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One-Step Fiber Laser Fabrication of Mesoporous and Compact TiO₂ Layers for Enhanced Performance of Dye-Sensitized Solar Cells

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Abstract: Mesoporous TiO₂ structure (mp-TiO₂) with a compact TiO₂ blocking layer (bl-TiO₂) has been recognized as an effective photoanode for high performance dye sensitized solar cells (DSSCs). However, producing both mesoporous and compact TiO₂ layers by conventional methods requires high temperature furnace process via a two-step manufacturing route. Here, a one-step laser technique has been successfully developed to generate both mesoporous and compact TiO₂ layers on tin doped indium oxide (ITO) coated glass by a millisecond pulsed fiber laser with a wavelength of 1070 nm in ambient atmosphere. Compared with conventional furnace processes, the laser process exhibits a significant reduction of overall fabrication time from 5 h 20 min to 2 min. More importantly, the DSSCs fabricated by the laser process shows a remarkable improvement with the maximum power conversion efficiency (PCE) by 34% compared with the DSSCs fabricated by the furnace. The short-circuit current density (J_{sc}) reaches 16.5 mA cm⁻² for the DSSCs fabricated by the laser process while 10.6 mA cm⁻² is obtained for that fabricated by the furnace process. The improvement is associated with the increased dye adsorption, decreased charge transfer resistance and increased electron lifetime of the TiO₂ photoanode fabricated by the laser process.

Keywords: DSSC; laser; one-step; mesoporous; compact; TiO₂

Introduction

Mesoporous TiO_2 (mp- TiO_2) has been considered as a benchmark material in a wide range of applications including hydrogen generation, photocatalysis and thin film photovoltaics, in conjunction with dyes sensitized, quantum dots, and more recently the metal-organic perovskites solar cells.¹⁻⁴ This is due to a combination of physical properties that are inherent to the TiO_2 and its particular structuring, in addition to its chemical/optical stability and commercial availability.⁵ For dye sensitized solar cells (DSSCs), mesoporous TiO_2 structure offers high surface area resulting in an efficient loading capacity of dye molecules.⁶ In addition, its fast electron transport ability and prominent light scattering effect makes it the most promising candidate for DSSC applications.⁷ However, the mesoporous structure results in direct contact between electrolyte and transparent conductive oxide (TCO) layer, enhancing electron/hole recombination. Therefore, some work has been reported to introduce a compact TiO_2 blocking layer (bl- TiO_2) at the interface to effectively increase the performance of DSSCs by reduction of the back-electron transfer and charge recombination.⁸⁻¹¹ The blocking layer has been also reported to be essential to maintain efficient charge generation under low light conditions, at which DSSCs perform well compared with common semiconductor-based photovoltaic devices.¹² However, fabrication of mesoporous and compact TiO_2 layers by conventional methods requires high temperature furnace process via a time-consuming two-step manufacturing route.

Firstly, conventional fabrication of mesoporous TiO_2 layer is carried out in furnace at 450-550°C for 30 min to remove organic binders and form appropriate interconnection between TiO_2 nanoparticles.¹³ If the time consumed from ramp-up and cool-down processes in furnace is taken into account, the entire fabrication process of TiO_2 mesoporous often takes

longer than 3 h.¹⁴ Such long process significantly limits the possibility of rapid manufacture of DSSCs, especially for roll-to-roll production of DSSCs on metallic substrate.¹⁵ In addition, occurrence of irregular bending of glass substrate was reported due to the thermal stress induced by the long thermal process.¹⁶ On the other hand, it is difficult to fabricate the multifunctional or integrated devices on the same substrate with the DSSCs due to the integral heating process by furnace or oven.¹⁷ Up to date, several alternative methods have been introduced to replace the conventional furnace or oven sintering process for the DSSCs. These methods includes flame annealing, UV irradiation, microwave irradiation, near infrared (NIR) heating, flame annealing and O₂ plasma sintering.^{14,15,18–21}

Secondly, formation of a compact TiO₂ blocking layer using chemical methods also requires a temperature above 450°C to achieve appropriate crystallization from amorphous phase,²² although atomic layer deposition, thermal oxidation, TiCl₄ chemical bath deposition as well as electro-deposition have been also reported in the literature.^{12,23–25} Among various chemical techniques, spin coating and spray pyrolysis are two representative solution processes.²⁶ Spin coating involves dipping a few drops of a solution containing a diluted titanium precursor onto TCO-coated glass, and then spinning at high spinning velocity and baking the substrate at 400-500°C in the furnace sequentially to form the compact TiO₂ layer.²⁷ Spray pyrolysis involves the use of an atomizer to spray a titanium precursor onto a heated substrate at a temperature of 450°C;² the precursor droplets thermally decompose simultaneously to form the compact layer.

