

Investigation on stability and photocatalysis of perovskites

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Abstract

Hybrid organic–inorganic perovskite materials have attracted a lot of attention with their facile synthesis process and high efficiency of light absorption. However, the poor stability is always a big barrier to commercial development. In this study, a new kind of organic perovskites MA_{0.6}(AA)_{0.4}PbBr₃ (AM-PE), which harnesses aniline as a replacement of conventionally used methylamine, was synthesized to increase the stability of MAPbBr₃ (M-PE). The decomposition process of MAPbBr₃ in acetone was investigated. Smaller PbBr₂ particles were formed in the decomposition process, causing the change of photoluminescence emission wavelength from 540 nm to 610 nm. The photocatalysis and photoluminescence properties of M-PE and AM-PE were also compared. As a result, the introduction of aniline reduced the decomposition rate of AM-PE significantly, and showed twice the catalysis efficiency of M-PE in the degradation of organic dye - malachite green. Copyright © 2018 VBRI Press.

Keywords: Perovskite, photocatalysis, stability, photoluminescence.

Introduction

Recently, a big breakthrough occurs in the photovoltaic field: the organic–inorganic hybrid perovskite materials, as light harvester, highly improved the photoelectric conversion efficiency of the solar cells [1-4]. This kind of perovskite materials has the same structure with CaTiO₃, and is called trihalide perovskite. This kind of trihalide perovskite (ABX₃) is a hybrid inorganic–organic direct-bandgap semiconductor, CH₃NH₃PbX₃ (X= Cl, Br, I) [5]. With its outstanding photo energy conversion, this perovskite MAPbX₃ has been investigated for application in photovoltaic and LED field [6]. For example, CH₃NH₃PbI₃ and CH₃NH₃PbBr₃ have achieved a big breakthrough on the photovoltaic technologies with efficiencies about 20% [7,8]. The LED device employing MAPbBr₃ offers remarkable photoluminescence quantum yield up to 85% and exhibits maximum EL of 10590 cd m⁻² at 12 V [9]. More importantly, the MAPbX₃ perovskites have the tunable bandgap with different compositions of the three halide ions. MAPbCl₃, MAPbBr₃ and MAPbI₃ demonstrated bandgaps of 3.3, 2.3, and 1.5 eV, respectively [6].

Photocatalysis is a promising technology to utilize the energy of either natural sunlight or artificial indoor illumination to realize the green chemistry and reduce the dependence on fossil energy [10-11]. Anatase-structured titanium dioxide (TiO₂) has been studied extensively as the photocatalyst for several decades due to its high catalytic activity and long-term stability [3]. However, its large band gap of 3.2 eV has limited its

light absorption in UV range and not active in visible light of photon energy ~1.7–3.1 eV. As the UV energy accounts only about 4% of the total energy in solar spectrum, the wide bandgap is considered as the main limitation to high photocatalytic efficiency [5].

So far the photocatalysis performance of organic–inorganic lead perovskite has not been reported, in particular the degradation of organic dyes under the light irradiation. Compared with the TiO₂ powders, the narrower bandgap of MAPbX₃ perovskite helps to harvest most part of the solar light to achieve higher efficiency of photocatalysis. In addition, these MAPbX₃ materials can be easily synthesized via low temperature solution processing [12]. So MAPbX₃ perovskite material is expected to be a promising candidate in the photocatalysis.

Conducting polymers and their derivatives have been used in the photocatalytic degradation of dyes [12-13] for a long time. For example, polyaniline (PANI) possesses high electron mobility and get easily excited under visible-light illumination [14]. In addition, it is much cheaper than TiO₂ and environmentally stable. We expect to incorporate aniline into perovskite, to stabilize its structure and accelerate its photocatalytic degradation of dyes.

Here, we synthesized a new kind of perovskite MA_{0.6}(AA)_{0.4}PbBr₃ (AM-PE) to increase the stability of perovskite crystal, and investigated the decomposition process of M-PE dispersion. Their photocatalytic performances were also compared in dye degradation.

Experimental

Materials

The PbBr₂ (99.999%) and methylamine (CH₃NH₂, 33% in ethanol) were purchased from Sigma-Aldrich. The HBr (47.0% - 49.0% in water) was purchased from Alfa Aesar. Malachite Green and aniline were purchased from J&K and Fisher Scientific.

Material synthesis

To synthesize the low concentration MAPbBr₃ dispersion for the PL test, we prepared three different molar ratios of MABr and PbBr₂ (2:1, 4:1, 6:1) in DMF solution and dispersed them into a certain amount of acetone. With three different precursor DMF solutions, a series of perovskite dispersion in acetone were formed with different concentrations.

