A study of Polystyrene microgel particles with conjugated polymers and perovskite solar cell

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy

in the Faculty of Science and Engineering

Submitted 2017

Mu Chen

School of Materials

The University of Manchester
# Table of Contents

A study of Polystyrene microgel particles with hole transfer materials and perovskite solar cell ........................................................................................................................................ 1

List of Figure .................................................................................................................................................................................. 6

List of Abbreviations ........................................................................................................................................................................ 13

List of Symbols .................................................................................................................................................................................. 15

Abstract ............................................................................................................................................................................................ 17

Declaration ......................................................................................................................................................................................... 19

Copyright Statement ........................................................................................................................................................................ 20

Acknowledgements ........................................................................................................................................................................... 21

Chapter 1. Introduction ...................................................................................................................................................................... 22

1.1 Aims of the study ........................................................................................................................................................................ 22

1.2 Survey of thesis .......................................................................................................................................................................... 22

1.3 References ............................................................................................................................................................................... 26

Chapter 2. Literature review ............................................................................................................................................................ 27

2.1 Microgels .................................................................................................................................................................................... 27

2.1.1 Free-radical polymerisation .................................................................................................................................................. 29

2.1.2 Emulsion polymerisation ................................................................................................................................................... 31

2.1.3 Surfactant-free emulsion polymerisation .......................................................................................................................... 32

2.2 Colloidal Stability ..................................................................................................................................................................... 33

2.2.1 Overview ............................................................................................................................................................................... 33
<table>
<thead>
<tr>
<th>Section</th>
<th>Title and Details</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2.2</td>
<td>Van der Waals forces</td>
<td>33</td>
</tr>
<tr>
<td>2.2.3</td>
<td>Electrostatic forces</td>
<td>35</td>
</tr>
<tr>
<td>2.2.4</td>
<td>DLVO theory</td>
<td>36</td>
</tr>
<tr>
<td>2.2.5</td>
<td>Stabilisation of MG particles</td>
<td>38</td>
</tr>
<tr>
<td>2.3</td>
<td>Conjugated polymers</td>
<td>40</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Semiconductors</td>
<td>40</td>
</tr>
<tr>
<td>2.3.2</td>
<td>Shockley-Queisser limit</td>
<td>41</td>
</tr>
<tr>
<td>2.3.3</td>
<td>Poly(3-hexylthiophene)</td>
<td>43</td>
</tr>
<tr>
<td>2.4</td>
<td>Solar cells</td>
<td>46</td>
</tr>
<tr>
<td>2.4.1</td>
<td>Electron transport processes in polymer solar cells</td>
<td>46</td>
</tr>
<tr>
<td>2.4.2</td>
<td>Efficiency of solar cell</td>
<td>47</td>
</tr>
<tr>
<td>2.4.3</td>
<td>Polymer Fullerene solar cells</td>
<td>48</td>
</tr>
<tr>
<td>2.4.4</td>
<td>Hybrid solar cells</td>
<td>49</td>
</tr>
<tr>
<td>2.5</td>
<td>Perovskites</td>
<td>51</td>
</tr>
<tr>
<td>2.5.1</td>
<td>Origin of perovskites</td>
<td>51</td>
</tr>
<tr>
<td>2.5.2</td>
<td>Perovskite solar cells</td>
<td>52</td>
</tr>
<tr>
<td>2.5.3</td>
<td>Advantages of perovskite solar cells</td>
<td>55</td>
</tr>
<tr>
<td>2.5.4</td>
<td>Preparation of perovskite solar cells</td>
<td>56</td>
</tr>
<tr>
<td>2.5.5</td>
<td>Principles of perovskite solar cells operation parameters</td>
<td>58</td>
</tr>
<tr>
<td>2.5.6</td>
<td>Current state of the perovskite</td>
<td>59</td>
</tr>
<tr>
<td>2.6</td>
<td>Instrumentation</td>
<td>60</td>
</tr>
</tbody>
</table>
Chapter 4. A study of the morphology, structure, optical properties of HTM-MG combine films

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Abstract</td>
<td>110</td>
</tr>
<tr>
<td>4.2 Introduction</td>
<td>112</td>
</tr>
<tr>
<td>4.3 Experimental</td>
<td>115</td>
</tr>
<tr>
<td>4.3.1 Materials</td>
<td>115</td>
</tr>
<tr>
<td>4.3.2 Polystyrene MG preparation</td>
<td>115</td>
</tr>
<tr>
<td>4.3.3 Preparation of methylammonium iodide</td>
<td>116</td>
</tr>
<tr>
<td>4.3.4 Preparation of MAPI(C) film</td>
<td>116</td>
</tr>
<tr>
<td>4.3.5 Preparation of HTM-MG blend film and MG encapsulated film</td>
<td>117</td>
</tr>
<tr>
<td>4.3.6 Physical measurements</td>
<td>117</td>
</tr>
<tr>
<td>4.4 Results and Discussion</td>
<td>119</td>
</tr>
<tr>
<td>4.5 Conclusions</td>
<td>137</td>
</tr>
<tr>
<td>4.6 References</td>
<td>138</td>
</tr>
</tbody>
</table>

Chapter 5. A study of microgel dual roles in perovskite solar cells

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Abstract</td>
<td>140</td>
</tr>
<tr>
<td>5.2 Introduction</td>
<td>141</td>
</tr>
<tr>
<td>5.3 Experimental</td>
<td>143</td>
</tr>
<tr>
<td>5.3.1 Perovskite solar cell fabrication</td>
<td>143</td>
</tr>
<tr>
<td>5.3.2 Physical measurements</td>
<td>145</td>
</tr>
<tr>
<td>5.3.3 Device Meaurements</td>
<td>145</td>
</tr>
<tr>
<td>5.4 Results and Discussion</td>
<td>146</td>
</tr>
</tbody>
</table>
5.4.1 Devices preparation and measurement ............................................. 146
5.4.2 Devices stabilities ........................................................................... 154
5.5 Conclusions ....................................................................................... 161
5.6 References ......................................................................................... 162
Chapter 6. Conclusion and future works ..................................................... 165
  6.1 Summary of conclusions .................................................................... 165
  6.2 Future works ...................................................................................... 167
  6.3 References ........................................................................................ 168
Appendix ..................................................................................................... 169
  Published works ..................................................................................... 169
  Co-author Works .................................................................................... 169

Words count 30210
List of Figure

Figure 1.1 The method used to prepare P3HT-MG composite film. Heating P3HT solution and MG dispersion at 70 °C and mixing them to spin coated onto a glass substrate. The x and y are the concentrations of MG and P3HT. ............................................................... 23

Figure 1.2 Schematic of the two methods for using MG to improve MAPbI3-xClx(MAPI(C)) solar cell performance. HTMs were mixed with MG and spinning coated onto MAPI(C) as a hole transport layers (HTL) shown on the left hand side. MG particles were spinning coated on.......................................................... 25

Figure 2.1A scheme of MG particle in a poor solvent (a) and a good solvent (b)† ................. 27

Figure 2.2 scheme of a polymer chain in a good solvent (a), theta solvent (b) and poor solvent(c)................................................................................................................................. 28

Figure 2.3 The generation of free radicals from Azo initiator............................................ 29

Figure 2.4 Possible types of addition of a monomer molecule to propagating radical......... 30

Figure 2.5 Termination of a propagating chain by (a) combination and (b) disproportionation ........................................................................................................................................ 31

Figure 2.6 The schematic diagram of three intervals in emulsion polymerisation............ 32

Figure 2.7 The schematic diagram of three intervals in emulsion polymerisation............ 34

Figure 2.8 Schematic illustration of two electrostatically stabilised particles using a negatively-charged surfactant............................................................ 35

Figure 2.9 schematic diagram of potential energies versus distance of two particles40 ...... 38

Figure 2.10 Schematic diagram of steric and electrostatic stabilisation between two MG particles26 ................................................................................................................. 39

Figure 2.11 A presentation of energy bands gap between the HOMO and the LUMO in metal, semiconductor and insulator. ........................................................................................................... 41
Figure 2.12 The schockley-Queisser limits for efficiency of a solar cell, and this curve is slightly wiggly because of the infrared absorption bands in the atmosphere\textsuperscript{35-36} .................42
Figure 2.13 group R is instead of hexyl group and the right top structure is regioregular P3HT (Head to tail) and the rest three are the regiorandom P3HT. .................................................44
Figure 2.14 Spectrum of light reaching the earth (AM1.5)\textsuperscript{43} ........................................44
Figure 2.15 The P3HT bipolaron form. ..................................................................................45
Figure 2.16 The processes of electrons transport .................................................................47
Figure 2.17 Device architectures and active layer structure of donor-acceptor bulk heterojunction solar cells\textsuperscript{48} ..............................................................................49
Figure 2.18 Architecture of a hybrid solar cell. .................................................................50
Figure 2.19 The perovskite mineral\textsuperscript{51}. ..................................................................51
Figure 2.20 the crystal structure of perovskite mineral ......................................................52
Figure 2.21 Structure of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}. Pb atoms are placed at the centre of the white octahedrons, purple spheres represent iodine atoms and red spheres represent the methyl ammonium cations .............................................................................................................53
Figure 2.22 The historic evolution of PSCs\textsuperscript{59} ..................................................................54
Figure 2.23 The architecture and efficiency principle of PSCs ............................................55
Figure 2.24 general processes for preparing PSCs. ...........................................................57
Figure 2.25 PCE of PSCs over the years(ref =a\textsuperscript{66}, b\textsuperscript{56}, c\textsuperscript{67}, d\textsuperscript{68}, e\textsuperscript{69}, f\textsuperscript{70}, g\textsuperscript{71}, h\textsuperscript{67}, I\textsuperscript{72}, j\textsuperscript{73}, k\textsuperscript{74}, l\textsuperscript{75}) .................................................................60
Figure 2.26 Schematic diagram of DLS\textsuperscript{77} ......................................................................61
Figure 2.27 Schematic diagram of SEM\textsuperscript{80} .................................................................64
Figure 2.28 Schematic of X-ray diffraction .........................................................................68
Figure 3.1 DLS size data of MG particles in water and ethylbenzene. ...............................89
Figure 3.2 SEM images of MG particles deposited form water (scale bar is 2 µm). ..........90
Figure 3.3 SEM images of MG particles deposited from ethylbenzene (scale bar is 1 µm)...

Figure 3.4 Morphologies of different MG films prepared from various concentration (a) M0.5 (b) M1.0 (c) M3.0 (d) M6.0 (scale bars in zoom out images are all 2µm, scale bars in the insert images are 500 nm)............................................................................................................................92

Figure 3.5 Optical microscopy image of the M3.0 film and a scratch in this film shown as red arrows (scale bar is 20 µm)...........................................................................................................................................................................................93

Figure 3.6 Diagram schematic of P3HT-MG composite films, the x axis and y axis of each point showed the concentration of MGs and P3HT composite film. The images are the films under optical microscopy and the dimension of each film is 25 mm x 20 mm. The black circles and blue squares indicate monolayer and multilayer of MG particles respectively. The numbers next to the symbols are the thickness (nm) of that film. The scale bars for images are 20 µm and for insert images are 2 µm. ..................................................................................................................95

Figure 3.7 The light path when the light goes through two different phrases. .........................96

Figure 3.8 Photographs of P3HT-MG blend films in reflection (a) and the labels of each film (b)........................................................................................................................................................................................................................................98

Figure 3.9 Colour change various for the thickness of a thin film31...........................................99

Figure 3.10 AFM images and profile line of M3.0 film (a) and (b) respectively and (c) is the thickness and diameters of MG particles changes versus the concentration of MG dispersion changes........................................................................................................................................................................100

Figure 3.11 The SEM images of M3.0P0.8 film (a) and M3.0P1.6 film (b) (all the scale bars are 1µm)......................................................................................................................................................................................................................................................101

Figure 3.12 AFM images of M3.0P1.6 film (a) and the profile line of M3.0P1.6 film (b) ...102

Figure 3.13 The XRD data showed datas of P1.6, L3.0, L3.0P1.6 M3.0 M3.0P1.6 films (a) and four probes measurement of some films showed conductivities of each film (b). ........103
Figure 3.14 The UV-Vis spectra of MxP0.8 films system (a), UV-Vis spectra of the reference films M3.0 and M6.0 (c) and the absorbance of each film at 525 nm (c).................................104
Figure 3.15 Effect of P3HT concentrations on the UV-Visible spectrum for P3HT-MG blend films (a). Variation of absorbance at 525 nm with y for M3.0Py and Py films (b). Absorbance of Linear polystyrene and linear polystyrene with MG blend film(c). PL data of P3HT-MG film and linear polystyrene MG films (d)..............................105
Figure 4.1 DLS data for MG particles dispersed in chlorobenzene, toluene and water respectively. .................................................................................................................120
Figure 4.2 SEM images of MG particles deposited from water (a), toluene(b) and chlorobenzene(c). DLS data for PS MG particles dispersed in water, toluene and chlorobenzene. Particle size data obtained from the SEM and DLS data are shown in the table (d)..........................................................................................................................121
Figure 4.3 Optical microscopy (a) and AFM image (b) of M3.0 film deposited from toluene. ....................................................................................................................................................................................122
Figure 4.4 Optical microscopy images of ITO/MAPI(C)/P3HT-MG film (a), ITO/MAPI(C)/Spiro-MG film (b) and ITO/MAPI(C)/PTAA-MG film (c). .........................123
Figure 4.5 AFM tapping mode image and line profile line of P3HT-MG /MAPI(C) film....125
Figure 4.6 AFM tapping mode image and line profile line of Spiro-MG /MAPI(C) film. ...127
Figure 4.7 AFM tapping mode image of PTAA-MG /MAPI(C) film. ........................128
Figure 4.8 DLS of MG particles in chlorobenzene in the presence of different concentration of Spiro-MeOTAD (in wt.%). The MG concentration was 0.10 wt.% The measurements were performed at room temperature. .................................................................129
Figure 4.9 The quenching showed in PL spectr a of MAPI(C) and MAPI(C)/P3HT films (a), and PL spectra of P3HT film on glass substrate (b). PL spectra of MAPI(C)/P3HT and
MAPI(C)/P3HT-MG films and corrected curves (c), UV-vis spectra of MAPI(C)/P3HT and MAPI(C)/P3HT-MG films (d) ......................................................................................................................................................................................... 131

Figure 4.10 PL spectra of MAPI(C), PTAA/MAPI(C) and PTAA-MG/MAPI(C) film (a), and UV-vis data of MAPI(C), PTAA/MAPI(C) and PTAA-MG/MAPI(C) film (b) ................................................................. 132

Figure 4.11 XRD data spectra of P3HT-MG/MAPI(c) (a) and PTAA-MG/MAPI(c) (b) films. ............................................................................................................................................................................................................................................................................................................. 133

Figure 4.12 AFM tapping mode images of MAPI(C) film (a) and MG encapsulated MAPI(C) film (b). The insert image is the profile-line for each AFM image. ................................................................. 134

Figure 4.13 PL spectra of MAPI(C) and MAPI(C)/MG encapsulation film (a) UV-Vis spectra of MAPI(C) and MAPI(C)/MG encapsulation film (b) ................................................................. 135

Figure 4.14 XRD data spectra of MAPI(C) film, MG encapsulated MAPI(C) film and HTM-MG films ......................................................................................................................................................................................... 136

Figure 5.1 Schematic of (a) normal PSC without MG (unmodified cells), (b) HTM-MG blend PSC and (c) MG encapsulated PSC ............................................................................................................................................................................................................................................................................................................. 147

Figure 5.2 Champion J-V curves for P3HT (a) and P3HT-MG cells (b) ................................................................. 148

Figure 5.3 Champion of J-V curves for PTAA (a) and PTAA-MG (b) cells ................................................................. 149

Figure 5.4 Champion JV curves for (a) Spiro and (b) Spiro-MG cells ............................................................................................................................................................................................................................................................................................................. 150

Figure 5.5 Cross-sectional SEM image for the P3HT solar cell ............................................................................................................................................................................................................................................................................................................. 152

Figure 5.6 Champion J-V curves for MG encapsulated PSC ............................................................................................................................................................................................................................................................................................................. 153

Figure 5.7 Cross-sectional SEM images for the MG encapsulated solar cell ............................................................................................................................................................................................................................................................................................................. 154

Figure 5.8 The photos of controlled humid chamber (a) and temperature and humidity controller (b) ............................................................................................................................................................................................................................................................................................................. 155

Figure 5.9 Accelerated aging perovskite film (a) and MG encapsulated perovskite film (b) XRD data obtained at 85% humidity at room temperature ............................................................................................................................................................................................................................................................................................................. 156
Figure 5.10 Accelerated aging perovskite film (a) and MG encapsulated perovskite film (b) UV-Vis data obtained at 85% humidity at room temperature. 500 nm (c) and 750 nm (d) are the absorbance of encapsulated film and normal film change trends vs time. .........................157

Figure 5.11 Accelerated aging cell four parameters data current density (a), open-circuit voltage (b), fill factor (c) and PCE (d) obtained at 85% humidity at room temperature. ......159

Figure 5.12 Long term performance for P3HT solar cell, MG encapsulated P3HT solar cell and P3HT blend solar cell stored in vacuum conditions. Four parameters of solar cells current density (a), open-circuit voltage (b), fill factor (c) and PCE (d) were measured. .......................160
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk heterojunction</td>
</tr>
<tr>
<td>CBZ</td>
<td>Chlorobenzene</td>
</tr>
<tr>
<td>DI-water</td>
<td>De-ionized water</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>DLVO</td>
<td>Derjaguin, Landau, Verwey and Overbeek</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DVB</td>
<td>Divinylbenzene</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-doped tin oxide</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HTM</td>
<td>Hole transfer material</td>
</tr>
<tr>
<td>IQE</td>
<td>Internal quantum efficiency</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MAI</td>
<td>Methyl ammonium iodide</td>
</tr>
<tr>
<td>MAPI(C)</td>
<td>Mixed halide perovskite</td>
</tr>
<tr>
<td>MG</td>
<td>Micorgel</td>
</tr>
<tr>
<td>MSSC</td>
<td>Meso-superstructured solar cell</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic photovoltaic</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PSC</td>
<td>Perovskite solar cell</td>
</tr>
<tr>
<td>PTAA</td>
<td>Poly[bis(4-phenyl)(2,5,6-trimethylphenyl)amine</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SFEP</td>
<td>Surfactant-free emulsion polymerisation</td>
</tr>
<tr>
<td>Spiro-OMeTAD</td>
<td>2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene</td>
</tr>
<tr>
<td>ssDSSC</td>
<td>Solid-state Dye-sensitized solar cell</td>
</tr>
<tr>
<td>TDB</td>
<td>Titanium diisopropoxide bis(acetylacetonate)</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultra-violet visible spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
### List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Constant</td>
</tr>
<tr>
<td>α</td>
<td>Radius of particles</td>
</tr>
<tr>
<td>$A_\lambda$</td>
<td>Absorbance</td>
</tr>
<tr>
<td>B</td>
<td>Peak breadth at half the full intensity</td>
</tr>
<tr>
<td>c</td>
<td>Concentration</td>
</tr>
<tr>
<td>D</td>
<td>Translational diffusion coefficient</td>
</tr>
<tr>
<td>d</td>
<td>Distance</td>
</tr>
<tr>
<td>$d_h$</td>
<td>Hydrodynamic diameter of the particle</td>
</tr>
<tr>
<td>e</td>
<td>Charge</td>
</tr>
<tr>
<td>$G(\tau)$</td>
<td>Correlation coefficients functions</td>
</tr>
<tr>
<td>H</td>
<td>Distance of two particles</td>
</tr>
<tr>
<td>I</td>
<td>Intensity of scattered light</td>
</tr>
<tr>
<td>$I_0$</td>
<td>Intensity of the incident beam</td>
</tr>
<tr>
<td>$J_{sc}$</td>
<td>Current Density</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$K_p$</td>
<td>Rate coefficient of propagation</td>
</tr>
<tr>
<td>$K_t$</td>
<td>Parameter of the total rate coefficient of</td>
</tr>
<tr>
<td></td>
<td>combination and disproportionation</td>
</tr>
<tr>
<td>$P_m$</td>
<td>Power at maximum power point</td>
</tr>
<tr>
<td>q</td>
<td>Scattering vector</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Rate of propagation</td>
</tr>
<tr>
<td>T</td>
<td>The absolute temperature</td>
</tr>
<tr>
<td>$V_1$</td>
<td>Molar volume of solvent</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$V_A$</td>
<td>Attractive interaction energy</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open-circuit voltage</td>
</tr>
<tr>
<td>$V_R$</td>
<td>Electrostatic repulsive potential</td>
</tr>
<tr>
<td>$V_T$</td>
<td>Potential energy of interaction</td>
</tr>
<tr>
<td>$V_u$</td>
<td>Volume of non-swollen particles</td>
</tr>
<tr>
<td>$z$</td>
<td>Valence</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Molar absorptivity</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Viscosity of medium</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Angle</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Debye screening parameter</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Parameter of potential</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Delay time of time interval</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Number of moles of cross-links</td>
</tr>
<tr>
<td>$\phi_a$</td>
<td>Average volume fraction</td>
</tr>
</tbody>
</table>
Abstract