Nowadays, lasers, as an advanced manufacturing tool, have been introduced to fabricate the mesoporous TiO₂ layers for DSSCs due to its advantages including being precise, selective, localize, non-contact, highly automated and scalable in the manufacturing process.²⁸ The use of laser sintering has shown the possibilities of locally fabricating integrated or

multifunctional devices on the same substrate which otherwise could be thermally damaged by conventionally integral heating methods.^{28,29} fabricating the DSSCs on the flexible substrates,³⁰ and preventing the bending of glass substrates due to its local heating feature.²⁸ It has been also calculated that the embodied energy (EE) required to sintering 1 m² of the mesoporous TiO₂ film by the laser process is comparable to that of the conventional oven and belt furnace treatments.¹⁷ Therefore, laser sintering can be considered as a highly promising alternative for manufacture of mesoscopic TiO₂ for DSSCs. Up to date, to the best of our knowledge, no work has been reported to generate both mesoporous and compact TiO₂ layers using a one-step laser process for DSSCs.

In this paper, we demonstrate a one-step fabrication of both mesoporous and compact TiO₂ layers on ITO-coated glass using a millisecond pulsed fibre laser at 1070 nm wavelength. It was expected to achieve thermal heating in a controllable manner allowing formation of mesoporous TiO₂ layer via vaporization of organic binder and interconnection between TiO₂ nanoparticles, as well as compact TiO₂ layer via nano-crystallization of TiO₂ precursor, without thermally damaging the ITO and glass substrate. Photovoltaic performance of the DSSCs with the laser-fabricated photoanodes were evaluated and compared to those with conventional furnace processed.

Experimental

Figure 1 schematically presents the three fabrication methods used in this work for generation of mesoporous and compact TiO₂ layers on ITO-coated glass. Detailed procedure can be found below.

Figure 1 Schematic representations of the fabrication methods in the experiments. (a) one-step laser fabrication of compact and mesoporous layers, (b) one-step furnace fabrication of compact and mesoporous TiO_2 layers, (c) two-step furnace fabrication of compact and mesoporous TiO_2 layers.

Mesoscopic structure fabrication by furnace process

ITO-coated glass substrate ($6\text{--}8\ \Omega/\text{sq.}$, Kintec Company, Hong Kong) was cleaned in sequence with ethanol, acetone, deionized water and then treated by UV-ozone for 15 min. For a conventional two-step furnace process, a compact TiO_2 layer was prepared by spin coating 0.2 M titanium diisopropoxide bis(acetylacetonate) (75 wt % in isopropanol, Sigma-Aldrich) solution in 1-butanol (Sigma-Aldrich) at 2000 rpm for 60 s on the ITO-coated glass and dried at 125°C for 10 min. Then, the ITO-coated glass with TiO_2 precursor was annealed in a furnace with 10 min ramping from room temperature to 500°C and kept at 500°C for 30 min, followed by cooling down for 2 h. The TiO_2 paste was prepared based on the description in Ref ³¹, and then deposited on top of the compact TiO_2 layer by screen-printing. The layer was dried at 125°C for 10 min and then sintered in a furnace with 10 min ramping from room temperature to 450°C and kept at 450°C for 30 min, followed by furnace cooling for 2 h.

In order to compare with the two-step furnace process, a one-step furnace process was also carried out, in which the deposition of 0.2 M titanium diisopropoxide in 1-butanol was achieved by spin-coating and drying at 125°C for 10 min, and then the TiO₂ paste prepared was screen-printed and dried at the same condition. Then, the samples were sintered in the furnace with 10 min ramping from room temperature to 450°C and kept at 450°C for 30 min, followed by cooling down for 2 h. Therefore, the overall fabrication time for the two-step and one-step furnace processes are 5 h 20 min and 2 h 40 min, respectively.

One-step laser fabrication of mesoporous and compact TiO₂ layers

Firstly, the 0.2 M titanium diisopropoxide in 1-butanol and TiO₂ paste were deposited on ITO-coated glass by following the same procedure as the one-step furnace process described above. Then, the laser processing was carried out using an IPG Fiber laser in ambient atmosphere. The laser beam with a power density of 85 W cm⁻² and variation of duty cycles from 75 ms/25 ms, 100 ms/25 ms to 125 ms/25 ms, irradiated on the sample surfaces for 1 min. After the laser irradiation, the substrates were cooled down for 60 s. Therefore, the entire laser process took 2 mins in total.

