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ARTICLE

Chemodosimetric approach for selective detection of Pb²⁺ ions using a Cesium based perovskite

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We report the preparation of a lead free inorganic perovskite by a facile wet-chemical method using HCl as solvent at room temperature. The cesium perovskite CsCuCl₃ material was characterized by powdered X-ray diffraction (p-XRD), field emission scanned electron microscopy (FESEM), and energy dispersive X-ray spectroscopy (EDX). Ultraviolet/Visible spectroscopy (UV-Vis) and steady state photoluminescence (PL) were also carried out on the material. CsCuCl₃ showed promising optical properties with a band gap of 2.6 eV. The material was tested as a fluorescent sensor for the detection of metal ions and as a selective fluorescent chemodosimeter for Pb²⁺ ions. The substitution of Cu²⁺ ions by Pb²⁺ in CsCuCl₃ proves the chemodosimeter approach for detection of Pb²⁺ ion.

Introduction

Recently hybrid perovskite materials have been emerged as promising candidates for use in photovoltaics, water splitting, light emitting diodes and photodetectors.¹⁻⁶ Solar devices based on the hybrid perovskite, CH₃NH₃PbI₃ have shown a power conversion efficiency greater than 20%.⁷ Such efficiencies belong to perovskite materials with the general formula ABX₃, where A is an organic cation, B is a metal cation and X corresponds to a halide or mixture of halides (Cl, Br, I).^{8,9} However, these hybrid perovskites have inherit instability that limits their commercial applications.^{10,11} Currently, research in perovskite materials is focused on the replacement of an organic cation with inorganic cation especially cesium (CsPbI₃). These materials have shown an improvement in electrical and optical properties, while retaining the main characteristics of CH₃NH₃PbI₃.^{12,13}

Inorganic cesium based perovskites have gained considerable attention because they do not have a dipole as compared to the methyl ammonium based hybrid perovskites.¹³ Therefore, distortion in the geometry is avoided in inorganic cesium lead halides. The cesium lead halides have greater thermal stability as compared to the hybrid perovskites.¹⁴ However the lead

content of inorganic perovskite materials has raised serious concerns due to their toxicity and accumulation in the ecosystem.¹⁴¹⁵⁻¹⁸ It is also important to develop an alternative class of lead free inorganic perovskites for photovoltaic and other applications. The first attempt was made to replace lead with tin in the perovskite family. However, Sn²⁺ can easily be oxidized to Sn⁴⁺.¹⁹

The developments of fluorescent sensors for the detection of metal ions have gained considerable interest being a simple, cost effective, sensitive method.^{20, 21} The fluorescent molecules may show photoluminescence enhancement or quenching with exposure to metal ions, both these properties have been used for the detection of metal ions.^{22, 23} Molecules with irreversible transduction of a fluorescent signal during analyte recognition are known as a chemodosimeter. They are different from simple fluorescent sensors due to their irreversible signal response whereas the latter is reversible.^{24, 25} The development of chemodosimeters for qualitative and quantitative analysis of various metal ions has recently become an active research field.²⁶⁻³⁰ In particular, the presence of lead ions in environment, has a toxic effect even at low concentration.³¹ The leaching of lead ions from paints, petroleum and batteries can cause anaemia, nervous system dysfunction, and reproductive dysfunction in humans.³² Therefore the detection of lead ions in ecosystems is important. Many organic chemodosimeters have been reported for the detection of various metal ions, with very few reported for lead ions.³³ Reports include triazole linked rhodamine,³⁴ 8-hydroxyquinoline³⁵ and amino acid³⁶ based chemodosimeters. However, to date there are no reports of inorganic chemodosimeters. Hence there is a potential to develop a selective inorganic fluorescent chemodosimeter for lead ion sensing.

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Herein, we report the synthesis of CsCuCl_3 , inorganic perovskite with an aim to use them as a fluorescent chemodosimeter for selective sensing of Pb^{2+} ions. The as-prepared compound was characterized by powdered X-ray diffraction (p-XRD), field emission scanned electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDX), Ultraviolet/Visible spectroscopy (UV-Vis), steady state photoluminescence (PL). The results have shown the superior selectivity of as-synthesized compound for Pb^{2+} ions.

Experimental

Materials

Cesium chloride (CsCl), copper chloride (CuCl_2), 37% hydrogen chloride solution (HCl), chromium (III) chloride, silver (I) nitrate, cadmium (II) chloride, cobalt (II) chloride, iron (II) chloride, mercury (II) nitrate, manganese (II) chloride, lead (II) bromide, zinc (II) chloride and anhydrous DMF were purchased from Sigma-Aldrich and used without further purification.