This thesis presents a study of polystyrene (PS) microgel (MG), hole transfer materials (HTMs) and perovskite solar cells (PSCs) and associated effects to combine them together to increase the stabilities of PSCs. PSCs are a disruptive technology which attract a lot of attention because of their remarkable power conversion efficiency (PCE). However, PSCs are very fragile and easy to be damaged by moisture and oxygen. The PS MGs are solvent-swellable, inherently colloidally stable, hydrophobic, and have good film-forming properties. In the study, we mixed PS MG with three different HTMs, poly(3-hexylthiophene) (P3HT), Poly[bis(4-phenyl)(2,5,6-trimethylphenyl)amine (PTAA) and 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD) to establish a diagram of concentrations of each component to form films. We investigated the morphology and light absorption and photoluminescence (PL) of HTM-MG films spin-coated from HTM-MG dispersions. The films containing flattened MG with an aspect ratio of around 10. MG islands containing packed particles were evident for both pure MG and P3HT-MG. The composite films were electrically conducting. An unexpected finding from the study was that the MGs dispersed well within the PTAA matrix. The HTM-MG films were used in PSCs to replace the HTM layer in PSCs and measured the PCEs of these new designed PSCs. The short-term (accelerating) stability test and long-term stability test were designed to investigate the MG based PSCs stabilities. Whilst MGs were used to form an encapsulation layer on PSCs as well, and the MG encapsulated PSCs were investigated using same method as HTM-MG PSCs to demonstrate their versatility. The PCE of these PSCs containing PTAA-MG and P3HT-MG decreased by only around 20% comparing to control PSCs containing PTAA and P3HT. The PTAA and P3HT in PTAA-MG and P3HT-MG only occupied around 35 vol.% of the composite films. Additionally, the open circuit voltages (V_{oc}) for the PSCs containing P3HT-MG increased by around 0.17 V compared to control PSCs containing P3HT. The
stabilities of PSCs containing PTAA-MG and P3HT-MG have a significant improvement comparing with control PSCs in both short-term test and long-term test. Hence, MGs can reduce the conjugated polymer use and increase the stability in PSC.
Declaration

The author declares that no portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Mu Chen
Copyright Statement

i. The author of this thesis (including any appendices and/or schedules to this thesis) owns certain copyright or related rights in it (the “Copyright”) and s/he has given The University of Manchester certain rights to use such Copyright, including for administrative purposes.

ii. Copies of this thesis, either in full or in extracts and whether in hard or electronic copy, may be made only in accordance with the Copyright, Designs and Patents Act 1988 (as amended) and regulations issued under it or, where appropriate, in accordance with licensing agreements which the University has from time to time. This page must form part of any such copies made.

iii. The ownership of certain Copyright, patents, designs, trademarks and other intellectual property (the “Intellectual Property”) and any reproductions of copyright works in the thesis, for example graphs and tables (“Reproductions”), which may be described in this thesis, may not be owned by the author and may be owned by third parties. Such Intellectual Property and Reproductions cannot and must not be made available for use without the prior written permission of the owner(s) of the relevant Intellectual Property and/or Reproductions.

iv. Further information on the conditions under which disclosure, publication and commercialisation of this thesis, the Copyright and any Intellectual Property and/or Reproductions described in it may take place is available in the University IP Policy (see http://documents.manchester.ac.uk/DocuInfo.aspx?DocID=487), in any relevant Thesis restriction declarations deposited in the University Library, The University Library’s regulations (see http://www.manchester.ac.uk/library/aboutus/regulations) and in The University’s policy on Presentation of Theses.
Firstly, I would like to thank my supervisor Prof. Brian Saunders for his excellent advice, encouragements and support since I was a master student. Without his expertise and patiently help, this thesis could not reach this form. His professionalism, preciseness and sincerity toward science are admirable to me and he is my academic role model.

I would like to thank all of the staff in the School of Materials, University of Manchester. In particular, I greatly appreciate Polly Greensmith for teaching me a lot of skills and techniques of the lab works and Eric Whittaker for helping me with device coating and measurement. Many thanks also go to Dr. Shicheng Li and Dr. Manrui Zhang for their generous care and assistance.

I would also like to thank to thank all of my group members for their efforts over my entire PhD life. I am so fortunate to have stayed in such a positive and friendly group. Specifically, I would like to thank Zhengxing Cui who was being five-year roommate with me. Thank you for sharing joys and supporting me over these years. I am grateful to Dr. Amirhossein Milani, Dr. Jane Bramhill, Dr. Junfeng Yan, Dr. Kyriaki Pafiti, Dr. Judith McCann, Dr. Robert Farley, Melody Obeng, Wenkai Wang, Qing Lian, Shanglin Wu, Mingning Zhu, Muhamad Sharan Musa, Aloïs Mispelon, Muhamad Zulhasif Mokhtar and Syazwani Mohd Zaki and I wish you all success and happy in the future. It is fantastic to work with your company.

Finally, I would like to give my deeply grateful to my family, especially my parents and my fiancée. Those warm words over the phone always gave me the strength and encourage me to complete this journey.
Chapter 1. Introduction

1.1 Aims of the study

MG particles are crosslinked polymer colloid particles which can swell in a good solvent\(^1\). PSCs are the most attractive solar cells nowadays due to their remarkable PCE. However, PSCs can be damaged by moisture easily\(^2\) and PS MG is a basic MG and hydrophobic\(^3\). The aim of this thesis was to investigate HTM-MG composite and establish a concentration system of film forming. Moreover, we used HTM-MG composite layer replaced the HTM layer in PSCs. HTM-MG composite layer could reduce the usage of HTM in PSCs and also increase the stabilities of PSCs. The MG encapsulated PSCs also showed good stabilities. These results from this study showed MG has a huge potential to mix with HTM and replace the HTM layer.

1.2 Survey of thesis

The main part of this thesis starts with a literature review (Chapter 2). It is followed by three experimental Chapters (3 – 5) to introduce independent. The thesis ends with an overall conclusion in Chapter 6. The literature review introduces key theories and background for the results and discussion chapters. This section includes an introduction to history and development of MGs, conjugated polymer and polymer solar cells especially PSCs.

Chapter 3 investigates composite films containing MG and P3HT. The PS MG was prepared using surfactant-free emulsion polymerisation (SFEP)\(^1\). The different concentrations of MG and P3HT mixed dispersion were prepared to investigate the morphologies of P3HT-
MG films. The method used to prepare P3HT-MG composite films are shown in Fig 1.1. The electrical conductivity and light absorption properties of the films are studied. The P3HT-MG composite films showed clear islands of crystalline MG particles. The data reveal that P3HT-MG films are electronically conducting and they have optoelectronic applications such as used as hole transfer layer in solar cell in the latter studies.

**Figure 1.1** The method used to prepare P3HT-MG composite film. Heating P3HT solution and MG dispersion at 70 °C and mixing them to spin coated onto a glass substrate.

Chapter 4 investigates HTM-MG films following Chapter 3. PTAA, P3HT, and Spiro were mixed with MG and spin coated to thin films. The HTM-MG films were investigated
using AFM, UV-vis Spectroscopy, and PL Spectroscopy. The MG particles dispersed well within the PTAA matrix and PTAA-MG films showed around 90% quenching under PL.

Chapter 5 describes the PCE and stabilities of PSCs containing HTM-MG. The HTM-MG films were replaced the HTM layer in PSCs. The PSCs architecture was shown in Fig 1.2. In this chapter, PSCs containing with HTM-MG were compared to control PSCs containing HTM. The designed PSCs were stored in an accelerating humid chamber for a short-term stability test and stored in a vacuum desiccator for a long term stability test.
**Figure 1.2** Schematic of the two methods for using MG to improve MAPbI3-xClx(MAPI(C)) solar cell performance. HTMs were mixed with MG and spin coated onto MAPI(C) as a hole transport layers (HTL) shown on the left hand side. MG particles were spin coated on
1.3 References


Chapter 2. Literature review

2.1 Microgels

Microgel (MG) particles are crosslinked polymer particles which can swell in a good solvent\(^1\). MGs were first reported by Baker in 1945 who identified the crosslinked polybutadiene particles\(^2\). In this term, M is “micro” which defines the particles size of MG in a range of 10 nm to 1 µm and G is “gel” which defines the polymeric networks between the each polymer chain and this networks cause the polymer cannot dissolve in solvent and only can be dispersed and swell in a solvent to form a gel\(^3\).

MG particles can swell in a good solvent until the swelling force reaches the restraining elastic force usually from attractive polymer-solvent interactions. Oppositely, in a poor solvent, MG particles can only collapse (shown in Fig 2.1). The particles of MG are spherical (Fig 2.1a) as in colloid dispersion, they can absorb solvent and swell in the dispersion (Fig 2.1b) and the collapsed form is called latex.

![Figure 2.1](image)

**Figure 2.1** A scheme of MG particle in a poor solvent (a) and a good solvent (b).\(^1\).
The average volume fraction ($\phi_\alpha$) of the MG is the ratio of the volume of non-swollen particles ($V_u$) to the swollen particle. The number of moles of cross-links ($\chi$) and molar volume of solvent ($V_1$) can affect volume fraction. The equation of average volume fraction is

$$
\phi_\alpha = \left( \frac{2\chi V_1}{V_u \left( \frac{1}{2} - \chi_12 \right)} \right)^{3/5}
$$

(2.1)

Where, the $\chi_{12}$ is the solvent-polymer interaction parameter\(^4\), which is the indicator of the solvent quality, for the polymer-solvent system and there are three kinds of solvents. When $\chi > 0.5$, the solvent is a poor solvent and the polymer-solvent contacts are minimised which result in chain collapse, clustering or precipitation\(^1\). When $\chi < 0.5$, the solvent is a good solvent and the polymer-solvent contacts are maximised which result in chain expansion. When $\chi = 0.5$ the solvent is known as a theta solvent and the polymer-solvent contacts are in balance which results in an ideal chain (shown in Fig 2.2).

*Figure 2.2* scheme of a polymer chain in a good solvent (a), theta solvent (b) and poor solvent(c).
2.1.1 Free-radical polymerisation

In this thesis, the polystyrene-co-divinylbenzene (PS-DVB) will be studied. Sieglaff et al. studied swelling of polystyrene MGs and they found the swollen MG particles can change the dimensions of analogous linear polymer in solution. There are four methods that have been reported for MG particles preparation: emulsion polymerization, cross-linking of neighbouring polymer chains, anionic copolymerization and inverse micro-emulsion polymerization. In this thesis, the initiator used azobiscyanopentanoic acid and DVB is crosslinker. Azobiscyanopentanoic acid is a free radical initiator which is used in free radical polymerisation.

Free-radical polymerisation is initiated by radicals generated from initiators such as azobiscyanopentanoic acid. There are four steps in the polymerisation: initiation, propagation, chain transfer and termination.

Initiation is the first step of free-radical polymerization. Azo initiator is a type of initiator system which is a non-redox initiator. In the Azo initiator, radicals are generated via homolytic scission (shown in Fig 2.3).

![Figure 2.3 The generation of free radicals from Azo initiator.](image)

Propagation is the second step of free-radical polymerisation. In this step, the free radicals are added on monomers. There two different types would appear during the propagation, head-to-
tail and head-to-head (shown in Fig 2.4). During the propagation, the head-to-tail addition is dominant for steric repulsion reasons.

\[ \text{head-to-tail addition} \]

\[ \text{head-to-head addition} \]

**Figure 2.4** Possible types of addition of a monomer molecule to propagating radical

The propagating radical normally terminate in two different ways, combination and disproportionation. Fig 2.5 shows these two different termination processes. The concentration of active centres and the coefficient of termination dominate the rate of termination. The rate of free-radical formation is equal to the rate of termination and the rate can be calculated as:

\[ R_p = k_p \left( \frac{f_k d}{k_t} \right)^{0.5} [M][I]^{0.5} \]  \hspace{1cm} (2.2)

Where, \( K_t \) is the parameter of the total rate coefficient of combination and disproportionation. \( R_p \) is the rate of propagation which can be calculated by a steady state condition in propagation when the generation and consumption rates are equal, and \( k_p \) is the rate coefficient of propagation\(^{10} \).
2.1.2 Emulsion polymerisation

Emulsion polymerisation is one of the most widely and common used methods for MG particles synthesis. The narrow polydispersity particles with a relatively rapid rate of free-radical based polymerisation are the main characteristics of emulsion polymerisation\textsuperscript{11}.

The monomers in emulsion polymerisation are insoluble in an aqueous solution and normally a surfactant is added into stable the monomers to form a latex. The initiator of emulsion polymerisation is using a water-soluble free-radical chemical. Hence, the polymerisation is initiated in an aqueous phase and the nucleation of particles begins to form at this stage that is known as interval I. The nucleation of particles begins to absorb monomers in the aqueous phase applied before or during the reaction by droplets to growth and maintain in a more stable colloidal dispersion than interval I, and this stage is known as interval II. The monomer begins to be exhausted and the reaction rate decreases after interval II, this stage is known as interval III\textsuperscript{5}. The schematic diagrams of three intervals in emulsion polymerisation showed in Fig 2.6.
The solubility of the monomer in water contributes to the rate of emulsion polymerisation. The different monomers in reactions have a distinct solubility that can result in non-uniform distribution of segments in the copolymer\(^5\).\(^{12}\). This non-uniform distribution can cause the different concentration of monomers in the reaction vessel and affect the reaction rate. The different reaction rate and concentration may cause the monomers in different interval stages.

### 2.1.3 Surfactant-free emulsion polymerisation

Polystyrene MG is one of the oldest MGs reported. In this thesis, we investigated MG mixing with perovskite (MAPI(C)), because of the hydrophobic features of polystyrene MG was attractive in our research. Polystyrene MG is usually crosslinked with divinylbenzene using surfactant-free emulsion polymerisation (SFEP) to prepare it.

SFEP is a special kind of emulsion polymerization which was first reported by Kotera et al\(^{13}\). In this method, surfactant is left out completely and an excess of initiator is used in the process. In SFEP, the monomer was in droplets because of high rotation speed and the initiator. The polymerization was happened in droplets and polymerization increased when two monomer droplets were closed to each other.
2.2 Colloidal Stability

Colloidal dispersion is defined as a phase containing dispersed particles, bubbles or foams and the sizes of this dispersion are in the range of 1 nm to 1000 nm\textsuperscript{14}. The phase of colloidal dispersion can be liquid, solid or gas\textsuperscript{14-15}. Colloidal dispersion is a heterogeneous system and commonly in everyday life as milk and beer, for example.

2.2.1 Overview

Because some colloids are relatively unstable, considering the kinetic stability is necessary. The stability of colloidal dispersion can be explained and described using DLVO theory. DLVO theory is named after Derjaguin, Landau\textsuperscript{16}, Verway and Overbeek\textsuperscript{17}. This theory divides colloidal stability into two forces, an attractive force Van der Waals forces and a repulsive force electrostatic force.

2.2.2 Van der Waals forces

Van der Waals forces are a type of intermolecular force; this force originates London dispersion forces is the weakest type of intermolecular force which is weaker than chemical bonds and hydrogen bonds. This term can be used loosely as a synonym for all the intermolecular forces\textsuperscript{4, 18}. In a colloidal dispersion, the attraction between two spherical particles can be explained by the equation of Van der Waals interaction. The attractive interaction energy $V_A$ for two identical spherical particles had the same radius $\alpha$, suspended in a phase with a distance $H$ (scheme showed in Fig 2.7) was derived by Hamaker\textsuperscript{19}

$$V_A = -\frac{A}{12} \left[ \frac{1}{x(x+2)} + \frac{1}{(x+1)^2} + 2 \ln \left( \frac{x(x+2)}{(x+1)^2} \right) \right]$$ (2.3)
Where $A$ is the Hamaker constant and

$$x = \frac{H}{2a}$$

(2.4)

If assuming, the two particles are very close, which means $H \ll \alpha$ or $x\ll 1$, the equation can be simplified as:

$$V_A = -\frac{A}{12} \cdot \frac{1}{2x} = -\frac{Aa}{12H}$$

(2.5)

Figure 2.7 The schematic diagram of van der waals force between two particles
2.2.3 Electrostatic forces

In the colloidal dispersion, electrostatic repulsive force contribute to the stability of the particles with surface charge\textsuperscript{20}. To obtain electroneutrality, counter-ions must exist near the surface ions. The counter-ions are able to diffuse back to the continuous phase, which causes a concentration gradient of the counter-ions away from the particle surface. This results in an electrical double layer consisting of a fixed layer of surface ions and a diffuse layer of mobile counter-ions in the aqueous medium\textsuperscript{21}. It is the electric potential of the diffuse layer that controls the particle stability. A schematic illustration of electrostatic stabilisation is shown in Fig 2.8\textsuperscript{22}.

![Schematic illustration of two electrostatically stabilised particles using a negatively-charged surfactant.](image)

**Figure 2.8** Schematic illustration of two electrostatically stabilised particles using a negatively-charged surfactant.
The electrostatic repulsive potential, $V_R$ between two same spherical particles have same radius $\alpha$ can be derived as

$$V_R = \frac{32\pi \varepsilon a k^2 T^2 \nu^2}{e^2 z^2} \exp(-\kappa H) \quad (2.6)$$

Here $\varepsilon$ is the permittivity, $\alpha$ is the radius of particles, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $\nu$ is a parameter of potential, $e$ is the charge, $z$ is the valence, $\kappa$ is the Debye screening parameter and $H$ is the distance between two particles. When the two particles are identical, the equation can be simplified to:

$$V_R = 2\pi \varepsilon a \psi_d^2 \exp(-\kappa H) \quad (2.7)$$

Here, $\psi_d$ is the potential at the Stern plane.$^{22d}$

**2.2.4 DLVO theory**

DLVO theory is used to quantitatively describe the electrostatic stabilisation of particles. The potential energy of interaction, $V_T$, of two electrostatically- stabilised can be expressed by the sum of the potential energy of Van der Waal’s force, $V_A$ and the potential energy of electrostatic repulsion, $V_R$. Hence, the total potential energy can be calculated by a sum of $V_A$ and $V_R$. The potential energy $V_T$ can be plotted against the distance $H$ between two spherical particles (Fig 2.9).