DSSC assembling

The TiO₂ photoanodes prepared by different fabrication methods were immersed in a solution containing 0.5 mM N719 dye in acetonitrile for 24 h. After rinsing off the excessive dye solution on the substrate, a Pt counter electrode (Dalian Heptachroma SolarTech) was sealed with the TiO₂ photoanodes by thermo-plastic hot-melt sealing film. The liquid electrolyte of Iodolyte Z-100 (Solaronix SA) was then injected through a hole made on the counter electrode to complete the assembling process.

Materials and Device Characterization

A VERSAS-TAT potentiostat connected with a solar simulator (Abet Technologies) with one Sun (100 mW cm^{-2}) under 1.5G air mass calibrated by a certified silicon solar cell was used to measure the power conversion efficiency (PCE) and electrochemical impedance (EIS) of the DSSCs. The impedance spectra were recorded at open voltage with a 10 mVAC signal over a frequency range of 100 mHz–100 kHz. The dye adsorption was measured by UV–vis absorption spectra of the N719 dye-desorption solution prepared by immersing the sensitized electrodes in a 0.1 M NaOH in a mixed solution (deionized water/ethanol = 1:1) for 2 h. The surface morphology and cross-sections of the compact and mesoporous TiO_2 layers were examined using a Sigma, Carl Zeiss Field Emission Gun Scanning Electron Microscopy (FEG-SEM). The phase constituents of the TiO_2 layers were measured using a Philips X'Pert MPD X-ray Diffraction at a fixed 2° angle of incident beam from a ($\text{Cu-K}\alpha$) standard X-ray source. The surface chemistry of the TiO_2 layers was examined by a Kratos Axis Ultra X-ray Photoelectron Spectroscopy (XPS). A Renishaw Raman Spectroscope with 514 nm excitation Ar^+ laser was used to examine the organic binder evaporation from the TiO_2 paste deposited and crystallization of the compact TiO_2 layers. A Bruker white light interferometry was applied for measurements of surface roughness.

Results and discussion

In the laser sintering process, three critical temperatures are needed. The first one is the temperature to completely remove the organic binders in the TiO_2 paste.¹⁸ A TGA measurement was performed to identify the evaporation temperatures of different organic components in the TiO_2 paste as shown in Figure 2a. A rapid weight loss of 60% in the range of 80-150°C is mainly caused by the evaporation of ethanol (as solvent to organic binders). Another significant weight loss of 7% in the range of 150-380°C is attributed to the

evaporation of the organic binders including ethyl cellulose and terpineol.³¹ Figure 2b shows the temperature profiles recorded by an IR thermal camera on the surface of the TiO₂ layers during the laser sintering processes at the power density of 85 W cm⁻² with a variation of duty cycles. The samples were irradiated by the laser for 60 s and then allowed for a cooling period of 60 s. As shown in Figure 2b, for the laser duty cycles of 75 ms/25 ms, 100 ms/25 ms and 125 ms/25 ms, the total time periods for vaporization of the organic binder are approximately 76 s, 83 s, and 88 s, respectively. The second critical temperature is to transform the TiO₂ precursor from amorphous to crystalline phase, usually above 450°C.¹² The third critical temperature of 450-550°C is required to form sufficient necking between TiO₂ nanoparticles.⁶ As shown in Figure 2b, with the increase of the laser duty cycles from 75 ms to 125 ms, the total periods of time for crystallization of TiO₂ precursor layer and formation of interconnection between TiO₂ nanoparticles increase from 52 s to 71 s. The peak temperatures measured during laser sintering also increase from 715.3°C to 786.2°C. No cracking or bending of the glass substrates is observed.

Figure 2 (a) TGA curve corresponding to the weight loss of TiO₂ paste, (b) Temperature profiles at the TiO₂ surface under constant laser power density of 85 W cm⁻² with variation of duty cycle of 75 ms/25 ms, 100 ms/25 ms and 125 ms/25 ms for irradiation of 60 s. The

dashed lines at 380°C and 450°C represent the temperatures of vaporizing organic binder and necking of TiO₂ nanoparticles respectively.