Characterization

XRD measurements were performed using a Bruker aXS D8 advanced diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 40 kV and 40 mA. Scanning electron microscopy (SEM) was carried out using a Philips XL30 FEG SEM. Energy-dispersive analysis of X-rays (EDAX) spectroscopy was performed using a DX4 detector. All samples were carbon coated using Edwards coating system E306A prior to SEM analysis. A Perkin-Elmer Lambda 20 UV-vis spectrophotometer was used to carry out optical measurements in the 200–1100 nm wavelength range at room temperature. Samples were placed in quartz cuvettes (1 cm path length) and the absorbance was recorded. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 luminescence spectrometer with xenon lamp over range of 200–800 nm. The samples were placed in quartz cuvettes (1 cm path length) and the excitation peaks were analysed and recorded. Thermogravimetric analysis was carried out at 20 °C heating rate using a Perkin Elmer Pyris 6 TGA upto 1000 °C in a closed perforated aluminium pan under N_2 gas flow.

Synthesis of CsCuCl_3

The cesium copper chloride powdered perovskite was synthesized by dissolving 0.537 g (4 mmol) of copper chloride (CuCl_2) in 2 cm^3 (81.73 mmol) of hydrogen chloride at room temperature. After complete dissolution of the copper chloride, 0.673 g (4 mmol) of cesium chloride was added. The mixture was stirred for 30 minutes to ensure the completion of reaction. The obtained precipitate was filtered and washed with ethanol.

Results and discussions

The cesium copper chloride was prepared at room temperature using HCl as a solvent. A brown colored precipitate appeared with the mixing of the precursor. To

remove excess acid, the precipitate was washed with ethanol. Fig. 1 shows the p-XRD pattern of the product. The sharp peaks at $2\theta = 20.66, 24.92, 32.48$, and 41.79° correspond to the (103), (110), (203) and (213) planes of hexagonal CsCuCl_3 (ICDD 00-018-0349).

The morphology of CsCuCl_3 was investigated by field emission scanning electron microscopy. The CsCuCl_3 has a stone-like appearance as shown in Fig 2. Energy dispersive X-ray spectroscopy (EDX) revealed $\text{Cs}:\text{Cu}:\text{Cl}$ atomic ratio of almost 1:1:3 which matches the expected CsCuCl_3 stoichiometry (supporting information, S1). The distribution of the Cs, Cu and Cl in the compound was investigated by EDX mapping. Fig 2 shows that the Cs, Cu and Cl are distributed uniformly in the interrogated area of the inorganic perovskite material.

Thermogravimetric analysis data of CsCuCl_3 indicates that the CsCuCl_3 perovskite is thermally stable up to 400 °C (Fig. 3). Decomposition of the compound occurs in two steps with the final temperature at approximately 900 °C. Fig 4 shows the absorption spectrum of CsCuCl_3 at room temperature in DMF. The inorganic perovskite material shows two absorption peaks, one at 439 nm and other at 296 nm. The band gap was determined by the Tauc plot which indicates that the compound has a direct band gap estimated to be 2.6 eV.

The PL emission spectrum of cesium copper chloride is presented in Fig 5. Upon excitation at 293 nm, the inorganic perovskite, showed three photoluminescence (PL) peaks at ca. 348 nm, 532 nm and 673 nm which suggest three distinct emission states in the compound.

The cesium copper chloride was then studied for its application as a fluorescent chemodosimeter to detect metal cations. A 20 mmol solution of cesium copper chloride in DMF was used to perform the selectivity test for various cations. It was observed that the presence of 50 μL of 20 mmol solution of Zn^{2+} , Co^{2+} and Cd^{2+} shows an enhancement in PL peaks lies at 348 nm and 673 nm whereas Pb^{2+} , Mn^{2+} and Cr^{3+} do not show significant enhancement in intensity of same peaks (348 nm and 673 nm) as shown in Fig. S2 (supporting information). However, Hg^{2+} , Fe^{2+} and Ag^+ in DMF results in the quenching of the all PL peaks of CsCuCl_3 (348 nm, 532 nm and 673 nm) while the Pb^{2+} solution with similar strength enhances the PL at 532 nm as shown in Fig 6(a), whilst no obvious change in PL was observed at the same peak (532 nm) with the addition of 50 μL solution of the other cations including Cr^{3+} , Co^{2+} , Cd^{2+} , Fe^{2+} , Mn^{2+} and Zn^{2+} .