When the two particles approach each other at a distance approaching their diameter, the potential energy will decrease to a minimum and this minimum is also known as the secondary minimum. When the depth of the secondary minimum is large enough, flocculation can appear in the dispersion. The flocculation is reversible because only small
amount of energy is required for separation. The depth of the secondary minimum increases when the concentration of particles size increases because of steric repulsion forces increasing.

After the secondary minimum, the energy increase to positive and there is a peak of energy, which is known as primary maximum and this primary maximum is also called energy barrier to prevent the particles approaching too close to each other. However, enough kinetic energy, can force the particles to be closer to the others and pass this barrier. When the energy is particles are forced close each other, the potential energy decreases rapidly to the primary minimum. In this condition, the particles are coagulated. Once the two particles are coagulated, the process is irreversible due to the extremely high energy required to separate the particles.
2.2.5 Stabilisation of MG particles

The solvophilic polymer chain in MG particles can extend from particles surface in a good solvent to form a loop or tail. The extended polymer chains can prevent the aggregation of particles and this is known as steric stabilisation\textsuperscript{24}. The repulsion force is from the imbalance of osmotic pressure in the overlapping orbits. Hence, the stabilisation of MG particles is the total energy effect from the DLVO theory and the steric stabilisation. The Fig 2.10 shows a
schematic illustrates the two types of steric repulsion, and most MG particles are surrounded with negative charges. Hence the electrosterics contributes to the MG particles stabilisation\textsuperscript{25}. 

**Figure 2.10** Schematic diagram of steric and electrostatic stabilisation between two MG particles\textsuperscript{26}. 

2.3 Conjugated polymers

Conjugated polymers are organic macromolecules which include a backbone chain and some double-and single-bonds. Normally there are benzene rings or other rings in conjugated polymers and the π-electrons in these rings are delocalised by the overlapping p-orbitals in double bounds. This relocation and overlapping can result in useful optical and electronic properties of conjugated polymers. Most conjugated polymers are soluble in organic solvents, which allow these polymers to be prepared as films by processes such as spin-coating, ink-printing and screen printing. All of these three processes can be performed at room temperature, and conjugated polymers can be performed as flexible films. For these reasons, conjugated polymers are potential excellent materials for commercial applications.

2.3.1 Semiconductors

Conjugated polymers are semiconductors that can absorb light with a certain energy and the π-electrons will be photoexcited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). In metals both the HOMO and the LUMO bands are partially occupied by electrons and there is no energy gap between the HOMO, Fermi level and the LUMO. In insulators, there are defined band gaps between the HOMO and the LUMO and the band gaps are relatively large and the electrons are excited from the HOMO to the LUMO hardly. However, the semiconductors are quite different from metals and insulators; they are situated in between metal-like conductors and insulators. In semiconductors, there are defined band gaps between the HOMO and the LUMO and the band gap is not that high (shown in Fig 2.11). A certain energy can cause the electrons of π-bonds to be transferred from the HOMO to the LUMO and π-electrons can be transferred from π to a π* excited state, which is known as an excitation. Whilst, the Fermi level in
semiconductors is not same as that of metals. The Fermi level was defined as the top of the collection of electron energy levels at absolute zero temperature. The Fermi level is between the HOMO and the LUMO, in some semiconductors, the Fermi level is closer to the HOMO (valence band), we call this kind of semiconductors as p-type semiconductor. In contrast, for other semiconductors, in which Fermi level is closer to the LUMO (conduction band) we call this kind of semiconductor n-type semiconductor.

![Figure 2.11 A presentation of energy bands gap between the HOMO and the LUMO in metal, semiconductor and insulator.](image)

2.3.2 Shockley-Queisser limit

In physics, there is a Shockley-Queisser limit which is the maximum theoretical efficiency of p-n junction solar cell. The Shockley-Queisser limit was first calculated by William Shockley and Hans-Joachim Queisser at Schokley Semiconductor laboratory in 1961. This limit was calculated a single p-n junction solar cell. When the device is placed under the sun, photons from the sunlight can be absorbed by p-n type semiconductor, which is resulted in
electrons in the valence band being excited to the conduction band and then the excited
electrons in the conduction band are not stable and the electrons will return to a level with
lower energy. This electrons excitation and returning composed current.

Absorption of a photon creates the electron-hole pairs, which potentially contributes to
the current, but the reverse process, recombination of electron-hole pairs cause the
emission of a photon always happens as well. This reverse process decreases the
efficiency of the electrons mobility in materials. The Shockley – Queisser limit was
calculated from this phenomenon, and the maximum efficiency versus bandgap was
shown in Fig 2.12. From the Shockley-Queisser limits, the best bandgap can provide
maximum efficiency is 1.5 eV, at that point the efficiency can reach around 33%.

![Figure 2.12](image)

**Figure 2.12** The Schockley-Queisser limits for efficiency of a solar cell, and this curve
is slightly wiggly because of the infrared absorption bands in the atmosphere^{35-36}.
The Shockley-Queisser limit is the only limit for a single p-n junction device, and it follows three assumptions, one electron-hole pair generated per photon; thermal relaxation of the electron-hole pair for energy more than the band gap and illumination with normal sunlight. There are several methods to exceed Shockley-Queisser limit\textsuperscript{35}, such as Tandem cells\textsuperscript{37} or Multi-junction cell\textsuperscript{38} and multi-exciton cell, or quantum dots\textsuperscript{39}.

### 2.3.3 Poly(3-hexylthiophene)

Poly(3-hexylthiophene) (P3HT) is a kind of polymerised 3-hexylthiophene, which is a presentative conjugated polymer. P3HT is a semiconductive material when the electrons are relocated from the conjugated \( \pi \)-orbitals under certain energy.

There are two types of P3HT, one is regiorandom P3HT and the other is regioregular P3HT (shown Fig 2.13). The regioregular P3HT has a better performance than regiorandom P3HT because the bandgap is around 1.9 eV\textsuperscript{40} which is near the best band gap from Shockley-Queisser limit than regiorandom P3HT, also regioregular P3HT is crystalline but regiorandom P3HT is amorphous\textsuperscript{41}. P3HT is highly stable and can absorb the photons between wavelengths of 350 to 650 nm\textsuperscript{42}, which means P3HT is able to capture around 21% of the incident photons (Fig 2.14).
Figure 2.13 group R is instead of hexyl group and the right top structure is regioregular P3HT (Head to tail) and the rest three are the regiorandom P3HT.

Figure 2.14 Spectrum of light reaching the earth (AM1.5)\textsuperscript{43}.

The electrons on P3HT will be delocalised along the backbone because P3HT is a conjugated polymer as said before. The electrons will usually move along the π-orbitals and this
movement causes the full electrons extension $\pi$-system appearance. When the electrons are removed from this kind of $\pi$-system a bipolaron is formed$^{40}$. (Shown figure 2.15)

![Diagram of bipolaron formation](image)

**Figure 2.15** The P3HT bipolaron form.
2.4 Solar cells

2.4.1 Electron transport processes in polymer solar cells

The process of charge generation and transport to the external circuit in the photoactive materials consisting of a donor and acceptor is showed in Fig 2.16 and there are six steps in the charge generation and transport. The first step is solar absorption (shown in Fig 2.16 (a)) and electrons absorb energy and become excitons and come to higher energy band (showed in Fig 2.16(b)). The excitons will dissociate if the energy difference between the LUMO for the donor and acceptor exceeded the maximum of exciton binding energy when excitons reached the donor / acceptor interface (Fig 2.16(d)). At last the separated electrons cross the photoactive layer and electrode interfaces to reach the external circuit (Fig 2.16(f)). This is the basic electrons transferring between multiple layers principle is suitable for all the polymer solar cells.
2.4.2 Efficiency of solar cell

Four parameters determine the power conversion efficiency (PCE) of a solar cell, they can be calculated:

\[
PCE = \frac{J_{sc}V_{oc}FF}{P_m}
\]  

(2.8)

Where \( J_{sc} \) is the current density of device (mA / cm\(^2\)), \( V_{oc} \) is open circuit voltage (V) FF is the fill factor of device and \( P_m \) is the power of device at maximum power point.
The value for $J_{sc}$ is determined by the external quantum efficiency (EQE) which is the ration of the number of electrons collected by a device to the number of total power of devices. Indeed, the integrated area of an EQE vs. wavelength plot is often used to test the validity of $J_{sc}$ measured from J-V plots. The value for $J_{sc}$ is controlled by the optical properties of the light absorbing phase and photons transfer efficiency ($E_{g}$ and $\eta$). In addition, a key factor controlling $J_{sc}$ is the electron mobility within the semiconductor. Photoactive layers with thicknesses that are small compared to the absorption length have low $\eta_{A}$ values. Although thicker films will absorb more of the light, the relatively low mobility of the semiconductors means that higher series resistance decreases FF and, hence, PCE. Low charge mobility also increases recombination. Most solar cells require a thickness trade-off to be made between light absorption efficiency and charge transport efficiency.

Solar cell efficiency calculated or measured from the laboratory is the converted energy via photostatic into electricity, which is not the efficiencies at all conditions. The sunlight and cloud can affect solar efficiency a lot, when the sun is high in the sky and less cloudy, the yield of device will be higher even much higher than that when sun is low in the sky and cloudy. For example, in central Colorado American, a standard solar panel with 20% efficiency and an area of 1 m$^2$ can produce 440 kWh annually, but the same panel in southern England the produce is only 175 kWh annually$^{44}$.

### 2.4.3 Polymer Fullerene solar cells

As a thin-film solar cell technology, organic photovoltaic (OPV) is a very attractive. Polymer-fullerene solar cell is in the categories of bulk heterojunction (BHJ) solar cell which performed extremely well in the field of OPV. The power conversion efficiency of polymer-fullerene solar cell can exceed 8% and even approaching 9% as now reported$^{45}$. The Success
of polymer-fullerene solar cell has been the Jsc values increase which improved the efficiency of the photogenerated charges.

The most widely used BHJ solar device is shown in Fig 2.17, in which the active layer is a kind of donor and acceptor component\textsuperscript{46,48}. There are two kinds of BHJ solar device, the one is so-called standard cells are ITO/PEDOT: PSS/Active layer/Cathode layer and the other is an inverted cell. The inverted cell appeared as an alternative architecture\textsuperscript{47}.

![Device architectures and active layer structure of donor-acceptor bulk heterojunction solar cells](image)

**Figure 2.17** Device architectures and active layer structure of donor-acceptor bulk heterojunction solar cells\textsuperscript{48}.

### 2.4.4 Hybrid solar cells

Hybrid solar cells are types of solar cells which contain photoactive layers and there are at least two components each with a distinct chemical composition (shown in Fig 2.18). The first hybrid polymer solar cell was established by Alivisatos et al\textsuperscript{49}. The design aim of hybrid solar cells is to use the strong light absorption of semiconducting nanoparticles to provide acceptors that increase the Jsc.
The structure of hybrid solar cells is a superimposition of layers, each of these layers with a unique purpose. The glass slide at the bottom was the support to the device and let light pass through it. The indium tin oxide (ITO) is used as anode because it is a transparent conductive oxide. The next is the hole transport layer and photoactive layer, and these two layers are the main parts of hybrid solar cells and perform the operations of light transforming, and charge separation. The top of this device is the cathode layer, which is used to collect electrons. Normally, the materials of cathode layer are a metal such as, aluminium, silver or gold.

![Figure 2.18 Architecture of a hybrid solar cell](image_url)

**Figure 2.18** Architecture of a hybrid solar cell\(^59\).
2.5 Perovskites

2.5.1 Origin of perovskites

Perovskite at first, is a kind of calcium titanium oxide mineral species composed of titanite (Fig 2.19), which was discovered in the Achmatovsk, Ural Mountains of Russia by Gustav Rose in 1839 and was named after Russian mineralogist Lev Perovski.50

![perovskite mineral](image)

**Figure 2.19** The perovskite mineral.51

Perovskite mineral is an orthorhombic crystal (Fig 2.20) and the chemical formula of it is $\text{ABX}_3$. Because the crystal structure and chemical formula of $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X}=\text{I,Br,Cl}$) are same as the perovskite mineral, the solar cells with $\text{CH}_3\text{NH}_3\text{PbX}_3$ are named as perovskite solar cells (PSCs).
2.5.2 Perovskite solar cells

PSCs were first reported in 2009 because of its remarkable Power Conversion Efficiency (PCE) is 3.8%\textsuperscript{52}. Because of the growth of quality of CH$_3$NH$_3$PbX$_3$ and hole transfer materials, the PCE of PSCs have now achieved 22.1%\textsuperscript{49}. The perovskite is a kind of organometallic materials and its general formula is (ANH$_3$)BX$_3$, where A is an organic group normally is Carbon named as MA-perovskite, B is a metallic ion and lead is the best metal can be used so far, and X is a halogen\textsuperscript{51}. Iodide is the most used halogen in perovskite and only one halogen in PSCs (normally is iodide) are single halide PSCs, and the chloride and bromine can mix with iodide and this kind of solar cells are named as mixed halide PSCs\textsuperscript{53}. All of these materials are called perovskite-type crystals and these perovskite-type crystals exhibit a remarkable optical absorption due to the crystal structures of perovskite-type crystals\textsuperscript{54} and the three dimensional crystal is shown in Fig 2.21\textsuperscript{54}.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{image}
\caption{The crystal cell of perovskite mineral (www.comsol.com)}
\end{figure}
Figure 2.21 Structure of CH$_3$NH$_3$PbI$_3$. Pb atoms are placed at the centre of the white octahedrons, purple spheres represent iodine atoms and red spheres represent the methyl ammonium cations.

The first PSC reported was a dye-sensitized solar cell (DSSCs)\textsuperscript{55}, but the efficiencies of these original DSSCs was very low (only between 0.4\% to 2\%)\textsuperscript{52}. After this the solid-state DSSCs (ssDSSCs) appeared and these solid-state layers were much more stable than DSSCs in which the perovskite absorber dissolved or decomposed in the electrolyte. In 2011, N. G. Park and co-workers improved PSC by using optimisation of the titanium surface and the efficiencies reached 6.5\%\textsuperscript{56}.

The meso-superstructured solar cell (MSSC) was investigated by Snaith et al\textsuperscript{57}, and they found the charge extraction rates were significantly faster for the perovskite-sensitized solar cells in comparison to conventional DSSCs\textsuperscript{57}. They used Al$_2$O$_3$ to replace the TiO$_2$ and the electrons transport was much faster and the open-circuit voltage increased by 200 to 300 mV, leading to a 10.9\% efficiency\textsuperscript{58}. Remarkably, the PSC reached a record efficiency of 22.1\% according to Seok’s group\textsuperscript{49}. In Fig 2.22, schematic illustrations of electrolyte DSSCs, ssDSSCS, MSSC are shown to explain the historic evolution of PSCs.
PSCs have a unique operation principle compared with other solar cells. Because the exciton binding energies of PSCs is very low, the excitons distribute in the perovskite layer at room temperature. The perovskite layer was spin coated on the nanoparticles (such as TiO₂ or ZnO), which has a built-in electric field and can drive electrons separation throughout the photoactive layer. Hence, there is a very small built-in voltage and this small voltage result in the hole-blocking and hole transporting layers that can guide electron and hole flow. Meanwhile, because of the very low binding energy of PSC, a bulk heterojunction is not necessary. Ponseca et al. have attributed the nearly ideal perovskite solar properties to highly mobile electrons and holes that form rapidly (within picoseconds) and mobilities for both species that are balanced and remain high for timescales of microseconds.

Even though PSCs already have excellent performance, there are still some methods to improve the efficiency. The best hole transporter is spiro-OMeTAD which is used to prevent contact between the perovskite and the metal anode. If there is a higher-mobility hole transporter, it could achieve a higher fill factors (FFs) which can increase the efficiency.
directly. Another of perovskite used now is CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$. The bandgap of this kind of materials is around 1.5 eV but from Fig 2.23 which is the best bandgap for solar cells efficiency from Shockley-Queisser limit.

![Figure 2.23](image-url) The architecture and efficiency principle of PSCs.

### 2.5.3 Advantages of perovskite solar cells

PSCs are normally designed using mesoporous TiO$_2$ and a stack layers, and the architecture showed in Fig 2.25. These layers are composed of indium tin oxide (ITO) or fluorine-doped tin oxide (FTO), an electron transport layer normally in form of mesoporous layer, the perovskite layer or “capping layer”, and a hole transport material layer with a metal gold or silver often. The characteristics of the electron transport layer, perovskite layer and hole transport layer can affect PCE of PSC. In 2009, Kojima and coworkers used TiO$_2$ as an electron transport layer with 8-12 µm thickness to achieve the first PSCs. In the following work, researchers using more concentrated precursor solution improved the TiO$_2$ thickness to achieve the record of efficiencies up to 22.1%\textsuperscript{49}. In only 7
years the efficiencies increase from 3.8% to 22.1% which is a huge progress and PSCs still have a potential to hit a higher efficiency and rival the traditional silicon solar cells and the efficiencies have been plotted in Fig 2.25.

At the beginning, perovskite layer was used MA and Br, in the 7 years research, MA is not the only cation in PSC, slightly larger formamidine ion (FA) was found to be used in PSCs and the band gap changes a little bit. Not only cation has been changed, but Br was changed to I and Cl as well, in recent days, MA to FA and Br to I exchange and mixing are done as well. There are some MA and FA mixing and Br and I mixing PSCs show the higher efficiencies.

Hole transport layers are using hole transport materials which are p-type semiconductor molecules. So far there are hundreds of p-type semiconductor molecules which affect the performance directly. Hence, the research of p-type semiconductor can improve the research of perovskite. These p-type semiconductors can be small molecules such as Spiro-MeTAOD or polymer such as P3HT and PTAA.

Therefore, the most important three layers in PSCs are still in an improvement moto-way and show a remarkable potential ability, the PCE of PSCs still can increase in the following years.

2.5.4 Preparation of perovskite solar cells

The PSC is thin film solar cell and they are after prepared by spin coating for several layers of film including quantum dots film, perovskite film and electron donor film.

In Timothy’s group, they used the ZnO to replace TiO₂. Comparing with the mesoporous TiO₂, the ZnO quantum dots layer could be much thinner and do not need sintering.
The efficiencies of ZnO quantum dots PSC can exceed 15% because ZnO could improve the performance of solar cell device on rigid substrate$^{64}$. 