To characterize the crystallinity of the compact layer, Raman spectroscopy, XRD and SEM were used. Figure 3a shows the Raman spectra of the compact TiO₂ layers obtained with no treatment, laser-treatment at 85 W cm⁻² with a duty cycle of 125 ms/25 ms for 60 s, one-step and two-step furnace treatment, respectively. Compared with the un-treated layer, all the treated samples exhibit the peaks at 144 cm⁻¹ (Eg)*, 399 cm⁻¹ (B1g)*, 519 cm⁻¹ (B1g)*, and 639 cm⁻¹ (Eg)*, corresponding to TiO₂ anatase phase.^{29,32} For the samples treated by the duty cycles of 75 ms/25 ms and 100 ms/25 ms, the peaks corresponding to TiO₂ anatase phase can be found as shown in Figure S1. The XRD patterns as shown in Figure 3b and Figure S2 further confirm the results by Raman spectroscopy. The crystallization of the TiO₂ precursor layers are essential for high performance DSSCs due to the benefits from the increase of electrical conductivity and charge transport ability compared with amorphous phase.³³

Figure 3 (a) Raman spectra and (b) XRD patterns of the un-treated, one-step, two-step furnace- and laser-treated compact TiO₂ layers at 85 W cm⁻² with a duty cycle of 125 ms/25 ms.

Figure 4 a-d shows the SEM images of both cross-sectional and surface views of the compact and mesoporous TiO₂ layers on ITO-glass under various treatment conditions. As seen in Figure 4a, the un-treated and spin-coated TiO₂ layer is uniform, smooth, free of cracks and pinholes with a thickness around 60 nm, representing a typical amorphous TiO₂ precursor layer. The compact TiO₂ layer fabricated by the one-step furnace at 450°C for 30 min clearly shows the crystal structure from both cross-sectional and surface views (Figure 4b), suggesting the occurrence of phase transformation from amorphous to crystalline structure. The thickness of the compact TiO₂ layer is reduced to around 50 nm. Similar morphology is also found on the two-step furnace-treated compact TiO₂ layer at 500°C for 30 min and then 450°C for another 30 min as shown in Figure 4c. The layer thickness is further reduced from 50 nm to around 40 nm. Figure 4d shows the layer treated by the laser at the power density of 85 W cm⁻² with the duty cycle of 125 ms/25 ms for 60 s. A similar crystal structure observed for the furnace-sintered is also evident. The thickness of the layer is around 40 nm, equivalent to the layer treated by the two-step furnace process. The SEM images of the compact TiO₂ layers treated by other laser duty cycles can be found in Figure S3.

Figure 4 FEG-SEM images of surface and cross-sectional views of (a) un-treated, (b) one-step furnace-treated, (c) two-step furnace treated, (d) laser-treated mesoporous and compact TiO₂ layers at 85 W cm⁻² with a duty cycle of 125 ms/25 ms (scale bar: 1 μ m on insets)

In order to investigate the formation of mesoporous TiO₂ structures, Raman spectroscopy, SEM and XPS were used. As shown in Figure 5, the Raman peaks corresponding to the organic binder ethyl cellulose at 2876 cm⁻¹, 2934 cm⁻¹ and 2976 cm⁻¹³⁴, presented in the un-treated TiO₂ paste are completely vanished after the laser sintering at 85 W cm⁻² with the duty cycle of 125 ms/25 ms for 60 s and furnace sintering at 450°C for 30 min. Both laser- and furnace-sintered mesoporous TiO₂ layers present the Raman peaks only corresponding to anatase, indicating no phase transformation from anatase to rutile as also observed by the XRD result and Raman spectra in Figures S4 and S5. It is vital to fully remove the organic binders in the TiO₂ paste in order to achieve an efficient charge transfer rate and appropriate dye absorption.³⁵

Figure 5 Raman spectra of the un-treated, furnace- and laser-treated TiO₂ mesoporous layers at 85 W cm⁻² with a duty cycle of 125 ms/25 ms.

Figure 6 shows the surface view of the mesoporous TiO₂ layers treated by different processes. As shown in Figure 6a, the TiO₂ paste was uniformly deposited on top of the compact TiO₂ layer without cracking or aggregation of the TiO₂ nanoparticles. After the furnace sintering at 450°C for 30 min, as shown in Figure 6b, interconnection of the TiO₂ nanoparticles is formed and the layer is still uniform and cracks-free. It is also noted that the particle size of the TiO₂ in the porous structure was slightly larger than that in the un-treated TiO₂ layer, further confirming the necking and growth of the TiO₂ nanoparticles occurred during the furnace process. As shown in Figure 6c, the laser-sintered mesoporous TiO₂ layer at the power density of 85 W cm⁻² with a duty cycles at 125 ms/25 ms are also uniform and crack-free. The HR-SEM image shown in Figure 6c reveals better interconnection between the TiO₂ nanoparticles compared with that of the furnace-sintered. This might be due to the peak temperature of 786°C achieved by the laser process which is higher than the furnace sintering temperature of 450°C, although the period of the laser irradiation time of 60 s is much shorter than that of 30 min for the furnace. This suggests that the sintering temperature seems to have

played a more important role than the duration time. Increase in the sintering temperature to 550°C by furnace was also reported to enhance interconnection of the TiO₂ nanoparticles,¹⁴ which benefited the improvement of photovoltaic performance of DSSCs.

