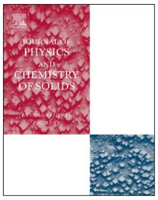
Journal of Physics and Chemistry of Solids 103 (2017) 164–169

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs



Modifying $CH_3NH_3PbBr_3$ nanocrystals with arylamines

Ruimin Zhu[a], Heyuan Liu[b], Li Shen[b], Dejun Sun[a,*], Xiyou Li[a,b,*]

[a] *Department of Chemistry, Shandong University, Jinan, Shandong 250100, China*
[b] *College of Science, China University of Petroleum (East China), Qingdao 266580, China*

ARTICLE INFO

Keywords:
$CH_3NH_3PbBr_3$ perovskite nanocrystals
Arylamine
Surface functionalization
Steric hindrance
Alkalinity

ABSTRACT

Chemically decorating $CH_3NH_3PbBr_3$ with a group of para-substituted arylamine (R-An) was investigated, where R ranges from electron-withdrawing trifluoromethoxy(-CF_3O), to hydrogen or electron-donating ethoxy (-EtO). Different ratios of R-An ammonium bromide and methylammonium bromide (MA) (R-An/MA=3/7, 4/6, 5/5, 6/4 and 7/3) were tested. XRD patterns revealed that the perovskite nanocomposite were cubic with good crystallinity. TEM and photoluminescence suggested that the perovskite nanocrystals were composed of 2D layered and 3D bulk structures. ^1H NMR and TGA experiments revealed that the non-substituted aniline can readily adsorb to the surface of perovskite at any ratios between R-An and MA. But an EtOAn/MA ratio ≥1 is needed to anchor the EOAn molecules on the surface of perovskite. For the arylamine with the electron-withdrawing -CF_3O group, it cannot adsorb to the surface of the perovskite at any concentrations. This result reveals that both steric hindrance and alkalinity can affect the anchoring of arylamine on the surface of $CH_3NH_3PbBr_3$ perovskite. I-V curves of the perovskite nanocrystal films prepared by spin coating suggest that proper surface modification can increase the conductivity significantly.

1. Introduction

Organic-inorganic halide perovskites can date back over a century ago [1]. A particular attention has been attracted since they were applied in photovoltaics by Miyasaka and Park, and performed good photon to electron conversion efficiency [2,3]. These reports triggered tremendous research interest in photovoltaics based on organic-inorganic halide perovskites [4–11]. In just a few years, the efficiency increased at a crazy pace and 20.2% was achieved in 2015 [12]. These star materials have the general formula of $APbX_3$, in which A refers to methylammonium ($CH_3NH_3^+$, MA) and/or formamidinium ($NH_2CH=NH_2^+$, FA), and X is I^- and/or Br^-. The incredible performance of perovskite solar cells (PSCs) is closely related to the intrinsic structure and properties of $APbX_3$. Firstly, strong optical absorption with direct band gap is critical to the outstanding performance of PSCs [13]. Secondly, its readily accessible self-organization from precursor solution and formation of polycrystalline thin film with slow non-radiative charge recombination rates and long lifetime photo generated electrons and holes, leading to large diffusion length for excitons [14,15]. Another striking attribute of the perovskites is their effective dimensionality of extended inorganic layer, which leads to low resistivity and high charge-carrier mobility [16–18]. Notably, PSCs with $CH_3NH_3PbBr_3$ as light absorber often have an extremely high open-circuit voltage, which is as high as 1.6 V in single-junction PSC [19] and 2.2 V in tandem PSC [20]. These are much higher than the applied bias voltage (1.23 V) for water-electrolysis, making PSCs based on $CH_3NH_3PbBr_3$ as promising candidates to achieve direct solar-to-hydrogen conversion. In addition, some other applications of the perovskite materials have been explored, such as in light emitting diodes [21,22], Li-ion batteries [23], and fluorescence sensors [24], in which the perovskite materials were used in the form of bulky thin solid films or confined nanomaterials.