In this project, TiO$_2$ are used for in PSCs preparation. At first, before the preparation the ITO glass needs to be clean efficiency because the dust or organic impurities may damage the film. The preparation of PSCs uses spin-coating the TiO$_2$, CH$_3$NH$_3$PbI$_3$ and poly (3-hexylthiophene) in order. Each layer must have a particular thickness. The thickness can affect the results greatly. In the whole preparation, the spin coater is the only special instrument used in following related work$^{65}$. As a TiO$_2$ film, the cells require a heating temperature of up to 500 °C to sinter. At last a metal (normally silver or gold) would be spin coated onto the PSCs.(shown in Figure 2.24)

![general processes for preparing PSCs](image-url)

**Figure 2.24** general processes for preparing PSCs.
2.5.5 Principles of perovskite solar cells operation parameters

Current density

There are some factors that limit the current density of PSCs, and these factors are very important to understand to analyse the device structure. The devices must minimise the photons losses and the photoabsorber should be at a proper thickness to capture as many as photons passing through. Internal quantum efficiency (IQE) is the term used to analyses the photons losses in the devices. IQE is the ratio of the number of charge carriers collected by the solar cell to the absorbed number of photons from an energy of beam shining on the solar cell outside. So that, the low value of IQE indicates the active layer of the device is not able to use the photons properly. Early studies showed current density was around 11 mA cm\(^{-2}\) and this number increases rapidly into more than 21 in 2013 and 22 in 2015. Correa-Baena and coworkers improved the IQE and minimised the losses and the current density is around 23 mA cm\(^{-2}\) and IQE is very close to 100%. The perovskite crystal size play an important role of IQE value, low and high IQEs are caused by small (40-100nm) and large crystallites (more than 150 nm).

Open circuit voltage

The open circuit voltage (\(V_{oc}\)) depends on the band gap of perovskite. Because of Shockley-Queisser efficiency limit, \(V_{oc}\) can approach the thermodynamic limit which is 1.33 V for perovskite because the band gap is around 1.6 eV. A broad absorption can decrease the \(V_{oc}\). Hence, a sharp absorption is beneficial for high \(V_{oc}\) performance. The coverage of perovskite layer affects the \(V_{oc}\) a lot, once the coverage of perovskite layer is 100% (there is no pinhole on the perovskite film), the \(V_{oc}\) of devices can
exceed 1V. Because the pinholes of perovskite layer could cause the HTM layer contact the TiO$_2$ which would result in short circuit and decrease the voltage. The charge transport layers affect the $V_{oc}$ as well, TiO$_2$ mesoporous layer is the most widely used charge transport layer so far.

**Fill factor**

The fill factor (FF) and $V_{oc}$ are linked and the maximum value of FF so far is around 82%. The low FF values are caused by the photons losses due to the charge extraction and this is showed as voltage, series resistances and shunt resistances. Recently report shows the thickness of perovskite layer affect the FF of device a lot, the FF, EQE, IQE and absorption of thin perovskite layers are lower than the thicker perovskite layer. This indicates the charge transportation was dominated by the thickness of perovskite layer.
2.5.6 Stability of perovskite solar cell

There is a big challenge of Perovskite solar cells (PSCs) which is stability especially long-term stability. Because main part of perovskite solar cells is very easy to degradation and moisture and oxygen play an important roll to accelerate the whole produce. The Oxygen molecular was found to oxidize the excited electron in conduction band and cause to material be photo-oxidized and water was found as a catalyst to decompose the MAPbI$_3$. Kelly et al. monitored the MAPbI$_3$ changes in perovskite under 80% RHE which resulted in an extremely rapid degradation and the mechanism was found.

$$4\text{CH}_3\text{NH}_3\text{PbI}_3 + \text{H}_2\text{O} \leftrightarrow 4\text{CH}_3\text{NH}_3\cdot\text{H}_2\text{O} \leftrightarrow (\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O} + 3\text{PbI}_2$$

The PbI$_2$ is the signature chemical when the MAPbI$_3$ decomposes and the associated formation and phase segregation of PbI$_2$ crystals limited the dihydrate phase $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ reverse back to MAPbI$_3$.

Therefore, the methods to increase the stability of perovskite solar is the major subject of perovskite recently and some remarkable efforts on the perovskite solar cell long-term stability were made. Commonly two methods were used to increase the stability of perovskite solar cell. Firstly is adding some addition in MAPbI$_3$ or change the structure of it to increase the water resistance of perovskite and the other one is using some chemicals to block and avoid contact perovskite layer. Snaith group found single-walled carbon nanotubes (SWCNT) could be added into to HTM to form a double layer HTL. Han et al. reported another method to added ZrO$_2$ and carbon in TiO2 mesoporous as a triple layer to
absorb and block the water contact perovskite layer. In this project we used MGs particles to increase to stability of perovskite solar cell, we tried using MGs particles mixed with MAPbI3 to increase to water resistance of perovskite and using MGs particles to cast a thin film as a wall to block to water contacting the MAPbI3.

2.5.7 Anomalous hysteresis

The current-voltage scans yield is also a major challenge for perovskite solar cell in contrast to the other solar cells. Because the hysteretic behavior of perovskite solar cell has been observed which depends on the scanning conditions especially scan direction and scan speed. The IV-curves of perovskite solar cell was quite different and the efficiency showed higher when the scan is backward, which mostly caused by polarisation of materials and ion movement and ferroelectric effects also affect hysteresis.

2.5.8 Current state of the perovskite

PSCs were first configurated in 2009 using TiO2 with 3.8% since that the perovskite layer was improved to serval different new materials and hole transfer materials had been changed to both macromolecule and small molecule materials, till this year, the efficiency reached 22.1%. the whole duration was less than 7 years. The following Fig 2.25 showed the PSC improved each year.
2.6 Instrumentation

2.6.1 Dynamic light scattering

The dynamic light scattering (DLS) is the most common used method for characterising the size of particles which are dispersed in a solvent. It is also referred to as photon correlation spectroscopy (PCS). The movement of particles in solvent as a function of time can scatter light and DLS is based on measuring this scattered light intensity and calculated the sizes of
particles from this intensity. The fluctuations can be converted to the average translational diffusion coefficient that can be converted to the particles size by using Stokes-Einstein equation. Fig 2.26 shows the set-up of DLS instrument. A laser beam passes through the filter lenses and hits on the sample of particle dispersion. The detector is fixed at a certain angle normally is 90°. The laser beam hits the particles in sample and light will scatter because of that. The detector can collect scattered intensity and then transforms the intensity to electrical signals via the associated digital correlator.

Figure 2.26 Schematic diagram of DLS
The MG particles in dispersion keep moving randomly all the time due to Brownian motion. Brownian motion of particles is relative to the sizes of the particles. The intensity autocorrelation of Brownian is as follow.

\[ G(\tau) = \langle I(t)I(t + \tau) \rangle \]  \hspace{1cm} (2.9)

Here, \( G(\tau) \) is the correlation coefficients functions and the \( t \) is the time, \( I \) is the intensity of scattered light at a given time. \( \tau \) is the delay time of time interval.

For monodisperse particles, the \( G(\tau) \) is

\[ G(\tau) = A(1 + 2Be^{-\Gamma\tau}) \]  \hspace{1cm} (2.10)

Here \( A \) and \( B \) are constants

The \( \Gamma \) value relates to translational diffusion coefficient, \( D \) and scattering vector \( q \) can be derived:

\[ \Gamma = Dq^2 \]  \hspace{1cm} (2.11)

The value of \( q \) can be calculated from:

\[ q = \frac{4nm}{\lambda_0} \sin \frac{\theta}{2} \]  \hspace{1cm} (2.12)

Here, \( n \) is the refractive index of the medium and \( \lambda_0 \) is the wavelength of the incident leaser and \( \theta \) is the scattering angle.

The translational diffusion coefficient \( D \) is related to Stokes-Einstein equation by:

\[ D = \frac{kT}{3\pi\eta d_h} \]  \hspace{1cm} (2.13)

The value for \( k \) is Boltzmann constant, \( T \) is the absolute temperature, \( \eta \) is the viscosity of medium and \( d_h \) is the hydrodynamic diameter of the particle.
2.6.2 Scanning electron microscopy

The scanning electron microscopy (SEM) is one of the most widely used instruments to obtain information of the morphology and elemental composition of samples can be detected as well. A diagram of SEM is shown in Fig 2.27. The electron beam is produced by the electron gun which is in the top of the SEM column and then passes through lenses and focuses on a tiny spot of specimens. When the electron beam hits on the specimens there are signals that come from secondary electrons, backscattered electrons, Auger electrons, X-rays and light. The detector can collect these signals and send them to the computer to transfer them to images. Subsequently, the sample displayed on computer screen is based on the variations in black and white. In the all signals, secondary electrons and backscattered electrons are the two major signals used for images displayed due to the high resolution and strong contrast for images. The X-rays can be used for elemental analysis.

The SEM instrument is made of an electron gun, electromagnetic lenses and apertures, collector system and deflectors. The electron beam is provided and accelerated by electron gun with energy from 1 to 30 keV in a high vacuum environment. The electron beam is demagnified by electromagnetic lenses and focused by apertures to ensure the beam hits a small spot with a diameter of 1 to 10 nm on the surface of the sample.

In this study, SEM is used to observe the morphologies of MG particles, spin-coated MG films, cross-section of perovskite devices. Because most of our samples include MG particles, which are easy to be damaged under a high energy beam, we can only use the low energy of electron beams. The low energy of the electron beam causes low contrast. All the samples in our study were coated thin platinum (around 10 nm) to increase the conductivity. The
energies voltage used for MG samples were kept 3 kV to 8 kV to avoid the sample damages and voltage energies voltage used for perovskite devices were kept at 20 kV\textsuperscript{86}.

**Figure 2.27** Schematic diagram of SEM\textsuperscript{80}.

### 2.6.3 Atomic force microscopy

Atomic Force Microscopy (AFM) is one of most common, high-resolution microscopy to measure samples from the micron range to nano-range\textsuperscript{81}. AFM is different from traditional, light based microscopes because it does not use the electromagnetic spectrum to form images. Instead, a hard and sharp probe typically made of silicon or silicon nitride is used\textsuperscript{82}. The probe interacts with the sample surface at atomic level can generate a force that can be measured by instrument.
An AFM image is obtained by scanning the tip over a sample surface while keeping up a constant distance between tip and the surface\textsuperscript{83}. As the sample height changes, the tip will respond by ascending and descending and these respond signals build up an image of the topographical nature of the sample. To obtain an image, the AFM tip must detect a very small topography changes and transfer the changes into image height. To detect the sample topography changes, the AFM possesses a force transducer to monitor the distance between sample and tip. The detector of AFM measures the deflection of the cantilever and transfers this deflection into an electrical signal.

There are three different modes of AFM, contact, non-contact and tapping mode. Both tapping mode and non-contact mode, the tip does not contact the surface of the sample. In the contact mode, the tip is dragged across the surface of the sample, but the non-contact and tapping mode is not similar like this. In non-contact mode, the cantilever is resonant frequency and the amplitude of it is typically less than 10 nm even a few picometers. In this distance, van der Waals forces are import and contribute to the image, but van der Waals forces are strongest from 1 nm to 3 nm above surface. The van der Waals forces can affect the frequency of cantilever with other long-range forces above the surface; hence the frequencies can be transferred to images. Typically, most of the samples have a liquid meniscus layer beyond the surface, hence when the tip is close to this liquid meniscus enough, the short-range forces can be detected\textsuperscript{84}. However, in this situation, the tip is very easy to stick to the surface and tapping mode can solve this problem. In tapping mode, the cantilever is driven to oscillate up and down at or near its resonance frequency but the amplitude of his oscillation usually much larger than 10 nm, normally around 100 to 200 nm\textsuperscript{85}. When the tip is very close the surface of sample, the van der Waals forces, dipole-dipole interactions and
electrostatic forces contribute to the frequency and amplitude of cantilever, and the instrument transfer those forces into AFM image\textsuperscript{86}.

In our study, the AFM was used to characterise MG particles film, HTM-MG blend film to determine the surface morphologies of these films. Because all the films in our study are including MG particles and they are soft samples, the tapping mode was used for all the films in this study.

**2.6.4 X-ray Diffraction**

X-ray diffraction (XRD) is a non-destructive characterisation technique which can identify the crystal structure and quantities of different materials. XRD is normally used for characterising crystalline materials, and it can be useful for characterising the position of atoms within amorphous samples\textsuperscript{87}. In film diffraction, the sample is placed in the path of a monochromatic beam of X-rays and the beam can pass though different spots of sample.

When the X-ray beam passes through the sample, the X-ray is scattered by the electron clouds in the crystal structure. In crystalline samples, the atoms stay with regular spacing (d-spacing), so the scattering only occurs at regular intervals. The most of angles can cause destructive interference between reflected X-rays, so that a certain angles result in phase, producing a strong, sharp signal\textsuperscript{88}. The coherent scattering can be determined by the Bragg equation, which is defined as:

\[
n\lambda = 2d \sin \theta
\]

(2.14)

Here, n is an integer, \( \lambda \) wavelength of incident X-rays, d is inter-planar spacing and \( \theta \) is the angle between plane and incident X-ray beam.
When a bulk material is characterised using XRD, the data present are the intense, extremely sharp peaks at the Bragg angles. This is evidence of ‘long range order’ (Atomic positions in a crystal exhibit a property called long-range order), caused by the presence of crystallite structures greater than 100 nm\(^89\). Because of the extensive crystal structure, there are many planes that will reflect X-rays. Subsequently, X-rays that reflect at any angle other than the Bragg edge will be inevitable out of stage with another reflecting X-ray, resulting in total destructive interference in all instances except Bragg angles\(^90\).

The crystal size can be calculated by the intensity picked up by the diffractometer. The crystal size contributes the breadth of the peak, Scherrer carried out the calculation of the crystal size by Scherrer equation\(^91\):

\[
D = \frac{K\lambda}{B \cos \theta}
\]  

(2.15)

Here, D is the diameter of the nanocrystal, K is the shape factor, set to 0.90 normally, \(\lambda\) is the X-ray wavelength used for a copper anode this is 1.54 Å. B is the peak full width at half maximum (FWHM) and \(\theta\) represents the Bragg angle.
2.6.5 Ultra-violet visible spectroscopy

Ultra-violet visible spectroscopy (UV-Vis) is an analytical technique that can be used to determine the structural characteristics, and dimensional properties of a wide range of materials\textsuperscript{92}. Light from the ultraviolet to visible regions of the electromagnetic spectrum (200-900 nm) is enough to induce electronic excitation\textsuperscript{93}.

UV-Vis system relies on the comparison of the intensity of the incident beam and transmitted beam. For a given wavelength, the absorbance can be calculated as:

\[
A_\lambda = \log_{10} \left( \frac{I_0}{I} \right)
\]  

(2.16)

Here, \(A_\lambda\) is the absorbance at wavelength \(\lambda\), \(I_0\) is the intensity of the incident beam and \(I\) is the intensity of the transmitted beam. The Beer-Lambert law is represented as:

\[ \text{Figure 2.28} \] Schematic of X-ray diffraction.
\[ A = \log_{10} \left( \frac{I_0}{T} \right) = \varepsilon cl \]  

(2.17)

Where, \( \varepsilon \) is molar absorptivity with a unit of \( \text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \), \( c \) is the concentration with a unit of \( \text{mol L}^{-1} \) and \( l \) is the path length of the beam in a sample with a unit of cm.

The molar absorptivity means the capacity of the sample to absorb light at a given wavelength, and the path length normally is known (a typical cuvette is 1 cm across). When both these values are known, it is a simple matter to rearrange the equation to determine the precise concentration of the sample.
2.7 Reference


44. Frs, D. J. C. M.; MacKay, D. J. C., Solar energy in the context of energy use, energy transportation, and energy storage.


Chapter 3. A study of the morphology, structure and light absorption of P3HT-Microgel photoactive layers

3.1 Abstract

Conjugated polymers are widely used because they are semi-conductors and they can be used in many fields such as solar cells. Microgel (MG) particles are quite different from conjugated polymer, they are insulating and hydrophobic. Because poly(3-hexyliothiophene) (P3HT) is conjugated polymer it can be used in a perovskite solar cell (PSC) as hole transfer material (HTM) layer. In this chapter we used P3HT to investigate the properties of conjugated polymer film. Hence, we were considering mixing MG particles and P3HT together and investigating the properties. We mixed P3HT and MG to make blend films and investigated morphology and light absorption. The blend films comprised flattened MG particles embedded in the P3HT matrix so the MG inclusion had an effect on P3HT-MG film morphology. The composition, morphology and photophysical properties of the P3HT-MG film were studied and model established. The absorbance of the P3HT-MG film was greatly increased by inclusion of MG particles and also the photoluminace (PL) intensity increased. Therefore, MG particles have a potential to be added in HTM layer for solar cells.
3.2 Introduction

In recent years, the interest of polymer solar cells was increasing, because these polymer solar cells show excellent performance and they have very low CO$_2$ emission exhausted$^1$. There are important kinds of solar cells containing polymer which are polymer-fullerene$^2,3$ hybrid polymer solar cells$^4,5$ and PSCs$^6$. The polymer-based solar cells are normally assembled from blends of semiconducting polymers (electrons donor) with nanometre-sized semiconducting particles (electrons acceptor). The acceptors are usually functional fullerene rings or semiconducting inorganic nanocrystals (quantum dots)$^7,11$. In many studies, the hole transfer materials (HTM) were used$^{12}$. In this chapter, we investigate one HTM poly(3-hexylthiophene) (P3HT) and a mixed P3HT with polystyrene MG system. This is because one approach to decrease cost is to include insulating (commodity) polymers within the photoactive layers. A recent publication showed the incorporation of insulating polymers such as linear polystyrene within polymer-fullerene solar cells$^{13}$ did not seriously decrease efficiency at relatively high volume fractions and even increased efficiency$^{14}$. An interesting question concerning the inclusion of insulating polymers within photoactive layers is whether insulating polymers that are ideally-suited to surface coating formation (e.g., MGs)$^{15}$ could maintain the performance of solar cells with reducing semiconductive polymer loading. In this chapter, we start to address this question by investigating the structure, morphology and light absorption properties of bi-component blends of P3HT and polystyrene MG particles. In this chapter, only the properties of composite P3HT and MG films were studied. Consequently, solar cells are not considered in this chapter. An aim of the study is to suggest design criteria for future polymer-MG composite layer for solar cells.

MG particles are crosslinked polymer colloid particles which can swell in a good solvent$^{15,16}$. MGs are versatile and a number of methods for incorporating semiconducting and fluorescent
nanocrystals into polystyrene particles are known\textsuperscript{17,18}. In this chapter, we investigated the behaviours of P3HT-MG films. We only the study blends of P3HT with polystyrene MG because it was important to first establish relationships between blend composition and film morphology.

MG dispersions are inherently colloidally stable because the constituent particles are swollen\textsuperscript{19}. MG also have some permeability to small linear polymer chains\textsuperscript{20} due to the average pore size. Depending on the hydrodynamic chain size and the nature of the interaction between the MG network and linear polymer\textsuperscript{21}, small linear chains particles could permeate through the MG but large chains are not included. MG particles also have excellent film forming properties and have been used in surface coatings\textsuperscript{22}. Polystyrene MGs, like all MGs, are deformable in the swollen state and flatten when deposited onto SEM grids\textsuperscript{23}. Polystyrene MGs can be prepared using surfactant-free emulsion polymerisation (SFEP)\textsuperscript{15}, which is a scalable process. Moreover, polystyrene MG particle size and degree of swelling can be controlled using different preparation conditions such as the pH of the latex and rotation speed. Polystyrene MG is the oldest reported class of MG and is usually crosslinked with divinylbenzene (DVB)\textsuperscript{24,25}. Whilst blends of conjugated polymers with linear polymers (insulating) have been well studied\textsuperscript{26}, there have been no reports of composite films prepared from mixtures of conjugated polymer solutions with dispersions of insulating MG particles.

