



Synthesis of PbS-CH₃NH₃PbI₃ core-shell nanoparticles with enhanced photoelectric properties



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ABSTRACT

A new method for synthesizing freestanding PbS-CH₃NH₃PbI₃ (MAPI) core-shell nanoparticles (NPs) with enhanced light absorption and photoelectric properties was reported. The transmission electron microscopy (TEM) and energy dispersive spectrometer (EDS) analysis confirmed the core-shell structure of the obtained sample. The Vis-NIR spectra proved the core-shell sample absorbed light both in visible and near infrared region. For comparison, oleic acid/oleylamine molecule capping PbS NPs, MAPI molecule capping PbS NPs, and PbS-MAPI core-shell NPs were used to fabricate Schottky solar cells. PbS-MAPI core-shell NPs based solar cells delivered a photocurrent response from both the PbS and MAPI, and achieved the highest overall PCE.

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1. Introduction

Semiconductor quantum dots (QDs) have aroused considerable interest as promising photovoltaic materials because of their extraordinary physical properties, such as band gap tunability by size control [1,2], intrinsic high extinction coefficients [3], and high dipole moments [4]. Particularly, PbS QDs have been widely used as light absorber in various solar cells due to its broad light harvesting capability over the UV, visible, to IR regions [5–8]. In the synthesis process of semiconductor QDs including PbS QDs, organic capping ligands were widely used to prevent aggregation, and passivate the particle [8–10]. Nevertheless, long-chain insulating organic ligands also hindered charge transfer and transport between QDs, and must therefore be removed for the integration of NPs into solid films as required for solar cells. The exchange of organic ligands with shorter ligands (e.g. mercaptopropionic acid, ethanedithiol, thio-glycolic acid) or smaller inorganic species (e.g. I⁻, S²⁻, CdCl₂) has been reported to decrease the distance between QDs, which greatly improved charge transport in QD films [11–15].

Ideally, the passivation state, i.e. the passivation state of QDs

capped by longchain organic ligands, will preserve after ligand exchange process. However, the ligand exchange with shorter or smaller species introduces many surface defects such as vacancies and dangling bonds, which increases the opportunity for trap-assisted recombination [16]. Therefore, it is necessary to passivate ligand-treated QD surfaces to fabricate high-efficiency QDs based solar cells. Introducing a passivation layer to prevent trap states is one of the methods for surface passivation. Basically, there are two strategies to prepare passivation layer. One utilizes the reaction between the surface of QD and the foreign agent to form the layer, which consumes QD itself. PbS-PbI₂, PbS-CdS core-shell QDs have been successfully synthesized via this strategy [17–19]. The other employs various film deposition methods, such as successive ionic layer adsorption and reaction [20], colloidal atomic layer deposition [21], etc., to deposit passivation layer on the QD surface. Diverse materials, including pristine materials (e.g. CdSe, CdS, ZnSe) [20–22], doped materials (e.g. Mn-doped CdSe, Cu-doped ZnS) [23,24], and composite (e.g. ZnS/Ga(OH)₃, ZnS/Ca(OH)₂, ZnS/Mg(OH)₂) [25] have been successfully coated on QDs as passivation layers through this strategy to improve the performance of QDs based solar cells.

In this work, the organic-inorganic hybrid materials, CH₃NH₃PbI₃ (MAPI) was employed as the passivation shell of PbS, and the properties of PbS-MAPI core-shell nanoparticles (NPs) were

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investigated. MAPI alone has exhibited very high potential for application in solar cells devices, due to its appropriate direct bandgap, high absorption coefficient, excellent carrier transport, and apparent tolerance of defects [26,27]. It is predicted that the introduction of MAPI shell can improve the photoelectric property of PbS QDs. A new method for preparing PbS-MAPI core-shell structure was proposed. PbS nanocrystals (NCs) were used as seeds, which were dispersed in PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ mixed precursor solution. By decreasing the polarity of precursor solution, MAPI was precipitated on the surface of PbS from solution, and the free-standing PbS-MAPI NPs were obtained. The core-shell NPs based solar cells exhibited higher efficiency compared with PbS core only solar cells.

2. Experimental

All reagents were purchased from Aladdin Industry Inc. and used without further purification.

2.1. Synthesis of PbS NPs

PbS NPs were synthesized by a two-liquid-phase method as our previous work [9]. In brief, 0.025 mmol PbCl_2 , 1.25 ml oleylamine (OLA) and 5 ml oleic acid (OA) were mixed together to form clear solution. Sulfur precursor was prepared by dissolving 0.02 mmol Na_2S in 5 ml dimethyl sulfoxide (DMSO) under sonication. PbCl_2 solution was added to Na_2S solution at room temperature of 20°C and reacted for 0.5 h. The surface of PbS particles formed at two liquid interface was capped by OLA or OA, which facilitated the dispersion of particles in the OLA/OA solution. The OLA/OA phase was extracted and a proper amount of ethanol was added to precipitate PbS particles, which were collected by centrifugation. The precipitate was washed three times with ethanol and then redispersed in hexane.