As indicated in Fig 6(b), only Pb^{2+} ions show the effective enhancement in PL with a high F/F_0 value as compared to other cations. In contrast, the Hg^{2+} and Ag^+ ions do not quench the PL effectively. These observations suggest that the perovskite material can be used as a chemodosimeter for Pb^{2+} ions.

For a compound to be an efficient chemodosimeter, it is necessary that its selectivity towards specific ions should not be affected by other competitive species. To confirm the

selectivity of Pb^{2+} ions, we investigated whether the Pb^{2+} can recover the PL of CsCuCl_3 which was quenched by the Hg^{2+} and Ag^+ ions. It was found that the addition of 50 μL of Pb^{2+} solution in the quenched sample by Hg^{2+} resulted in recovery of PL (supporting information, Fig. S3). On the other hand, the addition of Hg^{2+} solution into the solution containing Pb^{2+} with enhanced PL caused no suppression of the emission (supporting information, Fig S4). Similar results were obtained using Ag^+ solution. Based on these observations, it is concluded that some chemical reaction of Pb^{2+} occurs with cesium copper chloride, so that the enhancement of PL peak is irreversible. While Ag^+ and Hg^{2+} ions do not chemically interact with cesium copper chloride.

Quantitative PL titration was then performed in order to assess the sensitivity of the cesium copper chloride for Pb^{2+} ions. Fig 7 (a-b) indicates that PL of the compound increases monotonically with the increasing concentration of Pb^{2+} ions from 1×10^{-7} mole/l to 1.5×10^{-6} mole/L which indicates that the compound is sensitive for Pb^{2+} ions even at low concentration. It was observed that when the concentration of the as-prepared compound reaches 150 μL (1.5×10^{-6} mole/L) the fluorescence enhancement factor (F/F_0) reaches 70%. The as-prepared CsCuCl_3 showed moderate to good sensing activity in terms of selectivity and sensitivity.³⁷

We can conclude that the Pb^{2+} ions not only enhance the PL of the perovskite but also recover the PL that has been quenched by the Hg^{2+} ions. Therefore it can be expected that a much higher enhancement factor could be obtained if the PL of mixture of CsCuCl_3 and Hg^{2+} is considered as new sensing system. With this observation, a new sensor $\text{CsCuCl}_3 + \text{Hg}^{2+}$ was fabricated and used to detect Pb^{2+} ions. As expected, much higher enhancement was observed with this sensor by the addition of Pb^{2+} ions.

Mei *et al.* have reported the combination of L-Cys-AuNCs with Pb^{2+} as sensing system with enhanced fluorescent sensing of Al^{3+} ions.³⁸ On the similar basis, we have developed a new sensing system with the combination of CsCuCl_3 and Hg^{2+} for the sensing of Pb^{2+} ions. Fig 8(a) shows that PL spectrum of CsCuCl_3 , $\text{CsCuCl}_3 + \text{Pb}^{2+}$, $\text{CsCuCl}_3 + \text{Hg}^{2+}$ and $(\text{CsCuCl}_3 + \text{Hg}^{2+}) + \text{Pb}^{2+}$. Fig 8 (b) gives the comparison between the enhancement factor of two sensors cesium copper chloride and $\text{CsCuCl}_3 + \text{Hg}^{2+}$. It was observed that enhancement was approximately 25 times for Pb^{2+} using cesium copper chloride. However, the enhancement increases exponentially to 128 times using $\text{CsCuCl}_3 + \text{Hg}^{2+}$ as a sensor. This indicates that the sensor $\text{CsCuCl}_3 + \text{Hg}^{2+}$ has a higher sensing capacity than cesium copper chloride perovskite. Furthermore, the change in colour of (0.1 mmol) cesium copper chloride with addition of (0.1 mmol) Pb^{2+} ions is shown in Fig S5 (supporting information).

Based on the above discussion, it can be suggested that the Pb^{2+} ions may form a chemical interaction with cesium copper chloride compound which enhances the PL. To confirm this we have added equimolar amount of (0.5g, 1.6 mmol) CsCuCl_3 and (0.6g, 1.6 mmol) PbBr_2 in 5 cm^3 of DMF followed by sonication for 5 minutes. Then 10 cm^3 of acetone was added to the reaction mixture to form the precipitate. The p-XRD of the obtained precipitates confirms

the formation of CsPbCl_3 as shown in Fig. S6 (supporting information), which indicates that the Pb^{2+} have replaced the Cu^{2+} in the CsCuCl_3 perovskite.