The nano-structured perovskite has the advantages of easily surface-functionalization and property-adjusting, for which it has attracted much attention [25–28]. The nano-structured organolead perovskite can be prepared simply by adding the solution of perovskite precursor in polar solvent into a non-polar or low polar solvent [29,30]. The capping ligands with $-NH_2$ or $-NH_3^+$ head group can be added in the precursor, which can conveniently control the size and photoluminescence of the resultant nano-structured organolead perovskite [26,31–33]. In our recent work, we have successfully synthesized perylenetetracarboxylic diimide modified $CH_3NH_3PbBr_3$ nanoparticles. Efficient photo-induced electron transport from perovskite to the anchored ligand was observed. The result paved a convenient way to functionalize organolead perovskite [34].

Arylamine is a large family of compounds with structure diversity and flexibility. More importantly, it can be chemically modified easily in different positions of aromatic ring or heterocyclic ring. If arylamine

---

* Corresponding author at: College of Science, China University of Petroleum (East China), Qingdao 266580, China.
E-mail address: xiyouli@sdu.edu.cn (X. Li).

http://dx.doi.org/10.1016/j.jpcs.2016.12.018
Received 16 November 2016; Received in revised form 15 December 2016; Accepted 19 December 2016

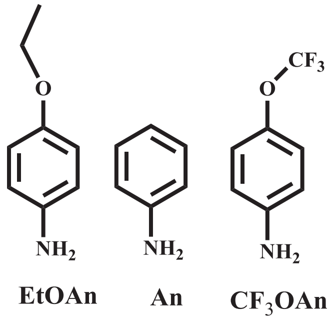


Chart 1. Structures of three arylamines used in paper.

can chemically decorate on the surface of perovskite, a great number of candidates can be used as ligands to tune the properties of perovskite and it should be a promising strategy towards novel properties and new applications of perovksite material. Among the arylamines, ortho- or meta-substituted arylamines have larger steric hindrance than para-substituted ones, which may hinder the adsorption of arylamine molecules on the surface of perovskite. Therefore, in the present work we chose three para-substituted arylamines (R-An), where R ranges from electron-donating ethoxy (EtO) to hydrogen, or electron-withdrawing trifluoromethoxy(CF_3O), to investigate whether arylamine can be chemically adsorbed onto the surface of $CH_3NH_3PbBr_3$. The molecular structures of the arylamines are shown in Chart 1.

2. Experimental section

2.1. Material and methods

All solvents were of analytical grade. DMF and acetone for preparation of perovskite NPs were dried by CaH_2 before use. All other chemicals were used as received without further purification. Arylamine bromine salts (R-AnBr) were prepared by the reaction of the corresponding arylamine with hydrobromic acid at 60 ℃ and then recrystallization with methanol/anhydrous ether. Methylammonium bromide (MABr) was prepared according to the reported method [3].

2.2. Preparation of An-MA perovskite nanocryatals

Oleic acid (96 mg) in 2 ml octadecene were stirred and heated at 80 ℃. R-AnBr was added into the hot solution. Then methylammonium bromide (MABr) in DMF (0.1 ml) and lead (II) bromide (36.7 mg, 0.1 mmol) in DMF (0.1 ml) were subsequently added. Yellow precipitates were formed by adding the hot reaction solution into hot acetone. The precipitates were collected by centrifugation (4000 rpm, 10 min). The molar ratio of R-AnBr/MABr ranges from 3/7, 4/6, 5/5, 6/4 to 7/3, and the total molar amount of ammonium salt was kept equal to the molar amount of $PbBr_2$. The resulted samples were labeled as *x*RAn-*y*MA, where x/y refers to the molar ratio of R-AnBr/MABr used in preparation.