The methodology of preparing P3HT-MG films in this chapter is depicted in Scheme 3.1. P3HT solutions and polystyrene MG dispersions were mixed and then films deposited by spin coating. Ethylbenzene is a good solvent for swelling polystyrene MG particles\textsuperscript{27-29} and was used. We found that P3HT could be dissolved in ethylbenzene at 75 °C. The P3HT was used at a low concentration to form the P3HT-MG film and retain the colloidal stability. This
Colloidal stability is very important because it enabled deposition of good quality composite films that did not contain aggregated particles.

Scheme 3.1 Depiction of the method used to prepare P3HT-MG composite films. The P3HT solution and MG dispersion are mixed and then spin-coated onto a glass substrate. The MG particles flatten upon film formation and a layer of P3HT encased the MG particles.

The first reported study of photoactive films comprising bi-component conjugated polymer insulating MG particle blends is presented here. Spin coated MG films were first examined to establish concentrations of MG where monolayer and multilayer films occur. The effects of P3HT and MG concentration on the morphology of P3HT-MG blends are then investigated and a morphology phase diagram constructed. The electrical conductivity and light absorption and photoluminescence properties of the films are also studied. The data obtained
are compared to those obtained using conventional P3HT/linear polystyrene blends. Inclusion of MG particles within the composite films caused the P3HT phase to adopt a more ordered structure, absorb more light and emit intensely when photoexcited. The results of P3HT-MG blend film showed a potential for the future polymer-MG composite solar cells to decrease the P3HT loading for solar cells.
3.3 Experimental

3.3.1 Reagents

P3HT had a regioregularity of greater than 95% and a molecular weight range (Mn) of 15,000 – 45,000 g/mol and was used as received (Aldrich). Linear polystyrene used was also supplied by Aldrich and had a weight-average molecular weight of 35,000 g/mol. Styrene (Aldrich, 99%) was purified by washing with sodium hydroxide solution and stored in the dark at 5 °C. Divinylbenzene (DVB, 80 %, Aldrich) was used as received. Ethylbenzene (Fisher 99.8 %) was also used as received. Doubly-distilled deionized water was used.

3.3.2 Preparation of polystyrene microgel

The method used to prepare the MG was based on earlier work. Styrene (Aldrich, 99%) was purified using with sodium hydroxide solution and stored in the dark at 5°C and used for MG synthesis. DI-water (265 ml) was adjusted to a pH of 9 using with 0.1 M aqueous NaOH, and then added into a 500 ml reaction vessel and stirred at 350 rpm using a Teflon stirrer blade. The vessel was placed in a constant-temperature water-bath and the temperature kept at 70 °C. DI-water (5 ml) was added into finely ground azobiscyanopentanoic acid (0.244 g, 0.871 mmol) and the pH of mixture was adjusted to 11.0 using 0.1 M aqueous NaOH. DVB (0.086 g, 0.661 mmol) was added to prepared styrene (28.6 g, 0.275 mol) and mixed them thoroughly then added into the vessel. The initiator solution was added with stirring to the mixture and all the steps were conducted under a nitrogen atmosphere for 16 hours. After the reaction, the cooled latex was filtered and kept in the dark at 5 °C. The cooled latex was washed and dispersed using with DI-water using five centrifugation cycles and freeze-dried sample was transferred to ethylbenzene.
3.3.3 Substrate cleaning

The DI water (150 ml) was heated to 75 °C in the crystallisation dish on a hot plate. Then, ammonia solution (35 % (w/w)) and H$_2$O$_2$ solution (> 30% w/v) (30 ml) were added into the water. The mixture bubbled vigorously when it was heated up 75 °C and the glass substrates was placed into the RCA bath and kept in the solution for 15 minutes. After that, the bubbles in mixture reduced and the substrates were removed from the solution and washed with running deionised water and dried under a flow nitrogen gas.

3.3.4 Preparation of P3HT-MG composite films

The P3HT-MG blends films are identified regarding the weight percentage of P3HT and MG used for their preparation i.e., MxPy. Pure MG and P3HT films are identified as Mx and Py, respectively. Furthermore, Lx and LxPy correspond to films prepared using linear polystyrene. So, M3.0P0.8 refer a blend film containing 3.0 wt.% P3HT and 0.8 wt.% MG particles.

The preparation method of MG and P3HT blends film is exemplified for the sample of M3.0P0.8 film. P3HT (2 mg) was dissolved into ethyl benzene (98 mg) at 70 °C. Freeze-dried MG (5 mg) was wetted by very small amount of methanol and then dispersed in ethyl benzene (95 mg) at 70 °C. Then 2 wt% P3HT solution (40 mg) and 5 wt% MG was dispersed (60 mg) at 70 °C and sonicated the mixture solution at 70 °C until the solution changed to same as the P3HT solution before. The mixture solution was drop cast onto a clean glass slide (used RCA cleaning) and spin-coating at 3000 r.p.m for 15 s and the film was kept in a dark and dry place. The other concentration films were prepared using
an equivalent method.

3.3.5 Physical Measurements

**Photon correlation spectroscopy (PCS)** measurements were performed using a BI-9000 Brookhaven light scattering apparatus (Brookhaven Instrument Cooperation), fitted with a 20 mW HeNe laser and the detector was set at a scattering angle of 90°.

**SEM** measurements were obtained using a Philips FEGSEM instrument. Samples were dried at room temperature.

**Wide-angle X-ray diffraction (WAXD)** was performed using a PANalytical X’pert diffractometer. Out-of-plane (OOP) diffraction patterns were obtained in this study and Cu Kα radiation was used.

**UV-visible** absorption spectra were obtained using a Hitachi U-1800 spectrophotometer, using a wave length from 200 nm to 900 nm.

**Photoluminescence (PL)** spectra were obtained using a L2T-SENS-9000 instrument (Laser2000 Corporation). Films deposited on glass substrate were examined using an excitation wavelength of 490 nm.
3.4 Results and Discussion

3.4.1 Preparation of polystyrene MG

The MG particles were prepared using SFEP, which is a well-known technique to synthesise MG particles. PCS was used to measure the particles size dispersed in water and ethylbenzene. Fig 3.1 shows the particle size (d_z value) in water was around 612 nm and in ethylbenzene it was around 1281 nm. The sizes increased in ethylbenzene because the MG particles were swollen in ethylbenzene that was a good solvent for PS MG.

![Figure 3.1 DLS size data of MG particles in water and ethylbenzene.](image)

A representative SEM image of MG particles deposited from water latex (Fig.3.2) shows the MG particles had low polydispersity. For SEM data, the number-average diameter of particles was 635 nm and the co-efficient of variation (CV) is 7.9%. The particle size value was very close to the d_z from water latex (612 nm). The value for D_{SEM} is smaller than d_z value for the particles dispersed in water. This difference is because d_z values are more...
strongly affected by the larger particles within a size distribution than number-average diameters determined by SEM.

![SEM images of MG particles deposited from water (scale bar is 2 µm).](image)

**Figure 3.2** SEM images of MG particles deposited from water (scale bar is 2 µm).

The particle size increased when the MG particles dispersed in ethylbenzene were deposited on SEM grids, because they are swollen, and the number-average diameter size increased to 895 nm and the CV is 9.2% (Fig 3.3). The swelling ratio is different because the flattening occurred during deposition of the swollen particles. In the 3.4.3 SEM image the particles are packed not as same as in DLS which causes by the solvent ethylbenzene, there is the lack of electrostatic repulsion between them.
The MG particles in ethylbenzene latex were investigated to make a MG thin film by spin coating. Fig 3.4 shows the different concentrations of MG particles in ethylbenzene and the morphology of these spin-coated films without added P3HT. Four different concentrations (0.5%, 1.0%, 3.0% and 6.0%) were examined and are shown in Fig 3.4 (a-d). The first two concentrations were not high enough to form a continuous film. However, from the concentration of 3.0 wt%, the MG dispersion could form a continuous film after spin coating. From the images, the number-average diameters of particles were 1260, 1115, 775 and 785 nm respectively. The first two samples (M0.5 and M1.0) have larger size compared to the particles deposited from ethylbenzene Fig 3.3 because spin coating caused the particles flatten on the substrate. The latter two samples (M3.0 and M6.0) have smaller particles sizes because of more particles around which compressed the particles laterally.

**Figure 3.3** SEM images of MG particles deposited from ethylbenzene (scale bar is 1 µm).
Figure 3.4 Morphologies of different MG films prepared from various concentration (a) M0.5 (b) M1.0 (c) M3.0 (d) M6.0 (scale bars in zoom out images are all 2µm, scale bars in the insert images are 500 nm)

Fig 3.5 shows an optical image of a M3.0 film and a scratch in this film. The image shows the film was continuous and uniform and the fragments demonstrated the film forming ability of the deposited MGs.
3.4.2 Film characterisation

![Scratch](image)

**Figure** 3.5 Optical microscopy image of the M3.0 film and a scratch in this film shown as red arrows (scale bar is 20 µm).

We investigated films prepared from different concentrations of MG and P3HT in ethylbenzene. It was found that when the P3HT concentration was higher than 2 wt% or the MG concentration was higher than 10 wt% the film was not smooth after mixture and spin coating. Hence, composite films were prepared using MG and P3HT concentration less than some special points were chosen to check the trend of different component mixture film (Fig 3.6).
Here, MG particles were mixed with P3HT to make a composite film. We investigated various concentrations to find the best mixture concentration (Fig 3.6). P3HT could be dissolved well in ethylbenzene at temperature up to 70 °C. Interestingly, the concentrated solution formed a gel when cooled to the room temperature. A similar observation was reported earlier when P3HT was dissolved in xylene, it is noted that ethylbenzene and xylene are isomers. The form change of P3HT/ethylbenzene solution to a gel was found to be reversible. The hot solution (70 °C) was used for spin coating and it could provide a smooth and uniform film. These P3HT-MG blend films had a mirror like appearance this suggests the films were smooth.
Figure 3.6 Diagram schematic of P3HT-MG composite films, the x axis and y axis of each point showed the concentration of MGs and P3HT composite film. The images are the films under optical microscopy and the dimension of each film is 25 mm × 20 mm. The black circles and blue squares indicate monolayer and multilayer of MG particles respectively. The numbers next to the symbols are the thickness (nm) of that film. The scale bars for images are 20 μm and for insert images are 2 μm.

In Fig 3.7 these six films showed quite different colours when we imaged reflection in the dark. These different colours indicated the thicknesses of the films are not same. The differences of the thicknesses could change the wavelength changed of light. When passes go through a slow phase from a fast phase the injection and reflection angles were changed according to Snell’s Law (following)
\[
\frac{n_1}{n_2} = \frac{\sin \beta}{\sin \alpha}
\]  \hspace{1cm} (3.18)

\[n_1 \neq n_2\]

**Figure 3.7** The light path when the light goes through two different phases.

The optical path length difference \(\Gamma\) for the light is given by:

\[
\Gamma = n_2(AB + BC) - n_1AD
\]  \hspace{1cm} (3.19)

Furthermore

\[
AB = BC = \frac{d}{\cos \beta}
\]  \hspace{1cm} (3.20)
\[ AD = (2d\tan \beta) \sin \alpha \quad (3.21) \]

Hence,

\[ \Gamma = 2n_2d \left[ \frac{1}{\cos \beta} - \tan \beta \sin \beta \right] \quad (3.22) \]

\[ \Gamma = 2n_2d \left[ \frac{1 - \sin^2 \beta}{\cos \beta} \right] = 2n_2d \cos \beta \quad (3.23) \]

The distance of light is a number of wavelength \( m \), times wavelength \( \lambda \) for maximum reflection.

\[ \Gamma = m\lambda \quad (3.24) \]

Hence,

\[ \Gamma = m\lambda = 2n_2d \cos \beta \quad (3.25) \]

Because of the phase change is 180° which is equal to \( \pi \)

\[ 2n_2d \cos \beta = (m - \frac{1}{2} \lambda) \quad (3.26) \]

\[ \lambda = 2(m - 2n_2d \cos \beta) \quad (3.27) \]
In the (3.10), wavelength \( \lambda \) was related to the thickness (distance) \( d \), which means the thickness of the film affects the colour.

<table>
<thead>
<tr>
<th>P0.8</th>
<th>P1.6</th>
<th>M3.0P0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>M6.0P0.8</td>
<td>M3.0P1.6</td>
<td>M3.0</td>
</tr>
</tbody>
</table>

**Figure 3.8** Photographs of P3HT-MG blend films in reflection (a) and the labels of each film (b)

Fig 3.9 shows the colours of reflection various for the thickness of a film. From the Fig 3.9 we could see the colours of reflection of films in Fig 3.8 are very close to the colours between 250 to 400 nm regions in Fig 3.9, which supports all these six films are very thin and the thicknesses are between 250 to 400 nm.
The AFM and profilometer were used to measure the height of flattened MG particles and the average thickness of MG film (Fig 3.10 (a)). From the AFM images, the line profile could be analysed and the height of MG particles are around 130 nm after spin coating and when they flattened on a glass substrate (Fig 3.10 (b)), and the width of these particles could be calculated as well, the diameters of them are around 1200 nm. Hence, the ratio of diameter to height is more than 9 which means the MG was extremely flattened after spin coating on a glass substrate.

We measured the thicknesses of various Mx films (Fig 3.10(c)). The M0.5 and M3.0 films were 110 and 143 nm, respectively, and M6.0 was 505 nm. The M0.5 and M3.0 films are similar. However, M6.0 was thicker than the first two films. The thickness increased when the MG concentration was more than 3 wt%. This indicate that when the concentration was more than 3 wt% the particles started to become compact and the value of the diameter was decreased when x was less than 3.0 and constant when x was greater than 3.0. Accordingly,
M3.0 is a critical value in these films. In this system, the MG particles value reached a critical value to form a single layer film. By contrast, M6.0 film is multilayer.

![AFM images and profile line of M3.0 film](image)

**Figure 3.10** AFM images and profile line of M3.0 film (a) and (b) respectively and (c) is the thickness and diameters of MG particles changes versus the concentration of MG dispersion changes.

According to the former discussion, M3.0 is a critical value. Hence, the different concentration of P3HT was investigated and the MG value was fixed at 3.0%. From the optical microscope images, M3.0P0.8 and M3.0P1.6 are quite similar (Fig 3.6), both are smooth and uniform. However when the concentration of P3HT is larger than 1.6% the film was no longer smooth. The films were examined using SEM (Fig 3.11(a) (b)) M3.0P0.8 and M3.0P1.6 appears to be similar from the SEM again. In terms of morphology, both optical microscope and SEM showed M3.0Py series were continuous and smooth as the P3HT pure film.
Figure 3.11 The SEM images of M3.0P0.8 film (a) and M3.0P1.6 film (b) (all the scale bars are 1μm).

M3.0P1.6 also has been examined by AFM and the results are shown Fig 3.12(a). The line profile is shown in (b). It is clear that there two different phases were present in AFM image (Fig 3.12(a)). P3HT can be seen around the MG particles. The line profile showed the height from top of MG particles to baseline was around 70 nm (The thickness of film was around 110 nm). This means the MG particles were surrounded by P3HT. Also, thickness of a pure P3HT film (P0.8) film was investigated using a Dektak profilemeter and the thickness was found to be around 38nm. These data support the view of images before, the MG particles were embedded into P3HT.
It was also very important to check whether molecular-level changes for P3HT had occurred. Structural order within the films was examined by WAXD (Fig 3.13 (a)). Peaks were evident at $2\theta = 5.5^\circ$, $10.5^\circ$ and $23.0^\circ$, which were assigned to primary $(100)$, secondary $(200)$ and face-to-face $(010)$ stacking, respectively. An increase in peak intensity indicates increased order. The $(100)$ peak originates from lamellae oriented perpendicular to the film plane. Interestingly the latter peak is strongest for M3.0P1.6 and P1.6 and L3.0P1.6 are lower in order. These results suggest that the stacking of P3HT perpendicular to the film plane MG particles was enhanced by the MG particles. This result is unexpected. Increasing the order of P3HT often results in improved photoactive performance of P3HT-based solar cells\(^{33}\).

The conductivity of the mixed films is also very important for potential applications. Therefore, conductivities of M3.0Py films were examined and L3.0P0.8 films and P1.6 films were also examined as controls (Fig 3.13 b). From the Fig 3.13 (b), all the films have conductivity which is from $10^{-6}$ to $10^{4}$ S m$^{-1}$. Comparing the P1.6 film and M3.0P1.6 film, we find that the conductivity is slight lower when the MGs mixed with P3HT.
The results imply that increasing the concentration of insulating MG did not affect the conductivity of these mixed films significantly. This indicates the MG particles were dispersed in the P3HT matrix.

![Graph showing XRD data and conductivity measurements.](image)

**Figure 3.13** The XRD data showed data of P1.6, L3.0, L3.0P1.6 M3.0 M3.0P1.6 films (a) and four point probe measurement of some films showed conductivities of each film (b).

We also investigated the light absorption properties of MxP0.8 films and M3.0Py films and compare the performance when x and y changed. In Fig 3.14 (a), the absorption of M_{x}P_{0.8} films were compared when x = 0, 1.0, 3.0, 4.5, 6.0. The spectra show strong contributions from P3HT in the form of vibronic bands in the 500 to 600 nm region. Interestingly, when the concentration of x increased, the absorption increased. Considering the light scattering from the MG particles could cause absorbance values increase, the M6.0 and M3.0 films were investigated to check the light scattering of these two films in Fig 3.14 (b). The absorbance spectrum of M6.0 film is slightly higher than M3.0 film. Overall there are more light scattering occurred when the concentration of MG increased. However this slightly difference is not same as the light absorption difference for MxPy films. These changes indicate the higher the concentration of MG in the blend, the higher P3HT absorbance. The
The maximum absorbance confirmed the increasing trend and the absorbance of M3.0 film and M6.0 film had a significant increased; these caused the light scattering from the MG particles. Fig 3.14 (c) also showed as x increased the absorbance for the composite films increased as well respectively. Interestingly, we found the absorbance of the films increased by a factor of 3 and the weight fraction of P3HT in the composite film decreased by a factor of 8. Thus, using MGs to dilute P3HT solution is a method to increase the absorbance of P3HT film.

**Figure 3.14** The UV-Vis spectra of MxP0.8 films system (a), UV-Vis spectra of the reference films M3.0 and M6.0 (c) and the absorbance of each film at 525 nm (c).

The effects of P3HT concentration at constant MG concentration were investigated using M3.0Px films (Fig 3.15 a). A 3.0 wt. % concentration of MG was chosen because this concentration of MG particles could form as a monolayer after spin coating (Fig 3.4). As expected, as the concentration of P3HT increased, the absorbance increased Fig (3.14(a,b)). The vibrionic bands for P3HT were most pronounced for M3.0P1.2 and M3.0P1.6. When the concentration is lower than 1.2 wt% the band was not that clear. The absorbance values are
plotted in Fig. 3.14 (b) and a consistently higher absorbance was present for M3.0P0.8 and M3.0P1.6 compared to the control P0.8 and P1.6 films. This result confirms that the presence of MG particles enhanced light absorption by the P3HT phase.

**Figure** 3.15 Effect of P3HT concentrations on the UV-Visible spectrum for P3HT-MG blend films (a). Variation of absorbance at 525 nm with $y$ for M3.0Py and Py films (b). Absorbance of Linear polystyrene and linear polystyrene with MG blend film (c). PL data of P3HT-MG film and linear polystyrene MG films (d).