Figure 6 SEM images on surface view of (a) un-treated, (b) two-step furnace-treated, (c) laser-sintered mesoporous TiO₂ layers at 85 W cm⁻² with a duty cycle of 125 ms/25 ms (scale bar: 100 nm on insets)

Another interesting observation is the variation of thicknesses of the TiO₂ layers by different treatments as shown in Figure S6. The thickness of the un-treated deposition of TiO₂ paste (Figure S6a) is 11.3 μm. The one-step and two-step furnace-sintered mesoporous TiO₂ layers (Figures S6b and c) are crack-free with no distortion and presented similar average thicknesses of 9.7 μm and 9.6 μm respectively. The reduction in the layer thickness is

associated with the evaporation of the organic binders and the interconnection of the TiO₂ nanoparticles which resulted in shrinkage of the layers.³⁶ All the layers sintered by the laser (Figure S6) at the power density of 85 W cm⁻² with the variation of the duty cycles are crack-free with good adhesion between the compact TiO₂ layers and the ITO-glass substrates, as well as between the mesoporous and compact TiO₂ layers. The thicknesses of the laser-sintered mesoporous layers at the duty cycle 75 ms/25 ms (Figure S6d), 100 ms/25 ms (Figure S6e) and 125 ms/25 ms (Figure S6f) are 10 μm, 9.6 μm and 9.3 μm respectively, indicating that the thicknesses of the layers decrease with increasing in the laser duty cycle due to the increased temperatures and longer duration time. Therefore, denser mesoporous TiO₂ layers can be achieved compared to the furnace treatment, when the duty cycles are 100 ms/25 ms and above. In addition, further increasing the thickness of the mesoporous TiO₂ layer to around 11 μm after furnace treatment showed the formation of cracks within the layers. Therefore, the optimized thickness of the mesoporous TiO₂ layer was fixed to be around 10 μm. The results on surface chemistry of the mesoporous TiO₂ layers fabricated by different processes are obtained by XPS (Figure S7), indicating that the overall differences in the concentrations of lattice defects, Ti³⁺ and oxygen vacancies, between the laser- and furnace-sintered mesoporous TiO₂ are not significant.

Typical J-V curves of the DSSCs with the TiO₂ layers treated by laser and furnace under simulated solar irradiation of AM 1.5 G (100 mW cm⁻²) are shown in Figure 7 and the corresponding photovoltaic parameters are summarized in Table 1, along with the dye adsorbed amounts. The average values of the PCEs with standard deviations were obtained from five samples for each condition, showing reproducibility of the measurements. The DSSCs with the photoanodes fabricated by the two-step furnace process presents an average PCE of 4.62%, which is higher than that of the one-step furnace process with an average PCE of 4.18%. For the laser process, with the increase of the duty cycles from 75 ms/25 ms to 125

ms/25 ms, the average PCEs of the DSSCs are remarkably increased from 4.08% to 6.01% and a maximum PCE of 6.50% is achieved with the optimized laser condition. This might be the result of increased dye absorption, surface roughness and peak sintering temperatures from 715.3°C to 786.2°C, and prolonged periods above the temperature of 450°C from 52 s to 71 s, which leads to better necking of the TiO₂ nanoparticles, effective removal of the organic binders as well as highly crystallization of the TiO₂ compact layers. In order to study the function of the compact TiO₂ layer in the DSSCs, a comparison of the photovoltaic performance of the DSSCs with and without compact TiO₂ blocking layer fabricated by furnace process was carried out. As shown in Table S1, the DSSCs with a compact TiO₂ layer shows the increase of the short-circuit current density (J_{sc}) from 9.7 to 10.6 mA cm⁻² and the fill factor (FF) from 56.4% to 62.7%. These results are in agreement with the other studies showing that a compact TiO₂ layer contributes to the reduction of the charge recombination between the interface of ITO and electrolyte, thus a better photovoltaic performance.^{11,37} The PCEs of DSSCs achieved in this work is comparable to several recent publications based on different TiO₂ nanostructures with N719 dye as shown in Table S2.