Scheme 1 shows the proposed mechanism for this reaction. The quenching of the PL emission when Hg^{2+} ions are added in CsCuCl_3 may also be due to the formation of chemical interactions with CsCuCl_3 compound. To confirm the proposed mechanism, an equimolar amount of (0.5 g, 1.6 mmol) CsCuCl_3 and (0.449 g, 1.6 mmol) HgCl_2 was sonicated in 5 cm^3 of DMF, for 5 minutes and then precipitated out by adding acetone. No change in p-XRD of CsCuCl_3 perovskite was observed which may suggest that Hg^{2+} is neither forming a permanent bond nor replacing copper in the structure of CsCuCl_3 as shown in Fig. S6 (supporting information). The conversion of CsCuCl_3 to CsPbCl_3 may also break the weak interaction of Hg^{2+} ions with CsCuCl_3 compound when the Pb^{2+} ions are added in the presence of Hg^{2+} ions in the solution. To investigate the competition between Hg^{2+} and Pb^{2+} to form a bonding with CsCuCl_3 we performed two experiments. In the first we added equimolar amount of (0.449 g, 1.6 mmol) HgCl_2 in solution of (0.6 g, 1.6 mmol) PbBr_2 + (0.5 g, 1.6 mmol) CsCuCl_3 . In second experiment, we dissolved equimolar amounts of (0.6 g, 1.6 mmol) PbBr_2 in (0.449 g, 1.6 mmol) HgCl_2 + (0.5 g, 1.6 mmol) CsCuCl_3 solution. The precipitates obtained from both of these solutions were analysed by p-XRD which showed conclusive formation of the CsPbCl_3 phase (supporting information, Fig.S6) confirming that the Cu^{2+} in CsCuCl_3 is selectively replaced by Pb^{2+} ions. However, PL enhancement at 532 nm can be attributed to the formation of either $\text{CsPbCl}/\text{Br}_2$, $\text{CsPbCl}_2/\text{Br}$ or CsPbBr_3 . These results suggest that CsCuCl_3 is a fluorescent chemodosimeter for the selective detection of Pb^{2+} ions.

Conclusions

We found simple and efficient method for the synthesis of lead free all inorganic perovskite (CsCuCl_3) using HCl as solvent. The as-prepared compound showed PL which was highly sensitive to different metal ions. The PL was quenched by Hg^{2+} and Ag^+ whereas it was enhanced by Pb^{2+} . Based on these observations the CsCuCl_3 was used as fluorescence turn on chemodosimeter for selective sensing of Pb^{2+} . A new sensing system was developed by using combination of CsCuCl_3 and Hg^{2+} ions. This perovskite (CsCuCl_3) material is not only useful as chemodosimeter for lead ions but also a highly potential material for photovoltaic applications.

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Chemodosimetric approach for selective detection of Pb²⁺ ions using a Cesium based perovskite

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Figure 1. p-XRD pattern of CsCuCl₃.

Figure 2. SEM-EDX Q-maps indicating the distribution of Cesium, copper and chlorine in the as-prepared all-inorganic perovskite compound CsCuCl₃.

Figure 3. Thermogravimetric analysis (TGA) spectrum of CsCuCl₃ perovskite.

Figure 4. Uv-Vis spectra of CsCuCl₃. Inset graph is the Tauc plot for band gap measurement.

Figure 5. Photoluminescence spectra of inorganic CsCuCl₃ perovskite.

Figure 6. (a) Photoluminescence spectra (532nm) of CsCuCl_3 in the presence of various metal ions and (b) is the corresponding selectivity of the cesium copper chloride (chemodosimeter) (F and F_0 are the fluorescence measured in the presence and absence of the metal ions respectively).

Figure 7. (a) Variation of PL intensity of CsCuCl₃ with different concentrations of Pb²⁺ at 532nm (b) the F/F₀ value with increasing concentration of Pb²⁺ ions.

Figure 8. (a) Comparative PL spectra of CsCuCl_3 , $\text{CsCuCl}_3 + \text{Pb}^{2+}$, $\text{CsCuCl}_3 + \text{Hg}^{2+}$ and $(\text{CsCuCl}_3 + \text{Hg}^{2+}) + \text{Pb}^{2+}$ (b) the corresponding enhancement factor using CsCuCl_3 and $(\text{CsCuCl}_3 + \text{Hg}^{2+})$ sensing systems

Scheme 1. Possible sensing principle of sensing system.

Chemodosimetric approach for selective detection of Pb^{2+} ions using a Cesium based perovskite

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Graphic

We have synthesized a Lead free inorganic perovskite as fluorescence turn on chemodosimeter for selective sensing of Pb^{2+} ions.