Linear polystyrene and P3HT blends film were also examined by using UV-visible spectrum in order to compare with the polystyrene MG particles blends. (Data for a linear polystyrene film (L3.0) and L3.0P1.6 also shown.) The L3.0P1.6 film showed a little lower absorbance as P1.6 film which was much lower than M3.0P1.6. This result shows the film with MG
particles have the higher absorbance than the pure P3HT film which is higher than the film with linear polymer.

PL data were obtained in order to probe the effect of polystyrene inclusion on radiative and non-radiative energy transfer processes following photoexcitation for P3HT. The PL efficiency is assumed to be proportional to the PL intensity$^{32}$. The efficiency decreased for the films in the order $M3.0P1.6 > L3.0P1.6 > P1.6$. This result showed that the PL intensity for P3HT films increased with increasing structural order. The reason for this phenomenon may arise from the change in structural hierarchy or another morphological effect. We propose that the relatively high PL efficiency for $M3.0P1.6$ is due to the increased structural order (as determined in Fig. 3.15 (a)) and relatively high light scattering. Both of these contributions to PL were caused by MG particles. The data presented suggest that polystyrene MG confer several factors on P3HT films that may translate to improved solar cells in the future. These factors include improved scattering, structural order of the P3HT phase and possibly light harvesting, as probed here by PL measurements.
3.5 Conclusions

In this chapter, MG particles were synthesised using SFEP method, it showed rigid 500 nm particles and it swollen a little when transfer from water to ethylbenzene. After spin coating on glass substrate, the MG particles are patterned, the width of the particles are almost 10 times their height. A method of uniform and continuous polystyrene MG film formation was established, and we found 3.0 wt% of polystyrene MG was the critical point to make a uniform film.

MG particles and P3HT blend film were investigated to find a suitable concentration for both MG particles and P3HT. A blend film making method was established to mix MG and HTM materials to make a uniform, continuous, hydrophobic and semiconductive film. As the concentration of MG particles increased in blend films, the light absorbance increased significantly. The photoluminescence and conductivity were not affected too much by MG.

We found M3.0P1.6 was the best film for all the different MG concentrations. It is a uniform and continuous film and the electrical and optical performances were still good. When the MG particles, insulating polymer were added in semiconducting polymer, P3HT, the morphology and photophysical properties of the film were not decreased as expect. Because our MG particles are hydrophobic, in the next step, we plan to add this kind of blend film in PSC, to replace the HTM layer and investigate the efficiency and stability changes of PSC.
3.6 References


28. Dawn Pro Dilution Evaluation
Chapter 4. A study of the morphology, structure, optical properties of HTM-MG combine films.

4.1 Abstract

Perovskite solar cells (PSC) have recently attracted a lot of attention due to their high power conversion efficiencies. However, this kind of cell is not very stable and easily decomposes. Moisture, UV-light, oxygen and temperature are the four key factors that affect the stability of perovskite cells. Microgel (MG) particles are crosslinked polymer colloids which swell in a thermodynamically good solvent and have excellent dispersion stability and form high quality hydrophobic films. We explore the ability of these qualities in order to improve the performance of PSCs. In this chapter we investigate the mixed halide perovskite films (MAPI(C)) with MGs. The MGs played two roles: a HTM extender and encapsulation agent. There were two different kinds of devices designed. The first used MGs as an encapsulating layer for a PSC. The second used mixing MGs within the hole transfer material (HTM). Three HTMs were used are P3HT, Spiro-OMeTAD and PTAA for blend mixture. Interestingly, the morphology of HTM-MG blend films and MG encapsulating films are different from the normal MAPI(C) film. The MG particles are clear to observe and arrange regularly. In the P3HT-MG film, the MG particles stay together to form a monolayer but in PTAA-MG film the MG particles are distributed separately well. By contrast Spiro-OMeTAD (which was able to penetrate the MGs) gave poor films which show micro-cracks. All films were investigated using UV-visible spectroscopy photoluminescence (PL) and WAXD. The UV-Vis performance of the HTM-MG films show a good absorbance which only have a slightly reduction. The PL data showed a strong quenching of the HTM and MAPI (C) film and
HTM-MG and MAPI (C) film showed the similar strong quenching as well. P3HT-MG and PTAA-MG blend films have good potential for the further devices research.
4.2 Introduction

The interest in PSCs has greatly increased in recent years which is driven in large part by the incredible increase of the power conversion efficiencies of research grade solar cells. The best values of the PCE are higher than 22%\textsuperscript{1-4}. New generation solar cells are needed as an energy resource because solar cells emit no carbon dioxide during their operation\textsuperscript{1-3}. In this chapter, we used the one-step preparation method for CH\textsubscript{3}NH\textsubscript{3}PbCl\textsubscript{x}I\textsubscript{3-x} (MAPI(C)) which is a common preparation method for PSCs\textsuperscript{5,6}. Three hole transport materials (HTMs) Spiro-OMeTAD (Spiro), poly(3-hexylthiophene) (P3HT)\textsuperscript{7} and poly(tiraryl amine)(PTAA)\textsuperscript{8} employed in PSC fabrication play important roles and dominate the performances of devices. Because MAPI(C) is fragile when humidity is high\textsuperscript{9-12} and MG particles are hydrophobic and have been extensively studied as model colloids and surface coating\textsuperscript{13,14}, we used MG particles in PSCs. The HTM provides opportunities to build a barrier to protect the underlying MAPI(C) layer. Hence we investigated MG particles as additives in HTM and tried to use MG particles to prevent damage from moisture.

The PSC efficiency and stability are affected by many factors\textsuperscript{15-17}, but the most harmful and likely reason is the decomposition of MAPI(C) caused by moisture in that case the MAPI(C) decomposed into CH\textsubscript{3}NH\textsubscript{2}, PbI\textsubscript{2} and other species\textsuperscript{18}. Oxygen and light can also cause decomposition to similar products\textsuperscript{19}. An aim of this chapter was to investigate degradation when polystyrene MG was included. In this chapter, we investigated the three HTMs mixed with MG particles. Because the MAPI(C) and HTMs combine layers are the main part of PSCs, this study presents a study of morphology and electrical properties of these blend. The work of this chapter is the base for new PSCs in Chapter 5. Our approach was to use MG particles as blend within the HTM with P3HT, PTAA and Spiro-MeOTAD. In this study, the HTM-MG blend films are not only type film we investigated, the MG encapsulated layer was
investigated as well. The morphology of MG encapsulated MAPI(C) was investigated and the morphology showed MG particles can form a good continuous HTM layer.

In the previously chapter, we found P3HT solution and polystyrene MG dispersion could be mixed and films formed by spin-coating\textsuperscript{20}. Importantly, in that work it was demonstrated that P3HT-MG composite films remained electrically conducting at high MG contents even though polystyrene is an insulator. Here, we designed two different films containing MGs, three of them contained MG blend HTMs where the hole transporting material was P3HT, Spiro-OMeTAD or PTAA, respectively (shown in scheme 1(b)). The other two were the standard control films without any MG particles (shown in scheme 1(a)). The last film contained the MG particles as an encapsulated material (shown in scheme 1(c)). After characterising the MGs we investigate their morphology and ability to coat MAPI(C) films. The MGs showed barrier properties as either an encapsulating layer or within the MG blend HTM and increased stability. Interestingly, the exclusion tendency of the MGs promoted performance benefits for the P3HT-based films and kept similar performance of the PTAA-based films. However, there was dramatically decreased performance of the Spiro-based films. The results indicate that MGs may mix with conjugated polymer HTMs slightly effective for the PSCs.
Scheme 1 Three samples are investigated in this study, MAPI(C)/HTM film (a), MAPI(C)/HTM-MG film (b) and MAPI(C)/HTM/MG encapsulation film (c). The structure of Spiro-OMeTAD (d) and PTAA(e).
4.3 Experimental

4.3.1 Materials

P3HT had a regioregularity of greater than 95% and a number-average molecular weight range of 25,000–35,000 g mol\(^{-1}\) (polydispersity < 2) and was used as received (Aldrich). 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spiropifuorene (Spiro-MeOTAD, Fenglin Chemicals, 99.5%) were also used as received. Poly(triaryl amine) (PTAA) was purchased from Aldrich and had a number-average molecular weight of 7,000 – 10,000 g/mol with a polydispersity of 2.0 – 2.2. Styrene (> 99%), divinylbenzene (DVB, 80%) 4,4’-azobis(4-cyanovaleric acid) (ACVA, 98%), toluene (99.8%), chlorobenzene (CBZ, 99.8%). Methyl amine solution (33 wt.% in absolute ethanol) and hydriodic acid (57 wt.%), titanium diisopropoxide bis(acetylacetonate) (TDB, 75 wt % in IPA), PbCl\(_2\) (98%), anhydrous N,N-dimethylformamide (DMF, 99.8%) were also purchased from Aldrich and used as received. Dyesol 18NRT titania paste (TiO\(_2\)) was also used as received. All water was of ultrahigh purity and de-ionised.

4.3.2 Polystyrene MG preparation

The method of MG preparation was based on Chapter 3. Water (265 ml) was adjusted to pH 9.0 using NaOH solution, and was then added into a 500 ml reaction vessel, and stirred at 200 rpm at 70 °C. ACVA (0.244 g, 0.871 mmol) was added into water (7.0 ml) and adjusted to pH of 11.0 using NaOH solution. DVB (0.086 g, 0.661 mmol) was mixed with styrene (28.6 g, 0.275 mol) and added to the vessel. The ACVA solution was then added into the de-oxygenated vessel under a nitrogen atmosphere and the mixture stirred for 16 h. The dispersion was purified using centrifugation and redispersion in water three times. After purification, the latex was freeze-dried and re-dispersed in toluene or CBZ. To aid this
process a few droplets of methanol were added to the dried powder to enable wetting by toluene. The MG had a nominal composition of 99.7 wt. % styrene and 0.3 wt. % DVB.

4.3.3 Preparation of methylammonium iodide

Methylamine solution (76 ml, 0.60 mol) was placed in a 250 ml round-bottom flask and hydriodic acid (80 ml, 0.60 mol) was added slowly to the reaction vessel. The mixture was stirred at 0 °C for 2 h. A white precipitate (methyl ammonium iodide, MAI) was isolated by vacuum evaporation at 60 °C for 4 hours, washed with diethyl ether and then stored at 4 °C.

4.3.4 Preparation of MAPI(C) film

Laser-patterned, ITO-coated glass substrates (20 Ω/sq) were cleaned by ultrasonication in a 2% Hellmanex solution, rinsed with deionized water and IPA, and dried. A TiO$_2$ hole-blocking compact layer (bl-TiO$_2$) (48 nm) was spin-coated at 2000 rpm for 60 s onto the ITO using TDP (0.15 M) solution in 1-butanol and subsequent heating at 125 °C for 5 min. The procedure was repeated using a TDB solution (0.30 M). Titania paste (70 µL, 1:5 in ethanol) was spin-coated onto the cleaned glass slides at 5000 rpm for 30 s to form a mesoporous scaffold (mp-TiO$_2$) with an average thickness of 250 nm. After cooling at room temperature, the MAPI(C) precursor solution was spin coated onto FTO/mp-TiO$_2$ substrate at 2000 r.p.m. for 60 s. The MAPI(C) was formed by spin-coating MAI and PbCl$_2$ (3:1 molar ratio) solution (30 wt.%) in DMF. The film was then dried at 100 °C for 45 min. The capping layer thickness as ~ 250 nm. All films were stored in a desiccator over P$_2$O$_5$ in the dark until investigation.
4.3.5 Preparation of HTM-MG blend film and MG encapsulated film.

The procedure to form the ITO/bl-TiO$_2$/mp-TiO$_2$/MAPI(C) films was described above. P3HT solution was prepared by adding P3HT (15 mg) to toluene (0.865 g) and heating to 70.0 °C. The P3HT solution was spin-coated onto MAPI(C) at 4000 r.p.m. for 30 s to give P3HT thickness of ~ 100 nm. P3HT-MG HTMs were prepared by mixing MG dispersion and P3HT solution. MG (64 mg) was wet by 2 droplets methanol and then added toluene to give a total weight of 1.0 g and then sonicated at 70 °C. P3HT solution (3.0 wt.%) was prepared by adding P3HT (30 mg) in toluene (total weight 1.0 g) and heating to 70 °C. The MG dispersion and P3HT solution were mixed at a weight ratio 0.47:0.53 at 70 °C. Spin-coating was conducted at 4000 r.p.m for 30 s to give a P3HT-MG thickness of ~ 160 nm. The Spiro HTM (450 nm) was spin coated by dissolving Spiro (20 mg) in CBZ. Spiro-MG composite HTMs (~ 160 nm) were prepared using the same procedure as described for P3HT-MG films and CBZ as the solvent. The same procedures as described above were used to prepare devices containing PTAA (~ 120 nm) and PTAA-MG (~ 180 nm) HTMs with the exception that the solvent was CBZ. Selected devices were encapsulated using MG dispersions (3.0 w/w%) in toluene spin coated at 3000 rpm for 30 s onto the top surface at room temperature. The thickness of the MG layer was ~ 145 nm.

4.3.6 Physical measurements

Dynamic light scattering (DLS) measurements were conducted using a 50 mW He/Ne laser operated at 633 nm with a standard avalanche photodiode (APD) and 90° detection optics connected to a Malvern Zetasizer Nano ZS90 autocorrelator. XRD patterns were obtained using a Bruker D8 Advance diffractometer (Cu-Kα). The MAPI(C) obtained in this work were scanned between 10 and 50° with a step size of 0.05. For these measurements the films were prepared and measured under a nitrogen atmosphere. Atomic force microscopy (AFM)
images were obtained using an Asylum Research MFP-3D operating in AC (“tapping”) mode. UV-visible spectra were obtained using a Hitachi U-1800 spectrophotometer. Film thickness measurements were conducted using a Dektak 8 Stylus Profilometer (Bruker). Contact angle measurements were performed using water and a Krüss Drop Shape Analysis (DSA100). PL spectra were obtained using an Edinburgh Instruments FLS980 spectrometer. A 550 nm cut off filter was used for all measurements and the beam was incident on the film surfaces. An excitation wavelength of 480 nm was used for all PL measurements. The substrates were ITO/bl-TiO₂/mp-TiO₂ for the films containing MAPI(C) or glass for P3HT and P3HT-MG.
4.4 Results and Discussion

In this chapter, the polystyrene MG was used in the blend (HTM-MG film) and encapsulated film (shown in scheme 1). The MG was synthesised using SFEP and the conditions of preparation were not same as that in Chapter 3. The rotation speed was significantly lower than that in Chapter 3. In this chapter, we used toluene and chlorobenzene as the two solvents to because these two solvents are good solvents to dissolve P3HT, spiro-OMeTAD, and PTAA, also they are bad solvents for MAPI(C). In Fig 4.1, the DLS data size distribution of MG particles dispersed in water, toluene and chlorobenzene are shown. The sizes of MG particles was smallest, in water $d_z$ value is 281 nm. This is because water is not a good solvent for polystyrene and the particles collapsed. In toluene the MG particles were swollen and $d_z$ value is 529 nm and in chlorobenzene the MG particles were less swollen ($d_z$ is 712 nm) were even larger than those in toluene ($d_z$ is 529 nm). The SEM images of MG particles from (a) water, (b) toluene and (c) chlorobenzene showed in Fig 4.2 in all these three solvent, polystyrene MG particles were monodisperse. The particles sizes in SEM images showed the diameter in water, toluene and chlorobenzene are 280, 300 and 514 respectively. The value shown in DLS is larger than the value shown in SEM because the particles contracted upon drying. The values of particles swelling ration ($Q_p=(d_z/d_z(\text{water}))^3$) could be calculated as 5.7, 6.7, 1.2 in water, toluene and chlorobenzene respectively.
Figure 4.1 DLS data for MG particles dispersed in chlorobenzene, toluene and water respectively.
Figure 4.2 SEM images of MG particles deposited from water (a), toluene(b) and chlorobenzene(c). DLS data for PS MG particles dispersed in water, toluene and chlorobenzene. Particle size data obtained from the SEM and DLS data are shown in the table (d).

<table>
<thead>
<tr>
<th>Dispersant</th>
<th>$d_{\text{SEM}}/ \text{nm}$</th>
<th>$d_{\text{i}} / \text{nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>280(5.7)</td>
<td>281</td>
</tr>
<tr>
<td>Toluene</td>
<td>300(6.7)</td>
<td>529</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>514(1.2)</td>
<td>712</td>
</tr>
</tbody>
</table>

* CV is the coefficient of variation
* $d_{\text{i}}$ is the average diameter

We investigated MG particles film, and Fig 4.3 (a) showed the coverage of MG film increased to 100% coverage when the concentration was 3.0 wt% which was same as the MG particles in Chapter 3. The optical microscopy image showed the surface morphology of M3.0 film (deposited from toluene dispersion), the film was continuous. The contact angle was measured as well, and water droplet was drop onto M3.0 film. The angle of this film was 102° and the film was hydrophobic. In Fig 4.3 (b) AFM images supported optical
microscopy that the morphology of M3.0 film is continuous, which was spin-coated on clean glass substrates from MG toluene dispersion, the MG particles spread to form a monolayer and no overlapped. The sizes of the MG particles were around 400 nm that means the MG particles were flatted after spin-coating.

![Image](image.png)

**Figure 4.3** Optical microscopy and water droplet contact angle (a) and AFM image (b) of M3.0 film deposited from toluene.

Mixed HTM-MG composite films were prepared and investigated in this chapter, from the system established in chapter 3, 3.0 wt. % MG and 1.6 wt. % HTM was used in this research. This concentration composite films are considered to M3.0H1.6 (could be M3.0P1.6 for P3HT-MG film, M3.0S1.6 for P3HT-Spiro film and M3.0T1.6 for P3HT-PTAA film) would be suitable composition to provide efficient polymer solar cells because the conductivities of M3.0P1.6 film showed similar properties as pure P3HT film (discussed in Chapter 3). This
blended HTM-MG films contained 35 wt.% HTM and 65 wt.% MG particles. This concentration could potentially decrease the concentration and cost of HTM comparing with pure HTM film and those where HTM was replaced by MG particles. For the P3HT, we used toluene as a used solvent and for Spiro and PTAA we used chlorobenzene. In Fig 4.4 we show images from these three HTM-MG blend films prepared uses optical microscopy. In Fig 4.4 (a) and (c) showed P3HT-MG film and PTAA-MG film. Both these two film showed a very good morphology. The P3HT-MG blend film is smooth under optical microscopy and PATT-MG film is even smoother than P3HT-MG film looks perfect. However, the Spiro-MG films have some micro-cracks which were absent for the P3HT-MG and PTAA-MG films (Fig 4.4 (b)). The micro-cracks appeared because of the properties of Spiro. These micro-cracks are form by small Spiro molecules cannot interdigitate. Comparing with Spiro, the P3HT and PTAA are obviously interdigitate because of they are polymers. The polymer chains form entanglements and crosslinks generated elastic films, which allow the local strain imbalances caused by the embedded MGs.