From Table 1, it can be seen that with the increase of duty cycles from 75 ms/25 ms to 125 ms/25 ms, the values of J_{sc} remarkably increased from 10.4 mA cm⁻² to 16.5 mA cm⁻², compared with the J_{sc} of 10.6 mA cm⁻² for the two-step furnace process. The increase in values of J_{sc} is mainly associated with two factors: dye amount adsorption and effectiveness of compact TiO₂ blocking layer. Firstly, the laser processed surfaces of the TiO₂ mesoporous layers exhibit higher surface roughness, measured by white-light interferometry (see Figure 8) and shown in Table 1. The average surface roughness (Ra) of the mesoporous TiO₂ layer fabricated by the laser process increases from 0.53 μm to 0.70 μm with the increase of the duty cycles from 75 ms/25 ms to 125 ms/25 ms, respectively, which are higher than the value of 0.49 μm for the two-step furnace processed. The increased surface roughness contributes

the larger surface area enhancing the adsorption of the dye molecules.³⁸ This is in agreement with the dye adsorption measurement, as shown in Table 1. The optimized laser processing condition with the duty cycles of 125 ms/25 ms results in the highest Ra which leads the highest dye adsorbed amount. Increased dye adsorption enhances the absorption of incident light;³⁸ thus, an improved photovoltaic performance was achieved by the DSSCs fabricated by the optimized laser duty cycles as shown in Table 1. In addition, the increase in surface roughness for the mesoporous TiO₂ layer was also reported to improve the light scattering effect which promotes the chances of capturing the incident lights.^{39,40} Therefore, it is believed that increased surface roughness of the mesoporous TiO₂ layers by the laser process makes a positive contribution to the improvement of PCEs for the DSSCs.

Secondly, as described earlier, the compact TiO₂ blocking layers prevent the direct contact between the electrolyte and the ITO layer. Therefore, the characteristics of the bl-TiO₂, including the adherence to the ITO glass, play an important role. These influential factors at the interfaces are discussed based on the EIS data analysis as follows. In addition, with the further increase of the laser duty cycles to 150 ms/ 25 ms, slightly bending of the glass was observed which could negatively affect the photovoltaic performance of the DSSCs. Therefore, the optimized laser duty cycle was chosen to be 125ms/ 25ms.

Figure 7 Current density-voltage (J-V) curves of DSSCs assembled with the photoanodes produced by one-step, two-step furnace treatment and laser-treated at 85 W cm^{-2} with variation of duty cycles under standard AM 1.5G condition.

Table 1 Summary of photovoltaic parameters of the DSSCs by laser and furnace treatments.

Treatment		J_{sc} [mA cm^{-2}]	V_{oc} [mV]	FF [%]	PCE best [%]	PCE average [%]	Dye amount adsorbed [$\times 10^{-8}$ mol. cm^{-2}]	Ra [μm]
Laser - sintered 85 W cm^{-2}	75ms/25ms	10.4	0.71	58	4.28	4.08 $\pm$ 0.15	20.1	0.53
	100ms/25ms	13.0	0.71	61	5.70	5.30 $\pm$ 0.29	21.9	0.67
	125ms/25ms	16.5	0.70	56.2	6.50	6.01 $\pm$ 0.37	22.9	0.70
Furnace	Two-step	10.6	0.73	62.7	4.83	4.62 $\pm$ 0.16	20.6	0.49
	One-step	10.0	0.72	60	4.32	4.18 $\pm$ 0.13	20.2	0.35

Figure 8. Surface roughness measurement of mesoporous TiO_2 layer sintered by furnace at 450°C for 30 min by (a) one-step furnace, (b) two-step furnace sintered and laser-sintered at the power density of 85 W cm^{-2} for irradiation of 1 minute with duty cycle of (c) 75 ms/25 ms, (d) 100 ms/25 ms, and (e) 125 ms/25 ms.

In order to further investigate the photovoltaic performance of the DSSCs and gain understanding of the fact that the laser-treated photoanodes present higher conversion efficiencies than those with the furnace-treated, electrochemical impedance spectroscopy (EIS) was used to provide information on the dynamics of electron transport at different interfaces of the DSSCs. Figure 9 shows the Bode plots of the DSSCs prepared by various methods. The equivalent circuit in Figure 9a is used to fit the EIS experimental data to appropriated electrical analogues of the DSSCs. The values of interfacial resistance and electron lifetime obtained from fitting the impedance data using Z-view software, photoelectrochemical parameters of the DSSCs are listed in Table 2.