Characterizations

A FLS920 fluorescence spectrophotometer (Edinburgh Instrument Ltd.) with a 450 W Xe lamp and 200 mW 808 nm laser diodes (LDs) was used to measure the photoluminescence emission (PL) and excitation (PLE) spectra. The degradation of dye solutions was monitored by UV-vis spectroscopy (UH5300 HITACHI). UV-Vis absorption and reflection spectra of the perovskite films were collected using a UV-vis diffuse reflectance spectrometer (Cary 3000) equipped with an integrating sphere.

The MAPbBr₃ and MA_{0.6}(AA)_{0.4}PbBr₃ were evaluated by their catalytic oxidation of malachite green (MaG) under visible light irradiation at room temperature. In a photocatalytic experiment, 50 mg of perovskite particles was dispersed in a 50 mL MaG solution with a typical concentration of 5.0 mg/L. The solvent used was chloroform. After stirred in the dark for 30 min, the samples were then irradiated by light sources (HITACHI 18 Watt F20T8/D Daylight lamp and PHILIPS TL-D 18 Watt UV lamp) to degrade the dye solutions. The light source optical power was recorded by Precision illumination-solar-UVA 3 in 1-meters (TENMARS, TM-208). At irradiation time intervals, a certain amount of solution (4ml) was taken out and tested by the characteristic UV-vis spectrometer at the absorption wavelength of 617 nm (MaG) to monitor the concentration change of dye solutions. Blank experiments that contain no catalyst were carried out with the samples and proved to have negligible dye degradation upon direct light irradiation.

Results and discussion

We developed a new kind of organic perovskites MA_{0.6}AA_{0.4}PbBr₃ (AM-PE) which harnesses aniline as a replacement of conventionally used methylamine. The introduction of aniline was expected to stabilize the perovskite particles in dispersions and slower their decomposition. The photoluminescence spectra of AM-PE and M-PE dispersions were measured on the

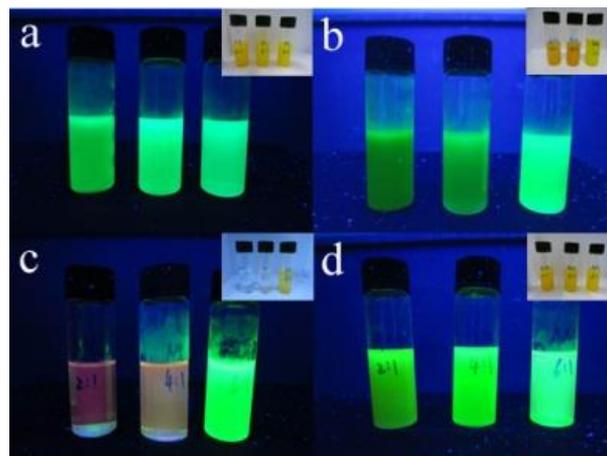


Fig. 1. Photographs of the M-PE and AM-PE dispersions in acetone with three molar ratios of MABr and PbBr₂ (2:1, 4:1, 6:1, from left to right) under UV light (365 nm): fresh M-PE (a) and AM-PE (b) dispersions, aged M-PE (c) and AM-PE (d) dispersions (6 hours). Inset: samples under ambient light.

Edinburgh FLS920 spectrofluorimeter. A comparison of the PL stability of AM-PE and M-PE over 6 h is shown in **Fig. 1**. The three molar ratios of MABr and PbBr₂ (2:1, 4:1, 6:1) of M-PE and AM-PE were prepared. All the as-synthesized perovskite dispersion exhibited strong green emission under UV lamps. AM-PE and M-PE dispersions both emitted green light of 540 nm by Xenon lamp excitation at 470 nm. Over only 6 hours, the PL performance of M-PE dispersion declined along with perovskite particles decomposition and reduction in particle size. In contrast, the AM-PE dispersion still kept the stable PL property and emitted green light under UV lamp. Therefore, the stability of PL performance was significantly improved by introducing aniline into M-PE, and AM-PE particles have a more stable structure than M-PE particles.

As the different perovskite dispersions with three molar ratios of MABr and PbBr₂ (2:1, 4:1, 6:1) showed, the dispersions of 2:1 and 4:1 became transparent gradually under ambient light, and the transform from the green emission to red emission under UV light also happened during 6 hours. The highest ratio of 6:1 exhibited a more stable PL performance. The different extent of the transparent performance indicated the M-PE needs more time to finish the transform process in the existence of extra ammonium.

