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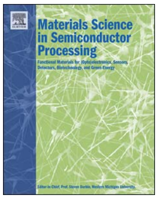

Enhanced photocatalytic activity of water stable hydroxyl ammonium lead halide perovskites

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ABSTRACT

Hybrid perovskite have shown a potential as structurally and chemically tunable materials with interesting optical properties. Herein, We describe the synthesis and characterization of two new perovskites, hydroxyl ammonium lead iodo chloride, $OHNH_3PbI_2Cl$ **(1)** and hydroxyl ammonium lead chloride, $OHNH_3PbCl_3$ **(2)** by wet-chemical route. The as-prepared **(1)** and **(2)** have shown promising optical properties with suitable band gaps 3.7 eV and 3.9 eV respectvely. Time resolved Photoluminescence (PL) results showed that hybride pervoskite **(2)** had a long lived PL whereas **(1)** exhibited a short PL life-time. Thermo-gravimetrical analysis (TGA) in nitrogen gas environment revealed that **(1)** and **(2)** are stable and do not show any sign of decomposition up to ~200 °C. Photocatalytical performance of as-prepared materials **(1)** and **(2)** under sunlight were mointerted using textile dye direct yellow. The compound **(1)** degraded dye in 20 min while **(2)** in 55 min with superior recyclablity.

1. Introduction

Organic-inorganic hybrid perovskites are a new class of materials which have received considerable interest across the spectrum of physical sciences due to their novel and enhanced optoelectronic properties.[1,2] Amongst the solar light absorbing materials, hybrid perovskites have attained promising attention, because of their facile synthesis, less toxicity and easy processing.[3,4] They have superseded the use of traditional dyes sensitized solar cells by absorbing across a wide range of the solar spectrum showing device efficiency over 20%.[5] The tunable band gap, high absorption/optical coefficient, and extraordinary charge carrier mobility are the important properties that make them potentially useful candidates for photovoltaic applications.[6–8] Structurally, organic-inorganic hybrid perovskite have ABX_3 stoichiometry, where, (A=small organic cation, B=divalent metal cation, X=halogen), BX^{6-} anion forms octahedral geometry with A component neutralizing the charge and fill the interstices.[4,9] [10] The spherical (e.g. inorganic) to non-spherical (e.g. organic or inorganic) A site component provide a basis to clearly distinguish between hybrid and inorganic perovskites.[10] The choice of a wide variety of organic and inorganic counterparts of perovskite can tailor electrical, mechanical, magnetic and optical properties. Therefore they have been considered suitable candidates for high efficacy solar devices, [11–16] light emitting diodes [17] and sensors.[18,19] However, organic cations impart moisture and thermal instability.[4, 20–22] These stability parameters are critical for the optoelectronic performance of devices. Various attempts have been made to improve the stability of hybrid perovskites by modifying the organic cation or halide ions. But, the effects of these measures were modest because of structure distortion and weak interaction between the organic and inorganic components.[23,24].

The industrial effluent contains a substantial amount of organic dyes which pose serious threat to aquatic life. [25,26] Degradation of such toxic dyes has been attempted by the use of ZnO,[27,28] TiO_2,[29,30] CuO [31,32] nanostructures. However, they need ultraviolent radiations to start degradation reaction, thus limiting their large scale use.[33–36] Further, due to nano size, the disposal of these materials needs special methods.[37–39] Pervoskite materials have superior visible light absorbing capacity.[25, 26, 40–42] Therefore, perovskites have a potential to be used as photocatalyst to degrade toxic wastes.

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In this work, we report the preparation of new hydroxyl ammonium lead halide perovskites **(1)** and **(2)**, using hydroxylamine precursor-an important intermediate in biological nitrification process,[43] instead of traditionally used organic moiety. The as-prepared compounds **(1)** and **(2)** were characterized by powdered X-ray diffraction (*p*-XRD), ultraviolent/visible spectroscopy (UV–Vis), steady state photoluminescence spectroscopy (SPL) and time resolved photoluminescence (TRPL). Further, the stability of as-synthesized compounds **(1)** and **(2)** was investigated in aqueous medium. The thermal stability was studied by thermal gravimetrical analysis (TGA/DTA) followed by visible light driven photocatalysis under ambient conditions. To the best of our knowledge, this aspect of prepared perovskite **(1)** and **(2)** have not been reported in the literature.

2. Experimental section

2.1. Materials

Hydroxyl ammonium chloride ($OHNH_3^+Cl^-$), lead chloride ($PbCl_2$), lead iodide (PbI_2) and anhydrous DMF were purchased from Sigma-Aldrich and used without further purification.

2.2. Characterization

Phase purity of synthesized materials were confirmed by powdered X-ray diffraction using X' Pert PRO PANalytical equipment with Cu Kα radiation (K=1.54178).

UV–Vis spectra were measured by using Shimadzu UV-1700 spectrophotometer at room temperature. The PL life-time was measured by using the standard instrument Flau Time 300 (FT-300) steady state and life-time spectrometer, PicoQuant GmbH, Germany. Thermal stability was tested by Shimadzu DTG-60/DTG-60A.

2.3. Synthesis of $OHNH_3PbI_2Cl$ perovskite (1)

Hydroxyl ammonium lead iodo chloride ($OHNH_3PbI_2Cl$) **(1)** was synthesized by treating 14 mmole of hydroxyl ammonium chloride ($OHNH_3^+Cl^-$) and 14 mmole of PbI_2 in DMF (10 cm^3) solvent at 80 °C for 12 h with stirring. The reaction mixture was kept at room temperature for two weeks. The pale yellow coloured crystals were than filtered and dried at room temperature.[44].