As shown in Figure 9a, the intermediate frequency region indicates the region corresponding to the charge resistance at the compact TiO_2 blocking layer/ITO interface ($R_{\text{TiO}_2/\text{ITO}}$) and the low-frequency region corresponding to mp- TiO_2 /dye/electrolyte (R_{ct}) interface. The laser-treated DSSC with a duty cycle of 75 ms/25 ms shows the highest impedance for both R_{ct} and $R_{\text{TiO}_2/\text{ITO}}$ among the DSSCs treated by different conditions as shown in Figure 9a and Table 2. The larger $R_{\text{TiO}_2/\text{ITO}}$ of 4.56 Ω obtained for the device by the laser process with a duty cycle of 75 ms/25 ms could be attributed to lower adherence between the compact TiO_2 blocking layer and ITO glass and also lower crystallinity of the TiO_2 due to the shorter period of sintering and lower sintering peak temperature compared with the DSSCs treated by other laser conditions. This is in agreement with ref⁴¹, that the improved adhesion between nanocrystalline TiO_2 layer and the ITO layer resulted in reduction of the $R_{\text{TiO}_2/\text{ITO}}$ interface resistance, which in turn led to improvement of the PCEs of DSSCs. Indeed, with the increase of the laser duty cycle to optimized condition (125 ms/25 ms), the $R_{\text{TiO}_2/\text{ITO}}$ shows a reduction from 4.56 to 3 Ω which is the lowest among all the fabrication conditions.

More importantly, the DSSC fabricated by the optimized condition (125 ms/25 ms) also shows a lowest R_{ct} of 0.78 Ω . This might be due to the better interconnection of the TiO_2 nanoparticles achieved by the optimized laser condition. This is further confirmed by a notably higher electron lifetime for the DSSC fabricated by optimized laser condition compared with the one-step furnace, two-step furnace, or laser treatments with other conditions as shown in Table 2. The calculation of electron lifetime is based on the impedance spectra of the phase plots as shown in Figure 9b. Three characteristic peaks are observed. The first peak was located at high frequency corresponding to the charge transfer process from counter electrode/electrolyte and the middle peak located at intermediate frequency is ascribed to the electron exchange from dye-sensitized nanocrystalline TiO_2 layer to electrolyte as well as the back reaction of electrons with I^{3-} via ITO layer, and the final peak is located at a low frequency associated with the I^{3-} diffusion in the electrolyte.^{42,43}

The electron lifetime (τ_e) in the TiO_2 layers was calculated from the intermediate peak according to the formula of $1/(2 \pi f_{max})$ ⁴⁴. From Table 2, the longest electron lifetime τ_e of 4.1 ms is obtained for the DSSC with the laser-treated at the 125 ms/25 ms. The improvement in the electron lifetime could be attributed to two reasons. Firstly, better interconnection of the TiO_2 nanoparticles contributes to an improved electron transport and reduction of the recombination sites in the mesoporous layer. Secondly, better adhesion of the compact TiO_2 blocking layer with ITO-glass also contributes to a reduction of back-electron transfer and recombination sites at TiO_2 /ITO interface.⁴⁵ The EIS data is in good agreement with the PCE results.

Table 2: EIS parameters of the DSSCs by laser and furnace treatments

Photoanodes		R_{ct} [$\Omega \cdot \text{cm}^2$]	$R_{\text{TiO}_2/\text{ITO}}$, [$\Omega \cdot \text{cm}^2$]	f_{max} , [Hz]	τ_e , [ms]
Laser-sintered at 85 W cm^{-2}	75ms/25ms	1.45	4.56	100	1.6
	100ms/25ms	0.8	3.19	63	2.5
	125ms/25ms	0.78	3	39	4.1
Furnace-sintered	Two-step	0.85	3.23	63	2.5
	One-step	0.87	3.52	100	1.6

Figure 9 Bode plots of the DSSCs with photoanodes fabricated by different methods.

Conclusion

This work has demonstrated a one-step rapid fabrication technique to generate both mesoporous and compact TiO_2 layers on ITO glass for DSSCs using a millisecond fiber laser with a wavelength of 1070 nm. The following conclusions might be drawn.

- 1) At the laser power density of 85 W cm^{-2} with 125 ms/25 ms duty cycle for stationary irradiation of 1 min, both mesoporous and compact TiO_2 layers are formed by complete vaporization of organic binder and inter-connections of the TiO_2 nanoparticle, and crystallization of TiO_2 precursor layer, without thermally damaging the ITO layer and the glass substrate.
- 2) Compared with the PCEs of 4.18% and 4.62% for the one-step and two-step furnace treatments, an average PCE of 6.01% with the highest individual PCE to 6.50% are achieved for the DSSCs with the laser-treated at 85 W cm^{-2} and 125 ms/25 ms.

