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Effect of thickness on the performance of hybrid solar cells fabricated using surfactant free lead sulfide quantum dots and poly(3-hexylthiophene-2,5-diyl) polymer

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ABSTRACT

Surfactant free lead sulfide (PbS) nanoparticles (NPs) had been synthesized by precipitation method using lead acetate and thiourea as precursor. Mechanical grinding using mortar pestle has been done to deagglomerate the NPs to obtain finer nanoparticles. Ground NPs were further sonicated using high power probe sonicator in chlorobenzene solution. The poly(3-hexylthiophene-2,5-diyl) (P3HT) polymer was added into the chlorobenzene solution containing well dispersed PbS quantum dots (QDs). The blends solution containing PbS QDs and P3HT polymer was spin coated at different rotation per minute to obtain an optimum thickness for efficient hybrid solar cells fabrication. Scanning electron microscopy, atomic force microscopy and transmission electron microscopy analysis showed a homogeneous distribution of PbS QDs in the P3HT matrix. Photoluminescence (PL) measurements performed on the blends solution showed strong PL quenching, which was very much dependent on the PbS QDs concentration, indicating that proper photoinduced electron and hole transfer occurred in PbS:P3HT blend. Hybrid solar cells with configuration indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS)/PbS:P3HT/Al had been fabricated with different active layer thicknesses. The device with optimum thickness showed the highest efficiency of 1.75% under Air Mass 1.5G illumination with the irradiation of 100 mW/cm^2. Morphological and optical investigations showed that improvement in the performance was achieved for the optimum thickness of the active layer due to good distribution and interconnection of surfactant free PbS QDs in P3HT matrix.

1. Introduction

Solution processed hybrid solar cells based on conjugated polymers and inorganic components have attracted much attention due to low fabrication cost and feasibility of large area devices on flexible substrates [1,2]. In recent years the hybrid solar cells efficiencies have increased markedly and reached >5% [3]. The superior mobility and chemical stability of inorganic materials make these hybrid solar cells technologies more promising. To date, hybrid solar cells have been fabricated using a wide range of inorganic materials, such as PbS [4], PbSe [5], CdS [6], CdSe [7], Sb_2S_3 [8] and ZnO [9] nanoparticles, along with many organic materials, such as conjugated polymers and small molecules [10]. In most of the systems the NCs are capped with long chain organic ligands, which inhibit the efficient charge transfer between polymer and NCs. Different approaches: (1) solution phase (octylamine, octanethiol) (2) post-deposition (acetic acid, 1,4-benzenedithiol) of ligand exchange have been used. Post deposition ligand exchange is found to improve the performance of the hybrid solar cells [11]. It is reported that optimum concentration of thiol is required for proper ligand exchange, over treated films result in the formation of cracks, which ultimately affect the device performance [12]. Capping the quantum dots (QDs) with short chain ligands can lead to clustering and limit the solubility. The ligand exchange process is challenging since often the increased clustering and limited solubility result in a more extensive phase separation and higher surface roughness. Ligands have a big impact on the electrical performance of the nanoparticles (NPs). Ligands that act as electrical insulators with large band gaps can severely reduce device efficiency by impeding charge transport between nanocrystals and reducing charge separation at semiconducting polymer-NP interfaces [13]. Complete removal of the surfactant ligands would provide direct contact between the nanocrystals and the polymer but it introduces the defect states on the nanocrystals [13,14].

Recently, oxygen plasma was applied to completely eliminate the ligands from the surface of QDs [15]. The obtained ligand free PbS QDs with low band gap polymer (PSBTBT) is used to fabricate the hybrid solar cells. The achieved efficiency is 1.7%. In another report [16], surfactant free CdS NPs, prepared using continuous spray pyrolysis (CoSP) technique followed by mechanical grinding using mortar pestle to obtained fine NPs, have been blended with conjugated polymers. The

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hybrid solar cells fabricated using spray technique showed an efficiencies of 0.6% and 1.06% with poly(3-hexylthiophene-2,5-diyl) (P3HT) and Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b;3,4-b′]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT) polymer. Surfactant-free PbS agglomerates prepared using CoSP technique deagglomerated into fine particles using mortar pestle and blended with P3HT polymer has also been reported [17]. The reduction of PbS concentration to 30 wt% is found to give the highest efficiency of 1.6%.

Here, we have demonstrated another facile method to directly synthesized ligands free PbS NPs of bigger sizes (size much greater than the Bohr exciton radius) with high yield using precipitation technique. Generally colloidal routes are commonly used to prepare capped QDs for fabrication of high efficiency hybrid solar cells. The synthesis of PbS QDs using these techniques require more attention to control the parameters like temperature, reaction time etc. and the use of toxic ligands and high boiling point solvent make these techniques more complicated. The method reported in this paper uses a deagglomeration method of to obtain fine QDs from the as prepared, bigger sized NPs yielded by the precipitation technique. The method involves mechanical grinding using mortar and pestle followed by sonication using a high power probe. This method has one disadvantage that it introduces the surface defect in the nanocrystals, which are not beneficial for solar cell devices. Here, our main aim is to show the impact of above mentioned method to create PbS QDs and hybrid solar cells fabrication. Using a blend with 30 wt% NPs in polymer matrix (following the effectiveness of surfactant free PbS NPs reported earlier), the effect of thickness on the performance of hybrid solar cells has been investigated.