2.4. Synthesis of $OHNH_3PbCl_3$ perovskite (2)

The synthesis of hydroxyl ammonium lead chloride ($OHNH_3PbCl_3$) **(2)** was carried out by reacting 14 mmole of hydroxyl ammonium chloride ($OHNH_3^+Cl^-$) with 14 mmole of $PbCl_2$ in 10 cm^3 of DMF at 80 °C for 2 h with stirring. The white crystalline powder was formed which was filtered and dried at room temperature.[44].

2.5. Procedure for photocatalysis

The photocatalytic activity of as-synthesized hybrid perovskites **(1)** and **(2)** was tested for the degradation of dye Direct Yellow 27. For the reproducibility of results all experiments were conducted under similar conditions. The degradation experiment was performed under natural light using same procedure as reported in literature.[45,46] The photodegradation experiment was carried out by adding 20 mg of synthesized hybrid perovskite in 40 ml of 5 ppm aqueous dye solution with initial concentration of 2 mg/ml. The reaction mixture was stirred in dark for 15 min at room temperature. The suspended catalyst was allowed to settle down by keeping the reaction mixture at room temperature for 10 min. The dye concentration was measured by UV–Vis spectroscopy. The reaction mixture was placed in sunlight at ambient laboratory condition and the samples were withdrawn after fixed time intervals to measure the concentration of dye until the complete degradation of dye.

2.6. Procedure for COD

The concentration of dye in the sample before and after the treatment with as-synthesized compounds **(1)** and **(2),** the COD experiment was performed by taking 50 ml of the sample into a 500 ml refluxing flask. Added 1 g of $HgSO_4$ and 5 ml of sulphuric acid reagent (5.5 g of Ag_2SO_4 per kg of concentrated H_2SO_4) and stirred the mixture till dissolution of $HgSO_4$. Then add 25 ml of 0.042 M $K_2Cr_2O_7$ solution and mixed well. To the resultant solution 70 ml of sulphuric acid reagent was added with stirring and allowed the mixture to reflux for two hours. Cooled and washed the condenser and collected the material. The volume of the sample was doubled by addition of distilled water and cooled the material to room temperature. Excess amount of $K_2Cr_2O_7$ was determined with Ferrous Ammonium Sulphate (FAS) titration using few drops of ferroin indicator. The end point indicated by colour change from blue green to reddish brown that persisted for more than one minute.[25,47].

The same procedure was repeated for blank sample using Deionized water as a sample COD value was calculated using following formula.

$\text{COD (mg } O_2/\text{L)} = \underline{(A-B) \times M \times 8000}/V_s$.

A=Volume of FAS used for blank in ml.

B=Volume of FAS used for sample in ml.

V_s=Volume of sample in ml.

M=Molarity of FAS solution.

3. Results and discussion

Hybrid perovskites **(1)** and **(2)** were prepared by a solution method.[44] The precursor hydroxyl ammonium chloride and lead halide were stirred at 80 °C. The reaction of compound **(1)** completed in 12 h while **(2)** in 2 h. Compound **(1)** and **(2)** were crystalized in DMF solvent at room temperature. Compound **(1)** gave yellow coloured crystals while **(2)** gave a white product. The powdered X-ray diffraction (p-XRD) showed that **(1)** and **(2)** have perovskite structure. Both compounds give sharp peaks indicating the highly crystalline nature of products. Fig. 1 shows that compound **(1)** have tetragonal peak pattern while compound **(2)** gave hexagonal pattern. Similar results are also reported in the literature.[48,49] Fig. 2(a) Shows the absorbance spectra of $OHNH_3PbI_2Cl$ **(1)** and $OHNH_3PbCl_3$ **(2)** measured at room temperature in DMF. The sharp absorption peaks of **(1)** and **(2)** indicate that these hybrid perovskites have direct band gaps which were calculated by using Tauc equation. The estimated band gap for $OHNH_3PbI_2Cl$ **(1)** is 3.7 eV and for $OHNH_3PbCl_3$ **(2)** is 3.9 eV. The data shows that the band gap decreases from 3.9 to 3.7 eV by the incorporation of iodine in the hybrid perovskites. The direct band gaps of hybrid perovskite semiconductors **(1)** and **(2)** predict that they could be potential candidates

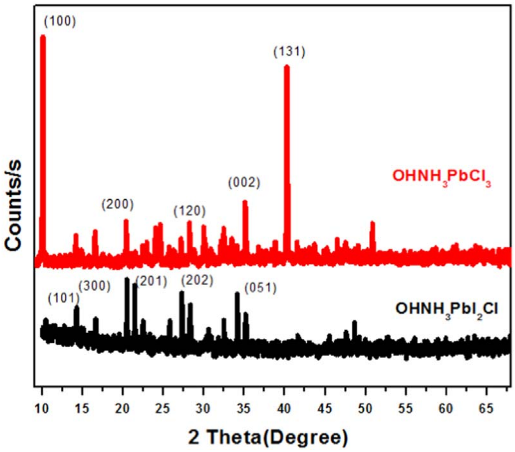

Fig. 1. *p*-XRD spectra of synthesized hydroxyl ammonium lead halides **(1)** and **(2).**