- 3) J_{sc} for the cell with the laser-treated at 85 W cm^{-2} and 125 ms/25 ms reaches 16.5 mA cm^{-2} compared with 10.6 mA cm^{-2} for the two-step furnace-treated, due to the significant increase in dye adsorption by mesoporous structure and enhanced effectiveness of the compact TiO_2 blocking layers produced by the laser.
- 4) The improvement of the photovoltaic performance for the DSSCs with the laser-treated is associated with increased dye adsorption, decreased charge transfer resistance and increased electron lifetime of the TiO_2 layers.

This work suggests that the use of the fiber laser with over 40% wall-plug efficiency offers an economically-feasible solution to potentially meet the demands for one-step rapid fabrication of large scale, mass production of mesoporous metal oxide with compact blocking layer for solar energy systems in the future, and also wider implications for a wide range of applications based on mesoporous metal oxides.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

XPS results, extra SEM images, Raman and XRD results and efficiency comparison table.

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Table of Content

Synopsis: Compact and mesoporous TiO_2 layers were fabricated by a one-step laser process for enhanced performance of dye-sensitized solar cells.

Supporting Information

One-Step Fiber Laser Fabrication of Mesoporous and Compact TiO₂ Layers for Enhanced Performance of Dye-Sensitized Solar Cells

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Figure S1. Raman spectra of the TiO₂ blocking layers (bl-TiO₂) with various conditions.

Figure S2. XRD patterns of the bl-TiO₂ layers on ITO coated glass with various conditions.

Figure S3. Top view SEM images of the bl-TiO₂ coated on ITO-glass substrates of (a) untreated, (b) one-step furnace-treated at 450°C for 30 min, (c) two-step furnace-treated at 500°C for 30 min, laser-treated at a power density of 85 W cm⁻² for 1 min at (d) 75 ms/25 ms, (e) 100 ms/25 ms and (f) 125 ms/25 ms.

Figure S4. XRD patterns of mesoporous TiO₂ layers (mp-TiO₂) sintered by the furnace at 450°C for 30 min and sintered by laser of constant laser power density at 85 W cm⁻² for irradiation of 1 min at various duty cycles of 75ms/25ms, 100ms/25ms and 125ms/25ms respectively.

Figure S5. Raman spectra of the mp-TiO₂ thin films sintered by the furnace at 450°C for 30 min, and by laser at the power density of 85 W cm⁻² for 1 min with variation of duty cycles.

Figure S6, FEG-SEM images of cross sectional view of the TiO_2 mesoporous layers of (a) un-treated, (b) one-step furnace-sintered at 450°C for 30 min, (c) two-step furnace sintered at 450°C for 30 min and laser- sintered at constant 85 W cm^{-2} at duty cycle of (d) 75 ms/25 ms, (e) 100 ms/25 ms and (f) 125 ms/25 ms.

Figure S7. High resolution Ti2p XPS spectra of the mp-TiO₂ layers for (a) furnace-sintered at 450°C for 30 min and laser-sintered at the power density of 85 W cm⁻² for irradiation of 1 min with duty cycle of (b) 75 ms/25 ms, (c) 100 ms/25 ms, and (d) 125 ms/25 ms.

Table S1. Summary of power conversion efficiency of the DSSC produced in our work compared to several recent publications.

Year	Nanostructures and Dyes	PCE (%)	References
Our Work	Compact TiO ₂ + Mesoporous TiO ₂ + N719	6.5	—
2018	Mesoporous TiO ₂ + 3D inverse opal TiO ₂ + N719	6.23	(Xu <i>et al.</i> , 2018, Advanced Functional Materials)
2017	Compact TiO ₂ + Mesoporous TiO ₂ + N719	4.5	(Santana Andrade <i>et al.</i> , 2017, ACS Applied Materials and Interfaces)
2018	Compact TiO ₂ + TiO ₂ nanotubes+ N719	4.04	(Monteiro <i>et al.</i> , 2018, ACS Applied Materials and Interfaces)
2017	Compact TiO ₂ + Au/TiO ₂ Hollow Spheres + N719	7.3	(Li <i>et al.</i> , 2017, ACS Applied Materials and Interfaces)
2017	3D-TiO ₂ Microspheres + N719	4.1	(Sadhu, Gupta and Poddar, 2017, ACS Applied Materials and Interfaces)
2018	Double-Wall TiO ₂ Nanotubes +N719	6.9	(Chen <i>et al.</i> , 2018, ACS sustainable chemistry & engineering)
2017	Mesoporous TiO ₂ + N719	2.46	(Moraes <i>et al.</i> , 2017, Journal of Power Sources)

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