Based on above experiment, the fresh M-PE dispersions (in acetone) transformed into transparent M-PE solution in several hours. The emission color of M-PE sample changed from green into pink under UV light as the fresh M-PE particles decomposed gradually.

To figure out the transform process, the fresh M-PE (2:1 ratio) dispersion and the transparent M-PE (2:1 ratio) dispersion were compared on the PL emission and excitation spectra. As **Fig. 2** showed, the excitation peak presented a blue shift from 470 nm to 340 nm for the fresh M-PE and transparent M-PE, while their emission peak showed a red shift from

540 nm to 610 nm. For the as-prepared M-PE dispersion, its excitation is active over a wide range of 320 ~ 500 nm, while its emission peak is very narrow around 540 nm. After 6 hours, the dispersion became transparent in visual observation, and emit pink light by excitation in a narrow range of 325 ~ 400 nm. Therefore, the beginning dispersion may consist of wide possible species having different luminescence properties. After aging of 6 hours, the mixture become narrower in composition and thus gave a narrow excitation peak.

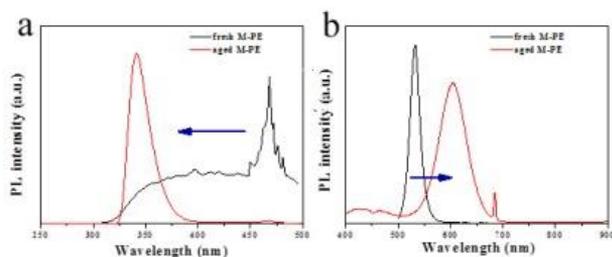


Fig. 2. PL excitation (a) and emission spectra (b) of the fresh and aged M-PE dispersions (detected at 540 & 610 nm for (a), and excited by 470 & 340 nm for (b), respectively).

To explore the photocatalysis mechanism for perovskite, the bandgaps of the perovskite particles were measured by UV-vis diffuse reflectance spectroscopy. The diffuse-reflectance spectrum showed that M-PE and AM-PE had the band edge at about 2.23 eV and 2.21 eV, respectively. Compared with TiO₂ (Degussa P25, band edge 3.2 eV), the perovskite materials (M-PE and AM-PE) have a wider absorption in solar light, which supports a higher photocatalysis efficiency. In addition, the introduction of aniline was proved successful to increase the perovskite absorption in visible light, thus may result in higher photocatalysis efficiency.

As above mentioned, AM-PE particles have a smaller size and better stability than M-PE particles, which will increase the contact area with dye molecules and working life, so AM-PE particles shall have a better photocatalysis performance. To test this hypothesis, a comparison of the photocatalysis activity of AM-PE and M-PE was performed under visible light (office lamp).

Fig. 3 showed the dye concentration change of the MaG solution under visible light in photocatalysis test. In the control sample, the MaG solution kept the constant concentration. Comparing M-PE and AM-PE, AM-PE showed almost twice the catalysis efficiency of M-PE in the degradation of organic dye: malachite green. The AM-PE particles were also assayed in darkness, which gave a slight reduction in the dye concentration. This dye reduction in darkness can be attributed to the physical adsorption of dye onto particles surfaces. In summary, AM-PE presented evidently improved photocatalytic efficiency by involvement of aniline molecules in perovskite structure.

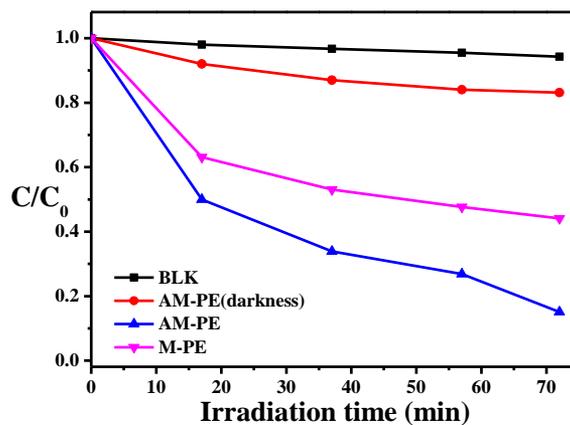


Fig. 3. Comparison of photocatalytic activity of the different photocatalysts: M-PE, AM-PE, AM-PE (darkness) particles in Malachite green solution (5.0 mg/L) under visible-light irradiation (20.5 w/m²).