![Optical microscopy images](image)

**Figure 4.4** Optical microscopy images of ITO/MAPI(C)/P3HT-MG film (a), ITO/MAPI(C)/Spiro-MG film (b) and ITO/MAPI(C)/PTAA-MG film (c).
AFM images of these three films were investigated as well. The AFM images of the P3HT-MG film are shown in Fig 4.5. Here, the particles could be observed clearly, compacted and tick together without aggregation and the phase between each particle were the P3HT deposited without MG particles. The profile line was analysed to investigate the height difference of P3HT and MG particles. From the profile line, the height difference between top of MG and top of P3HT was around 30 and the RMS roughness was 24 nm. This indicated these presentative particles are flattened. This result was very similar to the MG particles in Chapter 3(Fig 3.11 and 3.12). The only difference is the size of particle.
Spiro-MG blend films were much more different compared to the P3HT-MG film (Fig 4.6). The particles were very clear and they were stack with each other, barely could see the Spiro on this film. Also the height difference of the film are clear, this is a proof of the micro-cracks of Spiro-MG blend film. The micro-cracks only appeared in Spiro-MG film because the mechanical toughness of small molecule Spiro is much worse than large molecule.
polymer. When Spiro-MG dispersion was spin-coated on the substrate, the formation of the film resulting mechanical stress and this stress caused micro-cracks appeared\textsuperscript{22}. These micro-cracks in PSCs may reduce the PCEs of devices or even result the MAPI(C) layer contacts Au layer resulting in short circuit. This profile line was more like the profile line of M3.0 film (Fig 4.2). The morphology of Spiro-MG showed a problem using this kind of film replace Spiro layer because of the non-continuous of the film.
PTAA-MG blend films were observed using the same methods as P3HT-MG films with AFM. The surface morphology is unique under AFM. From Fig 4.7, the AFM images showed a remarkable result, because this AFM image showed the MG particles were well dispersed within the PTAA matrix because of the structure of PTAA and MG without any evidence of phase separation or aggregation.

Figure 4.6 AFM tapping mode image and line profile line of Spiro-MG /MAPI(C) film.
In order to clarify the reason of poor quality of Spiro-MG film, we mixed MG particles and Spiro with varying different concentration and used DLS to measure the particles size of each dispersion concentration. Fig 4.8 shows the DLS results of MG particles size varied the concentration of Spiro changed from 0 to 0.3 (in wt. %), and the concentration of MG particles were kept at 0.10 wt.%. In the range of concentration of Spiro from 0 to 0.10 wt.%, the particles size showed from DLS increased obviously and the peak became boarder which showed MG particles are aggregation. After the concentration of Spiro exceeded 0.15 the DLS data showed there were two clear peaks and the larger one at about 6,000 nm. Hence, Spiro caused the MG aggregation which would account for the less ordered morphologies and greater roughness of Spiro-MG film.
Figure 4.8 DLS of MG particles in chlorobenzene in the presence of different concentration of Spiro-MeOTAD (in wt.%). The MG concentration was 0.10 wt.% The measurements were performed at room temperature.

The surface morphologies of three kinds of HTM-MG blend films showed P3HT-MG and PTAA-MG films are thin continuous and smooth and very similar as pure HTM. Because the surface roughness of macromolecular polymers were very similar as pure HTM film but low molecule semi-conductive material such as Spiro-MeOTAD was not as good as the semi-conductive polymer. The PTAA-MG and P3HT-MG have the potential to be used in PSCs. In the following part of this chapter, we investigated the optoelectric properties of the two semi-conductive polymers, P3HT and PTAA.
Firstly, we investigated the photoluminescence of P3HT/MAPI(C) based combine films to observe the charge transfer properties of P3HT-MG/MAPI(C) combine films and P3HT/MAPI(C) combine films without MG. From the Fig 4.9, the MAPI(C) film showed two sharp peaks at around 720 and 780 nm, which are attributed to P3HT and MAPI(C), respectively. The PL signal from MAPI(C) was superimposed on the signal from P3HT. We measured P3HT film on glass comparing with P3HT/MAPI(C) to separate those two signals. There is a strong scattering of P3HT and P3HT/MAPI(C) films; hence we used the intensities to correct the spectra. Comparing the P3HT PL spectra to the MAPI(C) spectra and P3HT/MAPI(C) spectra, there is a quenching of the emission because of P3HT addition. From the corrected spectra, the quenching efficiencies (Q) can be calculated using $\frac{y-x}{y} \times 100\%$, where $y$ is the PL intensity counts for MAPI (C) and $x$ is the intensity counts for sample. There is around 57.8% quenching for P3HT/MAPI(C) considering there were around 32% light energy was absorbed by P3HT layer (according to the absorption of P3HT film is 0.5). The UV-vis spectrum for the P3HT-MG/MAPI(C) combine film shows a strong absorption in the region of 480 nm, which is stronger than P3HT/MAPI(C) film. However, the PL spectra of P3HT-MG/MAPI(C) film only shown Q=17%. This effect can be explained by the presence of close packed MG particles, which restricted pathways of holes movement from MAPI(C) to the P3HT matrix.
Figure 4.9 The quenching showed in PL spectra of MAPI(C) and MAPI(C)/P3HT films (a), and PL spectra of P3HT film on glass substrate (b). PL spectra of MAPI(C)/P3HT and MAPI(C)/P3HT-MG films and corrected curves (c), UV-vis spectra of MAPI(C)/P3HT and MAPI(C)/P3HT-MG films (d).

PTAA-MG films were different from the P3HT-MG films. PTAA did not cause the scattering. The PTAA/MAPI(C) and PTAA-MG/MAPI(C) composite films showed very strong quenching of the MAPI(C) signal shown in Fig 4.10 and most this quenching are from PTAA between MAPI(C) because the at 480nm the absorption of MAPI(C) is close or higher than PTAA/MAPI(C)and PTAA-MG/MAPI(C). Hence, the quenching efficiencies Q were 98% and 97.5% for PTAA/MAPI(C) and PTAA-MG/MAPI(C) respectively. This result was attributed to a higher efficient transfer of holes movement from the valence band of the
MAPI(C) to HOMO of the semi-conductive polymer than those for P3HT. That meant PTAA has a higher hole mobility and has been suggested to interact more strongly with MAPI(C) than P3HT\textsuperscript{22}. The UV-Vis spectrum of PTAA/MAPI(C) film was very close to MAPI(C) film, but the film with MG particles was more similar like that in P3HT system. The absorbance for the films was low at wavelengths higher than 350 nm and it increased significantly for the film below 350 nm due to light scattering, which indicates a degree of UV protection can provide by the film. UV protection has been found to enhance the stability of PSCs, which indicates, in terms of stability, MG particles had a power potentially.

\textbf{Figure 4.10} PL spectra of MAPI(C), PTAA/MAPI(C) and PTAA-MG/MAPI(C) film (a), and UV-vis data of MAPI(C), PTAA/MAPI(C) and PTAA-MG/MAPI(C) film (b).

The XRD was used to investigate the physical and chemical changes of MAPI(C) with HTM-MG film. From the former investigation, the MG particles have no effect on physical morphology. Hence XRD was used to detect the size and sharp of MAPI(C) crystal and analysed whether MAPI(C) was damaged by HTM-MG. From Fig 4.11, there were three peaks in both P3HT-MG and PTAA-MG MAPI(C) films on 14°, 28.5° and 33°. These three
peaks were MAPI(C) significant signal peaks, (110), (220), (310) and there was no signal of PbI$_2$ or PbCl$_2$ peak which meant the MAPI(C) layer was not damaged by MG additives.

**Figure 4.11** XRD data spectra of P3HT-MG/MAPI(c) (a) and PTAA-MG/MAPI(c) (b) films.

MG particles were to not only mix with HTM and spin coated as a continuous film; they could be used as encapsulation layers for PSCs. Here we spin coated 3.0 wt.% MG dispersion (M3.0) on to MAPI(C) film to make an encapsulated MAPI(C) film and investigated morphologies of this MG encapsulated MAPI(C) film. Fig 4.12(a) shows an AFM image of MAPI(C) film and (b) shows an MG film (MAPI(C)/MG encapsulation). Comparing (a) and (b), MAPI(C) did not cover the whole substrate and left some holes, after MG particles spin-coated on MAPI(C) the holes were filled by MG particles which indicate a good film ability of MG particles. The line profiles of MG encapsulated film is shown and the roughness of the MG encapsulated film was very close to the flatted MG particles which demonstrate the MG layer on MAPI(C) layer is a monolayer.
**Figure 4.12** AFM tapping mode images of MAPI(C) film (a) and MG encapsulated MAPI(C) film (b). The insert image is the profile-line for each AFM image.

The film-forming ability of MG particles is shown in Fig 4.12 because the full coverage of and the good morphology of this MG film could protect MAPI(C). Hence, the ability of this kind film was investigated in optical properties. Fig 4.13 showed the PL and UV-Vis spectra of the MG encapsulated MAPI(C) film. Comparing the UV-Vis spectra of normal MAPI(C) film, the MG encapsulated MAPI(C) film showed the absorbance had a slightly increase. This increase may have been caused by the scattering of MG layers beyond the MAPI(C) and there is no evidence showed the MAPI(C) layer was damaged by MG encapsulated layers.
Figure 4.13 PL emission spectra of MAPI(C) and MAPI(C)/MG encapsulation film (a), UV-Vis absorption spectra of MAPI(C) and MAPI(C)/MG encapsulation film (b).

Fig 4.14 shows the XRD spectrum of three different films. They were investigated to observe the crystals of MAPI(C) in these three kinds of films and compare the MG encapsulated MAPI(C) and blend film to normal MAPI(C) film to check whether the MAPI(C) crystals was damaged by MG. From the Fig 4.14, we could find the positions of the signal peaks of MAPI(C) showed in a correct position and we could use the width of 110° peak to calculation the size of MAPI(C) crystal.

The Scherrer equation could be used to calculation the size of crystals from the broadening of a peak$^{23}$.

$$\tau = \frac{K\lambda}{\beta\cos\theta}$$  \hspace{1cm} (4.28)

Where,

$\tau$ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size;

$K$ is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite;
\( \lambda \) is the X-ray wavelength;

\( \beta \) is the line broadening at half the maximum intensity (FWHM).

\( \theta \) is the Bragg angle (in degree).

From this equation, we used peak (110) to calculate the average size of crystals in MAPI(C) film, MG encapsulated film and HTM-MG/MAPI(C) are 148, 121 and 94 nm. The decreasing of crystal sizes when MG particles added in which may cause the current density of PSCs to decrease\textsuperscript{24}, but this change are not affect too much and polystyrene MG is an available insulating polymer which could be used in PSCs. These data predict the efficiencies of MG encapsulated and HTM-MG/MAPI(C) devices may not as good as MAPI(C) cells.

**Figure 4.14** XRD data spectra of MAPI(C) film, MG encapsulated MAPI(C) film and HTM-MG films.
4.5 Conclusions

We designed three different HTM-MG/MAPI(C) films and MG encapsulated MAPI(C) film; we measured morphologies and UV-vis and PL abilities of all these films. We found when the MG particles added into the MAPI(C) films, the blend films and MG encapsulated films presented different morphologies. HTM-MG/MAPI(C) film shows MG mixed with HTM and the MG form blocking island in HTM matrix, which is totally different from the morphology of MG encapsulated MAPI(C) film. In MG encapsulation MAPI(C) film, the MG shows an excellent film forming properties and the MAPI(C) layer can be covered well. For HTM-MG film, PTAA-MG and P3HT-MG films present the good morphologies because they are larger molecule polymer have a good mechanical properties. By contrast Spiro gave inferior blended films that tended to cracking and Spiro also causes MG particles aggregation which may result in low power conversion efficiency values when this film used in solar cell. PTAA-MG film and P3HT-MG film showed a great potential to replace the HTM layer in PSC. Whilst the MGs used here were based on polystyrene in this study, and there is a great deal of scope for varying the size and also functionalising them for groups that could help with Pb capture and these small size and functionalised MG have a potential to be used in HTM layer in the future. The present work shows that introduction of MG particles is a method that may be used in PSCs, and this is investigated in next chapter.
4.6 References


24 Kim, Mi Kyung, et al. "Effective control of crystal grain size in CH$_3$NH$_3$PbI$_3$ perovskite solar cells with a pseudohalide Pb (SCN) 2 additive." *CrystEngComm* 18.32 (2016): 6090-6095
Chapter 5. A study of microgel dual roles in perovskite solar cells

5.1 Abstract

Perovskite solar cells (PSC) have attracted a lot of interest due to their good performance. However, this kind of cell is not very stable and easily decomposes. Moisture, UV-light, oxygen and temperature are the four key factors that affect the stability of perovskite cells. In this chapter we use the microgel (MG) particles which were investigated in chapters 3 and 4 to enhance the stability of the PSCs. We used a film of MG particles as an encapsulating layer and also added MG particles into the hole transport material (HTM) layer to form a blend layer for PSCs. We found both of these two methods increased PSC stability and did not decrease the efficiencies greatly. We investigated three different HTMs in this chapter. Poly(3-hexylthiophene)(P3HT), poly(triaryl amine) PTAA and Spiro-OMeTAD (Spiro). The PTAA-MG blend layer PSCs showed a good result of efficiency which was better than Spiro-blend layer and P3HT-blend films PSC. The PTAA and P3HT used in these devices was around 35 Vol.%. The efficiencies for the PTAA-MG devices and P3HT-MG devices decreased by only around 20%. This result shows the MG particles diluted PTAA and P3HT matrix greatly but did not affect the devices by the same ration of dilute. We also found that the MG particles can be dispersed well within PTAA matrix and it can strengthen the quenching of the perovskite fluorescence. Moreover, the open circuit voltage ($V_{oc}$) for the P3HT-MG devices increased 0.17 V (around 20%) compared to the unmodified devices. The stabilities of P3HT based devices were investigated as well. The MG-blend devices and MG encapsulated devices showed better stabilities than normal unmodified devices. Results from stability tests supported the results of the
Both MG-blend devices and MG encapsulated devices remained operational for more than one month.

### 5.2 Introduction

Organmetal halide PSCs of the composition $\text{[MACH}_3\text{NH}_3\text{PbX]}$ (X=halide) have been widely studied recently, because of their impressive power conversion efficiencies (PCE)\textsuperscript{1-3}. The maximum PCE reported is over 20%\textsuperscript{3,4}. Although the perovskite solar cells (PSCs) have an extremely high PCE, the stability is the Achilles' heel of this kind of solar cell\textsuperscript{5,6}. Because the degradation of perovskite will result in lead (as lead ions) leaking out which is a highly poisonous to human body and also the stability restricts the PSCs applications outdoors\textsuperscript{7-9}. Perovskites are very sensitive to moisture, UV light, oxygen and temperature\textsuperscript{8-10}. Moisture is a key factor causing degradation which happens because $\text{H}_2\text{O}$ cause decomposition of perovskite\textsuperscript{10,11}. Hence, one of the key challenges of PSCs is keeping it away from water. The HTMs used in PSCs play a very important role in determining the device performance. Spiro-OMeTAD is the most widely-used HTM in perovskite and P3HT and PTAA are widely used as well\textsuperscript{12-14}. The cost of PTAA is much higher than P3HT and Spiro. However, Spiro and P3HT are still very expensive for commercialisation and widespread deployment\textsuperscript{15,16}.

MG dispersions are inherently colloidally stable because the constituent particles are swollen\textsuperscript{17-19}. MG particles can form excellent films and are used in surface coatings\textsuperscript{20}. Polystyrene MG was found useful and efficient at increasing the light absorbance and PL intensity of P3HT in Chapter 4. Here, we used polystyrene MG particles because like all MG particles they are deformable in the swollen state and flatten when deposited onto SEM grids.
MG particles are interesting here because they can form continuous and smooth films easily and can be functionalised for many other usages\textsuperscript{21,22,23}.

In the previously chapter, we found all three hole transfer materials (HTMs), PTAA, P3HT and Spiro solutions and polystyrene MG dispersion could be mixed and films made by spin coating\textsuperscript{21}. Here we designed two different PSCs using MG particles. One used MG as an encapsulated layer and the other used MG particles mixed into HTM solutions (Fig 5.1). The MG-HTM blend films replaced the HTM layer of PSCs \textsuperscript{5,24,25}. Previous research has used Al\textsubscript{2}O\textsubscript{3} was used as an atomic layer\textsuperscript{26} and Teflon casted from solution\textsuperscript{27,28} has been reported. However, in these encapsulation methods, high vacuum or specialist equipment are needed. Here, we use MG dispersion which has a good film forming properties that can offer a simple and low-cost encapsulation layer. We investigated that the performance of MG encapsulation devices and placed the cells in a humidity of 85\% humidity chamber to accelerate the degradation.

In this chapter we first compare the three HTMs in devices. We found the MG particles did not affect PCE of cells greatly for P3HT-MG or PTAA-MG devices. But spiro-MG devices did not show the same result as P3HT and PTAA devices. All of the four parameters decreased which meant MG particles affected the Spiro greatly. Therefore, MG plays a dual role in P3HT-MG and PTAA-MG devices. MG particles can dilute P3HT and PTAA matrix in PSC with a slightly decreasing of efficiencies, also the stabilities of PSCs increase significantly with MG particle in both MG encapsulation devices and HTM-MG blend devices. Also we studied stability the cells under a normal environment as a control. MG encapsulation devices could maintain performance for over one month which is three times longer than normal unmodified devices. Interestingly, P3HT-MG encapsulation devices showed elatively good stabilities which were similar as MG encapsulation device.
and they could operate for one month as well.

5.3 Experimental

5.3.1 Perovskite solar cell fabrication

The solution used to prepare the mixed perovskite was prepared as follows. MACl and PbI₂ (3:1 molar ratio) were added into anhydrous N,N-dimethylformamide (DMF) at room temperature to achieve a 30 wt.% solution. P3HT precursor solution preparation was prepared by adding P3HT (15 mg) into toluene (0.865 g) and heating to 70.0 °C. and Li-TFSI salt and t-BP (10 µl each) in acetonitrile were then added into the P3HT solution. ITO glass substrates with a sheet resistance of 20 Ω sq⁻¹ were cleaned by ultrasonication in a 2% Hellmanex solution, and rinsed with boiling water, IPA, 1M sodium hydroxide solution and dried. The PSCs were fabricated on cleaned ITO-coated glass substrates. A TiO₂ blocking layer (bl-TiO₂) was spin-coated at 2000 rpm for 60 s onto the clean substrates using TDB solution in 1-butanol (0.15 M) and subsequent heating at 125 °C for 5 min. The procedure was repeated using TDB solution (0.30 M). TiO₂ paste (70 uL 1:5 in ethanol) was spin-coated on bl-TiO₂ layer and annealed at 500 °C for 30 min to form a mesoporous scaffold (mp-TiO₂) layer. After cooling to room temperature, a MAPI(C) precursor solution was spin-coated onto the mp-TiO₂ layer at 2000 r.p.m. for 60 s. After the MAPI(C) layer was deposited, the P3HT precursor solution was spin coated onto MAPI(C) at 4000 r.p.m. for 30 s. Finally, a gold layer (80 nm) was deposited by thermal evaporation at 10⁻⁷ mbar.

M3.0P1.6 film was made by mixing the MG dispersion and the P3HT solution. MG (64 mg) was wet by 2 droplets methanol and then added toluene till the total weight was 1.0 g then
sonicated at 70 °C and P3HT solution (3.0 wt.%) was prepared by adding P3HT (30 mg) into toluene (total weight 1.0 gram) and heating to 70 °C. The MG dispersion and P3HT solution was mixed as weight ratio 0.47:0.53 and then heating the mixture blend at 70 °C and LiTFSI and t-BP in acetonitrile were added into mixture.