2.3. Measurements

^1H NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer with chemical shifts reported in ppm (TMS as internal standard). Thermogravimetric analysis data were collected on *TGA/DSC1 STAR* e *System* with the resolution of 1 microgram (Mettler Toledo). The samples were heated from 30 to 800 ℃ at the rate of 10 ℃ min^{-1} with a nitrogen flux of 40 ml min^{-1}. Powder X-ray diffraction (XRD) patterns were obtained by D8 Advance X-ray diffractometer (Bruker, Germany) with Cu Kα radiation. Energy-dispersive X-ray spectroscopy (EDS) was carried on 7593-H (Horiba). All the measurements were conducted at room temperature. Steady-state fluorescence spectra were recorded on F-7000 FL Spectrophotometer (Hitachi). TEM graphs were taken by H-7650 microscope (Hitachi) at an accelerating voltage of 200 kV. I–V curves were recorded on Keysight B2910A precision source/measure unit with an incorporated direct current voltage supply. The microscopic images were obtained on Swin probe station (EPS-4) with×90 amplification.

3. Results and discussion

3.1. Composition analysis

3.1.1. ^1H NMR spectroscopy method

^1H NMR spectroscopy is a powerful method to identify ligands on the surface of colloid quantum dots [35]. It can verify the presence of organic components because different organic molecules show a unique spectral signature. In our experiment, DMSO-d_6 was used as solvent to dissolve the nanocrystals. ^1H NMR spectrum can give the ratio of R-An^+ and MA^+ in the nanocomposite. The characteristic signature of MA^+ is the peak at 2.32–2.40 ppm (Fig. S1a), which was ascribed to the H of -CH_3. The amount of MA^+ can be calculated by the integration of the peak area. The characteristic signatures of R-An^+ is the signals of phenyl ring in the range of 6.95–7.51 ppm and the content of the aromatic amines can be estimated from the integration of the corresponding peak area (Fig. S1). The ^1H NMR spectra of An-MA series are shown in Fig. 1. The characteristic peaks at the range of 6.95–7.51 ppm were observed. The ratio between An and MA estimated from the integrated peak area between the phenyl Hs and methyl Hs increases with the amount of AnBr added, indicating that the number of An cations anchored onto the perovskite surface increases sequentially. The related experimental results are summarized in Table 1. Obviously, very small amount of An cations anchored onto the surface of perovskite when the ratio of AnBr/MABr was less than 5/5, but it started to increase sharply when the ratio was up to 5/5. It reveals that larger feeding molar ratio of AnBr/MABr favors the surface-modification of perovskite by aniline. When the feeding ratio of AnBr/MABr was raised to 7/3, the actual molar amount of anchored An on the surface of resultant perovskite nanocrystal can reach 39.7% relative to MA.

In contrast, for EtOAn-MA series (Fig. S2), no peaks were observed in the range of 6.95–7.51 ppm in the ^1H NMR spectra of 3EtOAn-7MA and 4EtOAn-6MA in which the ratio of EtOAnBr/MABr used in preparation were 3/7 and 4/6, respectively, suggesting that no EtOAn cations existed in the corresponding perovskite nanocrystals. However, with the ratio of EtOAnBr/MABr increased to 5/5 or more than 5/5, such as 5EtOAn-5MA and 6EtOAn-4MA, very weak signals of phenyl H can be identified in the ^1H NMR spectra, suggesting the presence of trace amount EtOAn in the samples. When the feeding ratio of EtOAnBr/MABr increased to 7/3, the actual molar amount of EtOAn cations in the resulted perovskite was greatly increased to 22.7% relative to MA.

However, when CF_3OAnBr was used, completely different results were obtained. There is not any trace of CF_3OAn cations can be identified in the ^1H NMR spectra even when the ratio of CF_3OAnBr/MABr added is increased to 9/1 (Fig. S3). Therefore, CF_3OAn cations cannot anchor onto the surface of perovskite, probably due to the electron-withdrawing property of -CF_3O, which reduced the alkalinity of the amino group.

3.1.2. Thermogravimetric analysis

The composition of the resulted nanocrystals can also be characterized by thermogravimetric method. The TGA curves of RAn-MA are shown in Fig. 2 and the details of weight loss are list in Table 2. The weight loss stage between 500 and 680 ℃ of these three series compounds is in good accordance with the thermal decomposition of $PbBr_2$ part of perovskite [32,36]. The significant difference among the samples is the decomposition temperature of organic components of perovskite. TGA curve of MABr salt shows that it begins to decompose