2. Experimental details

2.1. Materials

Lead acetate (CDH, India Ltd.), thiourea (Merck), deionized water (Milli-Q, Millipore), chlorobenzene (Merck), regioregular P3HT polymer (Sigma-Aldrich) and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Baytron P VP A1 4083) were used as obtained. Patterned indium tin oxide (ITO) coated glass substrates were purchased from Moser Baer, India.

2.2. Synthesis of PbS nanoparticles

PbS nanoparticles were synthesized by the precipitation method, in which lead acetate (0.1895 g, 0.005 M) was injected to the deionized water with continuous stirring. Thiourea (0.038 g, 0.005 M) was introduced into the solution with continuous vigorous stirring for 15 to 20 min. The pH of the solution was maintained by drop wise addition of liquid ammonia. The solution turned from light milky to light blackish which indicates the formation of PbS NPs. Finally, centrifugation was done to collect the PbS NPs. The NPs were dried in vacuum oven at 80 °C for 60 min. The as synthesized PbS NPs were mechanically ground using mortar and pestle followed by sonication using a high power probe sonicator (PCI Analytics Pvt. Ltd., Mumbai) to de-agglomerate the NPs and to yield PbS QDs. The entire process of creating PbS agglomerates and then PbS QDs was accomplished within 90 min. Without having to use any expensive chemicals and time consuming chemical processing as reported for other techniques [18]. The simplification of PbS QDs fabrication using PbS NPs from the precipitation method is a major achievement by itself.

2.3. PbS:P3HT blend solution preparation

First, PbS NPs were ground using mortar and pestle to deagglomerate the NPs into fine particles. The ground NPs were then sonicated using high power probe sonicator (pulse amplitude 60%, on time 10 s., off time 2 s.) in chlorobenzene solution. The stable solution containing well dispersed PbS QDs was obtained after the probe sonication. Second, P3HT polymer from Sigma Aldrich (molecular mass = 15,000–45,000 Da, regioregularity ≥95%, polydispersity index ≤2 and mobility range 10^{-4}–10^{-1} $cm^2/V \cdot s$) was added into the QDs solution with stirring for 2 h at 50 °C. 10 mg of P3HT polymer and 30 wt% of PbS QDs in 1 ml of chlorobenzene solution were used to fabricate the devices. For optical studies uniform thin films of pristine P3HT and PbS:P3HT blend were prepared on cleaned glass substrate using spin coating technique. The films were annealed at 120 °C for 25 min.

2.4. Characterization

Elemental analysis of the PbS NPs was obtained using ZEISS EVO MA10 Microscope. Phase analysis of the as synthesized PbS NPs was done using X-Ray diffractometry (XRD, Phillips X'PERT PRO), with a CuKα incident beam ($\lambda = 1.54056$ Å). Particle size of PbS NPs and PbS:P3HT blend morphology were seen from the TECNAI G2T30 transmission electron microscopy (TEM). Absorption of PbS NPs and PbS:P3HT blend solutions were measured with UV–Vis-NIR spectrophotometer (Perkin Elmer Lambda-1050). Room temperature photoluminescence spectra of blend solutions were recorded using Perkin Elmer LF 55 spectrophotometer (in the wavelength range of 500–850 nm). Scanning electron microscopy (ZEISS EVO-50 model) was used to study the surface morphology of the PbS:P3HT blend. The surface roughness and topography were measured using Bruker Dimension Icon atomic force microscopy (AFM) in tapping mode. The film thicknesses for all the samples were measured using Dektak surface profilometer using 2 μm stylus tip. The EQE spectra were recorded at

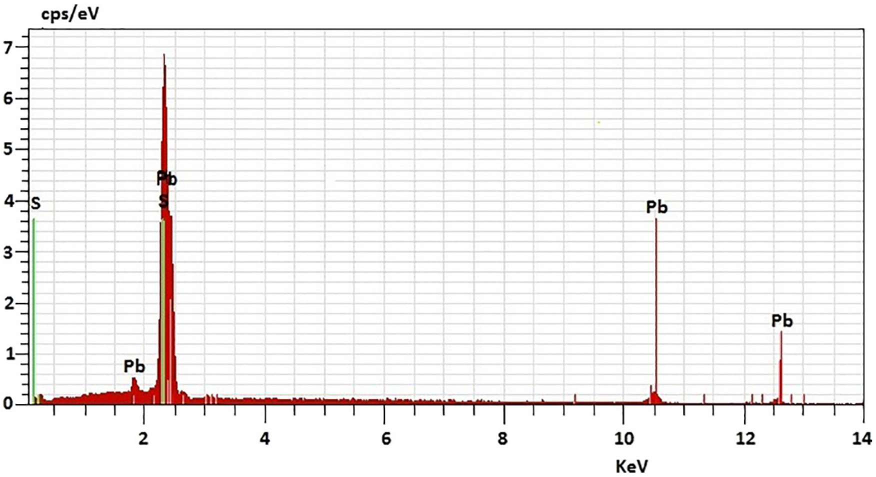

Fig. 1. EDX plot of PbS nanoparticles.