The mixture was spin coated onto the substrate at 4000 r.p.m for 30 s. MG (46 mg) was wet by 2 droplets methanol and then added toluene until the total weight reached 1.0 gram and then sonicated under 70 °C. The MG dispersion was spin coated after gold coating using 3000 r.p.m for 30 s to form a MG encapsulation device.

M3.0S1.6 film was made by mixing MG dispersion and Spiro solution. MG (64 mg) was wet by 2 droplets methanol and then added chlorobenzene until the total weight was 1.0 g and then sonicated at 70 °C. Spiro solution was prepared by adding Spiro (30 mg) into chlorobenzene (total give a total weight of 1.0 g) and heated to 70 °C. The MG dispersion and Spiro solution was mixed as weight ratio 0.47:0.53. The mixture blend was heated at 70 °C and LiTFSI and t-BP in acetonitrile were added into mixture. The mixture blend was spin coated onto the substrate at 3000 r.p.m for 60 s.

M3.0T1.6 (T is used as the symbol for PTAA) film was made by mixing MG dispersion and PTAA solution. The MG dispersion was prepared using MG (64 mg) in CBZ at room temperature with a total dispersion weight of 1.0 g. PTAA solution (3.0 wt.%) was prepared by adding PTAA (30 mg) to CBZ (total weight 1.0 g) at room temperature. The MG dispersion and PTAA solution were then mixed at a weight ratio 0.47:0.53. LiTFSI (15 μl, 170 mg/ml) and t-BP (7.5 μl) were added. The PTAA films were formed by spin-coating at 4000 r.p.m for 30 s.

Devices were encapsulated using MG dispersions (3.0 w/w%) in toluene spin coated onto the top surface at room temperature.
5.3.2 Physical measurements

XRD data were obtained using a Bruker D8 Advance diffractometer (Cu-Kα). Films were scanned between 10 and 50° with a step size of 0.05. The films were prepared and measured under a nitrogen atmosphere.

UV-visible spectra were obtained using a Hitachi U-1800 spectrophotometer.

Film thickness measurements were conducted using a Dektak 8 Stylus Profilometer (Bruker).

5.3.3 Device Measurements

The current density-Voltage (J-V) curves were measured using a sourcemeter (2440A, Keithley at 100 mA/cm² illumination AM 1.5G and a calibrated Oriel Si-reference cell certificated by NREL (National Renewable Energy Lab) with a solar simulator (Oriel SOL3A, Orient). There were 8 devices in one substrate for each of three cells were measured using a metal mask with 0.025 cm² active areas. The data shown are from the reverse scan and the sweep rate was 100 mVs⁻¹.
5.4 Results and Discussion

5.4.1 Devices preparation and measurement

In the last chapter, we investigated different HTMs containing MG particles. They showed the ability to form continuous and semi-conducting films. Hence, in this chapter these films were used in PSCs and we compare these cells to a standard PSC device (without MG particles) and MG encapsulated PSCs. In Fig 5.1 the architectures of three different solar cells containing MG particles are shown and the MG encapsulated cell PSC is also shown.
Figure 5.1 Schematic of (a) normal PSC without MG (unmodified cells), (b) HTM-MG blend PSC and (c) MG encapsulated PSC.
In Fig 5.2 (a) the champion J-V curves of P3HT PSC are shown and the curves of P3HT-MG cells are also shown (Fig 5.2(b)). The average current density of P3HT PSC is around 14.7 mA/cm² which is much larger than the P3HT-MG blend PSC (less than 10.9 mA/cm²). However, a remarkable and unexpected result from table 5.1 is that the voltages of these two kinds of solar cells are changed unexpectedly. After MG added in, the $V_{oc}$ value of the P3HT-MG cells is much higher than unmodified P3HT device and the improvement was almost 0.2 V. The $V_{oc}$ of P3HT-MG blend device measured as around 0.9 V and is similar to that reported by Gatti et al²⁹. From the P3HT-MG devices shown, MG particles could increase the $V_{oc}$ of P3HT-MG devices, because the MG particles reduce the contact of P3HT and the mp-TiO₂. Less contact can result in decreasing of the shunt resistance.

**Figure 5.2** Champion J-V curves for P3HT (a) and P3HT-MG cells (b).

The J-V curves of PTAA based PSCs (PTAA unmodified devices and PTAA-MG blend devices) are shown in Fig 5.3 The average PCE value of PTAA unmodified device is around 11.23% which was much higher than P3HT base devices and both $J_{sc}$ and $V_{oc}$ increased which caused the PCE value increase. The PTAA-MG blend devices showed a high PCE value as well. The $J_{sc}$ of PTAA-MG blend device was lower than the PTAA device and the
$V_{oc}$ was slightly higher (shown in Table 5.1). The PTAA based devices did not have the same results as the P3HT devices and $V_{oc}$ did not increased For PTAA-MG devices. This is because of a better MG distribution than P3HT-MG blend film and MG did not affect the contact of HTM and mp-TiO$_2$ and hence the shunt resistant was not.

![Figure 5.3 Champion of J-V curves for PTAA (a) and PTAA-MG (b) cells](image)

The J-V curves of Spiro-MeOTAD as HTM (Spiro and Spiro-MG blend) are also shown in Fig 5. 4. The average PCE for the unmodified device Spiro was 8.6% , the current density was around 21.4 mA/cm$^2$ and the $V_{oc}$ was around 0.88V which is comparable to other mixed halide perovskite device but when the MG added in the device. Spiro-MG blend solar cells were quite low efficiency from P3HT and PTAA based PSCs. The PCE value of the Spiro-MG device was only 1.0% and was much lower than the other two MG-blend cells. This effect may be caused by the poor film-forming properties of M3.0S1.6 film (this was mentioned in last chapter). The M3.0S1.6 film showed a lot of micro-cracks even from optical microscopy, and these microcracks undermined the integrity of the Spiro layer and would have allowed Au come into contact with perovskite and reducing performance.
Table 5.1 shows the average of the four the parameters for all the MG-blend perovskite device and unmodified perovskite devices. From this Table, we can see all the MG containing device had lower PCE values compared to the unmodified P3HT and PTAA devices. The remarkable and unexpected result was the P3HT-MG and PTAA-MG devices only contained 35 wt % of HTM (P3HT and PTAA) compared conventional P3HT device and PTAA device, but the efficiencies of P3HT-MG and PTAA-MG devices do not decrease in same ratio. The decrease of P3HT-based devices and PTAA base devices were 20.0% and 21.7% respectively. In terms of the total mass of P3HT and PTAA was 65% less than conventional devices and the decrease for MG-based devices, the result showed that the MG particles could be used to the economics of conjugated polymers as HTMs for PSCs. Meanwhile, if the PCE / weight fraction of conjugated polymer used in the HTMs are compared then the values for the PTAA-MG and P3HT-MG devices are a factor of ~ 2.3 higher than those for the respective PTAA and P3HT devices.

Table 5.1 Four solar cell metrics of the devices.
<table>
<thead>
<tr>
<th>Device.</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>14.7 ± 0.62</td>
<td>0.71 ± 0.02</td>
<td>0.64 ± 0.04</td>
<td>6.64 ± 0.65</td>
</tr>
<tr>
<td>P3HT-MG</td>
<td>10.9 ± 0.7</td>
<td>0.87 ± 0.01</td>
<td>0.56 ± 0.05</td>
<td>5.31 ± 0.44</td>
</tr>
<tr>
<td>P3HT/MG(en)</td>
<td>13.5 ± 0.48</td>
<td>0.68 ± 0.04</td>
<td>0.56 ± 0.03</td>
<td>5.06 ± 0.45</td>
</tr>
<tr>
<td>Spiro-MeOTAD</td>
<td>21.4 ± 2.0</td>
<td>0.88 ± 0.04</td>
<td>0.46 ± 0.02</td>
<td>8.62 ± 0.34</td>
</tr>
<tr>
<td>Spiro-MG</td>
<td>4.0 ± 1.5</td>
<td>0.42 ± 0.12</td>
<td>0.38 ± 0.02</td>
<td>0.60 ± 0.12</td>
</tr>
<tr>
<td>PTAA</td>
<td>17.8 ± 0.46</td>
<td>0.99 ± 0.01</td>
<td>0.67 ± 0.01</td>
<td>11.23 ± 0.51</td>
</tr>
<tr>
<td>PTAA-MG</td>
<td>13.7 ± 0.23</td>
<td>0.96 ± 0.04</td>
<td>0.66 ± 0.02</td>
<td>8.79 ± 0.46</td>
</tr>
</tbody>
</table>

Fig 5. 5 showed cross-section of P3HT base PSC, and this could be compared with structure showed in Fig 5.1(a). The SEM cross-section showed thicknesses of each layer. The blocking TiO$_2$ layer was around 50 nm, the mp-TiO$_2$ and perovskite capping layer was around 500 nm. The P3HT and Au layers were 100 nm and 80 nm respectively.
MG particles could not only be used in HTM layer, but they could be used as an encapsulation layer. The MG encapsulated devices showed different result as P3HT-MG blend devices and P3HT devices. The $J_{sc}$ was around 13.5 mA/cm$^2$ and the $V_{oc}$ was around 0.68 V.
Figure 5.6 Champion J-V curve for an MG encapsulated PSC.

Fig 5.7 showed cross-section of MG encapsulated P3HT PSC, and this could be compared with structure showed in Fig 5.1. The SEM cross-section showed thicknesses of each layer can be measured. The blocking TiO$_2$ layer was around 50 nm, the mp-TiO$_2$ and perovskite capping layer was around 500 nm. The P3HT and Au layers were 100 nm and 80 nm respectively, all of these thicknesses were very close to the P3HT PSC and beyond Au layer there was a MG encapsulated layer which was around 140 nm thick. The thickness of MG encapsulated layer is much smaller than the diameter MG particles because after spin-coating the MG particles are all flattened.
5.4.2 Devices stabilities

Because P3HT is cheaper than PTAA (around one to ten), it is possible to scale up P3HT-MG devices to commercial usage. We used P3HT base device as basic system to investigate the stability improvement of PSC. We used two different methods to investigate the stability, accelerated aging and normal aging. In accelerated aging, we kept films and devices at room temperature in a humidity chamber (shown in Fig 5.8) of which the humidity was at 85%. We used XRD to detect the perovskite crystals changes after keeping in humidity chamber for 0, 15, 30 and 45 mins. MG encapsulated perovskite film was compared with pure perovskite film. In Fig 5.9, the peaks of normal perovskite films (non-encapsulated) before exposure to humid air showed diffraction peaks at 14.6°, 28.6° and 43.3° confirmed the MAPI(C) structure with lattice parameter with $a = b = 8.85 \text{ Å}$ and $c = 12.64 \text{Å}$. There was no evidence of a PbI$_2$ peak (at 12.6°) for those films. After exposing the normal perovskite films to humid air the PbI$_2$ emerged after 15 min for the non-encapsulated film (Fig. 5.9 b). This peak showed the MAPI (C) layer begins to decompose. Whereas, the same peak emerged after 30 min for the MG-encapsulated film (Fig. 5.9 a). The degradation of the non-encapsulated...
MAPI(C) layer is much faster than MG encapsulated MAPI(C), because the MG layer prevents moisture coming in the device and improves the stabilities of MAPI(C). The changes were quantified using the amplitude fraction of the perovskite (110) peak with respect to the PbI$_2$. These data confirm that the encapsulating MG particles were able to slow the rate of PbI$_2$ formation.

**Figure 5.8** The photos of controlled humid chamber (a) and temperature and humidity controller (b)
Figure 5.9 Accelerated aging perovskite film (a) and MG encapsulated perovskite film (b) XRD data obtained at 85% humidity at room temperature.

The UV-Visible spectra for MG encapsulated film, P3HT-MG blend film and normal P3HT film were investigated (Shown in Fig 5.10). The MG encapsulated film and P3HT-MG blend film changed a little over 45 mins in humid chamber at 85% humidity. In contrast, the spectra
for the non-encapsulated normal film showed major decreases in the absorbance at 500 and 750 nm even in 15 mins. Following the latter, the absorbance at 500 nm (Fig 5.10(c)) and 750 nm (Fig 5.10(d)) was used to monitor stability in terms of light absorption. The relative absorption for the MG encapsulated film and P3HT-MG film was unchanged after 45 min; however, for the unprotected film changed this parameter decreased substantially after 30 min. These data demonstrate that MG prolonged perovskite stability.

**Figure 5.10** Accelerated aging perovskite film (a) and MG encapsulated perovskite film (b) UV-Vis data obtained at 85% humidity at room temperature. 500 nm (c) and 750 nm (d) are the absorbance of encapsulated film and normal film change trends vs time.
To investigate the ability of MG encapsulation to improve device stability the cells with and without encapsulation, we placed MG encapsulated devices, P3HT-MG blend devices and normal P3HT perovskite devices into the humidity chamber and scanned the J-V curve at a regular intervals. The four major parameters of devices revealed the significant differences for these three kinds of perovskite devices. The unmodified device (non-MG added in) degraded very rapidly and effectively ceased functioning after 20 min. The data for the device containing MG (both encapsulated and blend) degraded more slowly and retained their function at 45 min. The initial degradation of the MG encapsulated device was slowest. These results demonstrate the MG slowed the rate of moisture attack, which is attributed to an increase in hydrophobicity of the films and the tendency of MG particles to form intermeshed domains.
Figure 5.11 Accelerated aging cell four parameters data current density (a), open-circuit voltage (b), fill factor (c) and PCE (d) obtained at 85% humidity at room temperature.

Devices were also stored in the laboratory environment with 40% humidity for a long term period to investigate cell ageing (Fig 5.12) Once again, the rate of degradation for the encapsulated film was greatly diminished compared to the unmodified device. The PCE for the MG encapsulated device did not significantly decrease for ~ 30 days which agrees favourably with the results of Hwang et al\textsuperscript{17}. They used a Teflon coating for encapsulation. In contrast, the PCE for the unmodified device decreased to zero within 2 days. The half-life of the device ($t_{1/2}$) is defined as the time taken for the PCE to reach half the original value. Accordingly, the $t_{1/2}$ values for the P3HT, P3HT-MG and MG encapsulated devices were 0.5,
26 and 41 days, respectively. It is remarkable that the P3HT-MG blend showed improved stability which demonstrates the within the HTM the MG particles were able to play a dual role of HTM extender and stability enhancer. It is noted that at the longest times studied (77 days) the PCE of the device was actually higher than that for the MG encapsulated device. The inability of the MG particles to prevent very long term degradation may be due to ingress of moisture and oxygen.

Figure 5.12 Long term performance for P3HT solar cell, MG encapsulated P3HT solar cell and P3HT blend solar cell stored in vacuum conditions. Four parameters of solar cells current density (a), open-circuit voltage (b), fill factor (c) and PCE (d) were measured.
5.5 Conclusions

In this study, we designed four different PSCs. HTM-MG layers were used to replace HTM layers in devices and normal perovskite cells with MG encapsulation. We measured the PCEs of all three MG-containing cells and found that the MG particles added into the PSC mostly preserved the PCE for the P3HT and PTAA-containing systems. Indeed, due to percolation this enabled around 65% less HTM to be used. This good result made possible by the good MG dispersion stability prior to spin coating. By contrast Spiro-MeOTAD gave worse blend films which tended to crack which results in low PCE values. The good film formation tendency and hydrophobicity of MGs enabled them to be used to provide an encapsulation layer over the perovskite which increased device stability. Also, the MG particles used here were based on polystyrene and there is plenty of scope for varying the size and also functionalising their link groups that could help with lead ion capture. The stabilities of P3HT-MG devices and PTAA-MG devices increased significantly when measured in short term accelerating tests or long term tests. Consequently, the MG particles had dual roles in PSC. They more than halved the conjugated polymer weight fraction/PCE ration for the PSCs, and provided increased stability The present work showed that introduction of polystyrene MG particles (which could be made on the tonne scale) is a method that may increase the cost-effectiveness of conjugated polymers within future large scale PSCs.
5.6 References


Chapter 6. Conclusion and future works

6.1 Summary of conclusions

The main aim of this research is to design a HTM-MG system to form the most suitable composite films to replace the HTL in PSCs. We found the dual usage of MG to increase the stability of PSCs. The morphology, conductivity, photophysical property, PCE and stability were measured in the research to study MG, HTM-MG film and PSCs containing HTM-MG.

In Chapter 3 the morphology and photophysical properties of P3HT-MG composite film have been investigated for the first time. Both monolayer and multilayer P3HT-MG films were prepared and the transition to multi-layer films was determined by the concentration of MG. The MG was highly fattened in film form. However, they became less flattened as the concentration of P3HT increased. The MGs were able to scatter light effectively and this contributed to improved P3HT light absorption. Hence, we established a system of the concentrations of MG dispersion and P3HT solution. We compared with morphology and absorbance, structural order, thickness and PL intensity. The results of this study imply that the light absorption of conjugated polymer is enhanced by the inclusion of MGs within the conjugated polymer composite films. We found 3.0 wt.% for MG is the maximum concentration for monolayer formation and has a strong effect on light absorption. In our system, the composite of the M3.0P1.6 film has the most promising future in PSCs because the MG particles were deposited as a monolayer with large portions of closely packed MG particles. The film also had thicknesses within the normal PSC range and strong P3HT light absorption and PL intensities were evident.
After the P3HT-MG system was established, in Chapter 4, we used other two hole transfer materials Spiro and PTAA, and P3HT to mix with MG particles. We prepared three different HTM-MG films with concentration of MG 3.0 wt.% and HTM 1.6 wt.% and investigated these three kinds of composite films using SEM, AFM, UV-Vis and PL. PTAA-MG film showed an unexpected morphology, the MG particles dispersed well in the film and the PL showed a strong quenching for this film. However, Spiro-MG film showed some micro-cracks after spin-coating, which could result in relative low PCE of PSCs. Also, MG encapsulated MAPI(C) films were investigated as well. The MG particles can form a good continuous film on MAPI(C) layer, and the stabilities of MAPI(C) increased significantly when the films were stored in a 85% humid chamber.

In Chapter 5, we replaced HTL layer in PSCs by HTM-MG composite film and measured the PCE. The PCE values for devices containing P3HT-MG and PTAA-MG films decreased only around 20% compared to the control PSCs containing P3HT and PTA respectively. This is despite the fact that the concentrations of HTM in PSCs decreased by around 65%. Interestingly, the $V_{oc}$ values of P3HT-MG devices increased around 0.17 V. The stability of P3HT-MG, PTAA-MG and MG encapsulated devices were measured and compared with control devices. The stabilities of MG containing devices (both HTM-MG composite devices and MG encapsulated devices) increased significantly. Consequently, MG particles can play dual roles in PSCs. MG particles can halve the conjugated polymer weight fraction / PCE ration for PSCs and increase the stabilities of PSCs as well.
6.2 Future works

The results of this research showed MG particles have a good potential in PSCs. We only studied PS MG particles can increase the stability of PSCs in dual ways, the functionalised MG usages in PSCs are worthy of digging further. One possible proposal was using MG to capture the Pb ion\(^1\) when the PSCs decomposed and MG can make PSCs more eco-friendly. Moreover, there the sizes of MG are several hundred nm, the smaller size gel such as nanogel can be investigated as well. The sizes of nanogel are smaller and can form a smoother film. The light sensitive nanogel\(^2\) also can be tried in PSCs.

In this study, we only investigated MG particles mixed with HTM. However, the mixture of MG and other layers can be investigated. Both mp-TiO\(_2\) layer and MAPt(C) layer could be tried in our method.
6.3 References


Appendix

Published works


Co-author Works