Conclusion

In this paper, a detailed decomposition process of M-PE dispersion was studied: the emission light color of M-PE sample changed from green into pink under UV light as the fresh M-PE particles reduced gradually. The rapid decomposition was accompanied with the formation of smaller PbBr₂ particles. A new perovskite MA_{0.6}(AA)_{0.4}PbBr₃ (AM-PE) was successfully synthesized to improve the stability of perovskite particles in dispersion. By comparing the PL and PC property of AM-PE and M-PE particles, we found the AM-PE particles presented more stable photoluminescence performance and much higher photocatalytic efficacy than M-PE particles.

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Author's contributions

Conceived the plan: YW, BF; Performed the experiments: YW; Data analysis: YW; Wrote the paper: YW, BF. Authors have no competing financial interests.

References

- Gao, P.; Gratzel, M.; Nazeeruddin, M. K. *Energ Environ Sci* **2014**, *7*, 2448.
DOI: [10.1039/C3EE43214A](https://doi.org/10.1039/C3EE43214A)
- Gratzel, M. *Nat Mater* **2014**, *13*, 838.
DOI: [10.1038/nmat3979](https://doi.org/10.1038/nmat3979)
- Zhang, W.; Anaya, M.; Lozano, G.; Calvo, M. E.; Johnston, M. B.; Míguez, H.; Snaith, H. J. *Nano Lett* **2015**, *15*, 1698.
DOI: [10.1021/acs.nanolett.5b02888](https://doi.org/10.1021/acs.nanolett.5b02888)
- Kim, H. S.; Lee, C. R.; Im, J. H.; Lee, K. B.; Moehl, T.; Marchioro, A.; Moon, S. J.; Humphry-Baker, R.; Yum, J. H.; Moser, J. E. et al. *Sci Rep-Uk* **2012**, *2*.
DOI: [10.1038/srep1317](https://doi.org/10.1038/srep1317)
- Luo, S. Q.; Daoud, W. A. *J Mater Chem A* **2015**, *3*, 8992.
DOI: [10.1039/C5TA02888A](https://doi.org/10.1039/C5TA02888A)
- Pathak, S.; Sakai, N.; Wisnivesky Rocca Rivarola, F.; Stranks, S. D.; Liu, J.; Eperon, G. E.; Ducati, C.; Wojciechowski, K.; Griffiths, J. T.; Haghighirad, A. A. *Chemistry of Materials* **2015**, *27*, 8066.
DOI: [10.1021/acs.chemmater.5b02888](https://doi.org/10.1021/acs.chemmater.5b02888)
- Yang, W. S.; Noh, J. H.; Jeon, N. J.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I. *Science* **2015**, *348*, 1234.
DOI: [10.1126/science.1254043](https://doi.org/10.1126/science.1254043)

8. Bi, D. Q.; Tress, W.; Dar, M. I.; Gao, P.; Luo, J. S.; Renevier, C.; Schenk, K.; Abate, A.; Giordano, F.; Baena, J. P. C. et al. *Sci Adv* **2016**, 2.
DOI: [10.5185/sbm-2010-01](https://doi.org/10.5185/sbm-2010-01)
9. Ling, Y.; Yuan, Z.; Tian, Y.; Wang, X.; Wang, J. C.; Xin, Y.; Hanson, K.; Ma, B.; Gao, H. *Advanced materials* **2016**, 28, 305.
DOI: [10.5185/sbm-2010-01](https://doi.org/10.5185/sbm-2010-01)
10. Han, D. H.; Cha, S. Y.; Yang, H. Y. *Water Res* **2004**, 38, 2782.
DOI: [10.5185/sbm-2010-01](https://doi.org/10.5185/sbm-2010-01)
11. Horikoshi, S.; Saitou, A.; Hidaka, H.; Serpone, N. *Environ Sci Technol* **2003**, 37, 5813.
DOI: [10.5185/sbm-2010-01](https://doi.org/10.5185/sbm-2010-01)
12. Wei, J. H.; Zhang, Q.; Liu, Y.; Xiong, R.; Pan, C. X.; Shi, J. *J Nanopart Res* **2011**, 13, 3157.
DOI: [10.5185/sbm-2010-01](https://doi.org/10.5185/sbm-2010-01)
13. Riaz, U.; Ashraf, S. M.; Aqib, M. *Arab J Chem* **2014**, 7, 79.
DOI: [10.5185/sbm-2010-01](https://doi.org/10.5185/sbm-2010-01)
14. Zhang, L. X.; Liu, P.; Su, Z. X. *Polym Degrad Stabil* **2006**, 91, 2213.
DOI: [10.5185/sbm-2010-01](https://doi.org/10.5185/sbm-2010-01)