2.2. Ligand exchange and preparation of the PbS-MAPI core-shell NPs

$\text{CH}_3\text{NH}_3\text{I}$ was synthesized via the method reported in the previous literature [28]. 20 ml methylamine (40% in methanol) and 30 ml hydroiodic acid (45 wt% in water) were mixed in a 250 ml round-bottom flask and maintained at 0°C for 2 h with stirring. After reaction, the solution was putted on a rotary evaporator and removed the solvents at 50°C . For purification, the yellowish raw product $\text{CH}_3\text{NH}_3\text{I}$ was washed with diethyl ether for three times, and finally recrystallized from a mixture of diethyl ether and ethanol. The solid was filtrated and dried at 60°C in a vacuum oven for 24 h.

The ligand exchange, replacing OA and OLA on the surface of PbS particles with lead halide perovskite, was conducted before preparing core-shell structure. The ligand exchange process was similar to the steps reported by Dirin [29] with a little modification. Typically, 0.03 mmol PbI_2 and equimolar $\text{CH}_3\text{NH}_3\text{I}$ were dissolved in 2 ml *N,N*-Dimethylformamide (DMF) to obtain lead halide perovskite solution, which was mixed with 1 ml colloidal solution of PbS NPs in hexane. The mixture was stirred vigorously for hours, until most PbS NPs migrated from hexane to DMF phase as shown in Fig. 1.

After ligand exchange, the DMF phase was extracted and rinsed 3 times with pure hexane. The obtained colloid solution was the mixed solution of PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ with dispersive PbS NPs in DMF. To obtain MAPI molecule capping PbS, NPs were precipitated by adding acetone, centrifuged and redispersed in DMF. To obtain core-shell NPs, the mixed solution of PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ with dispersive PbS NPs in DMF was added drop by drop to the 20 ml

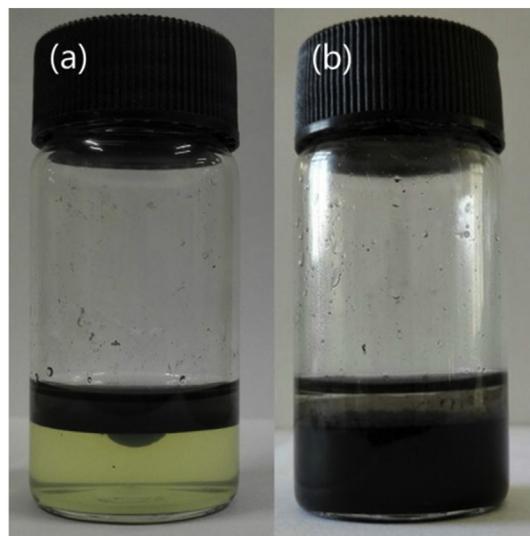


Fig. 1. Photographs of PbS colloid (a) before and (b) after ligand exchange. The top liquid phase was hexane, and the bottom liquid phase was mixed solution of PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ in DMF.

toluene under slow stirring. Then the NPs were collected by centrifugation and washed with toluene.

2.3. Fabrication of the Schottky solar cells

Fluorine-doped SnO_2 -coated transparent conducting glass substrate (FTO; $14 \Omega/\text{sq}$, Nippon Sheet Glass) was pre-patterned by etching with Zn powder and 25 wt% HCl solution for about 1 min. The etched FTO glass was ultrasonically cleaned in water, ethanol and then acetone, respectively. The cleaned FTO substrate was subsequently coated with a compact TiO_2 layer by spin coating 0.2 M butyl titanate petroleum ether solution and heating at 450°C for 30min. OA/OLA capping PbS (OCP), MAPI capping PbS (MCP), and PbS-MAPI core shell NPs (CSP) was respectively deposited on top of the TiO_2 compact film by drop casting. A small volume ($15 \mu\text{L}$) of the colloid (5 mg ml^{-1}) was drop-casted on the cleaned FTO glass. The films were dried at 60°C for 30min and then heated at 100°C for 5min under vacuum. Finally, the counter electrode was deposited by thermal evaporation of Al. The active area of the cells was 0.25 cm^2 .

2.4. Characterizations

The detailed microscopic characterization of the samples was analyzed using transmission electron microscope (TEM). The morphology and composition of the products were analyzed by field-emission scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector. The light absorption property was tested with Shimadzu Lambda750.

The photocurrent-voltage (*I-V*) curves were measured by Keithley 2400 source meter under an illumination of a solar simulator (Newport Oriel 91192) at 100 mW cm^{-2} . The incident photo to current conversion efficiencies (IPCE) of the fabricated solar cells were measured at the excitation wavelengths of from 450 to 1900 nm with Solar Cell Scan 100.

3. Results and discussion

Fig. 2 illustrates the formation process of the PbS-MAPI core-shell particles. A simple solution phase method to synthesize MAPI

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