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Synthesis of thiol modified CdSe nanoparticles/P3HT blends for hybrid solar cell structures

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ABSTRACT

Thioglycolic acid (TGA) capped cadmium selenide (CdSe) nanoparticles were synthesised in aqueous medium through wet chemical method using sodium selenite as the selenium source. The synthesised particles were transformed into organic medium using 1-dodecanethiol through efficient partial ligand exchange strategy. The UV–visible spectra recorded for the particles reveal the size distribution in water as well as in organic solvent. TEM analysis of the synthesised particles shows the size and the nature of distribution of the particles in solution. The phase transferred particles were blended with the polymer poly-3-hexyl thiophene (P3HT) in chloroform. UV–visible and photoluminescence spectra of the polymer with various volumes of the nanoparticles clearly indicate the effective coupling and the efficient charge transfer process in the blend. SEM analysis of the CdSe–P3HT blends confirms the effective distribution of the nanoparticles in the polymeric matrix. AFM studies reveal the morphology of the nanoparticles and the phase separation process in the blends.

1. Introduction

Semiconductor nanoparticles have a wide variety of applications in optoelectronics particularly in photovoltaics due to their size dependent properties [1,2]. Due to the limitation of the poor charge carrier mobility, organic acceptor molecules like fullerenes and PCBM are being replaced by semiconductor nanocrystals such as CdSe, CdTe, CdS, ZnO and TiO_2 to fabricate the hybrid solar cells based on the bulk heterojunction concept [3–9]. In recent years, the blends of these nanocrystals with semiconducting polymers have shown wide range of applications in the photovoltaics. CdSe is of great interest and useful in hybrid and quantum dot sensitised electrodes for solar cells [10,11] due to the size tunability nature and low bandgap ($E_g = 1.74$ eV in bulk form). Moreover, the absorption wavelength of nano sized CdSe could be tuned to near-IR region which shows its applicability in solar cells. CdSe nanoparticles were synthesised mostly in organometallic medium with trioctyl phosphine oxide (TOPO) as the capping ligand. Then surface treatment with pyridine was carried out with polymer, the blend was used as active layer in hybrid solar cells [12–14]. CdSe nanoparticles synthesised with TGA in aqueous system have major setback in many useful applications as they are immiscible in organic solvents. To eliminate this problem, the phase transfer chemistry has been proposed. Phase transfer of semiconductor nanoparticles from aqueous to organic medium is being carried out using different methods [15–17]. Gaponik et al. [18] have proposed a suitable method which helps to transfer the aqueous synthesised CdTe nanoparticles into organic medium through the long chain 1-dodecanethiol. This method is a simple and convenient one for the photovoltaic applications. Also, the 1-DDT capping has shown considerable application in

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HgTe nanoparticles for electroluminescent devices [19]. The ligand TOPO is toxic, hazardous in nature and it requires pyridine treatment of the particles for application as active layer in solar cells. Hence, the alternative pathway to produce CdSe nanoparticles soluble in the organic solvent with the suitable ligand for the active layer application was highly motivated. Recently, 1-DDT ligand capped semiconductor nanoparticles were shown as potential candidates for photovoltaic applications [20]. Since these ligands play a major role in the morphology and the efficiency in charge transport of the active layer, significant efforts were focussed for their selectivity. The non-TOPO based synthesis of the CdSe nanoparticles for hybrid solar cells has been achieved using the Aerosol Flow Growth Technique at high temperature using 1-DDT as the capping agent [21]. Further, the ligand 1-DDT can give a better spatial resolution than the short chain ligand thioglycolic acid (TGA) that can be used effectively for the phase transfer process. Moreover, 1-dodecanethiol acts as the very good additive in the performance of P3HT:PCBM blends [22]. Phase transferred particles capped by 1-DDT can readily be blended with P3HT polymer without surface treatment which eliminates the pyridine treatment (toxic) reaction. In this paper, the synthesis of TGA capped CdSe nanoparticles at low temperature (90 °C) in aqueous medium is reported. The synthesised particles were phase transferred through the partial ligand exchange process using 1-dodecanethiol. The phase transferred particles were blended with the polymer P3HT in chloroform. The optical properties and morphological analysis of the blends were evaluated.

2. Experimental section

2.1. Chemicals

Precursors in the form of cadmium chloride ($CdCl_2$) SRL (97%), sodium selenite (Na_2SeO_3) CDH (99%), thioglycolic acid (TGA) SPECTROCHEM (95%) , sodium borohydride ($NaBH_4$) MERCK (95%) , sodium hydroxide (NaOH) SRL (98%), trisodium citrate dihydrate (($C_6H_9Na_3O_9$) SRL (99%), chloroform ($CHCl_3$) MERCK (99%), regioregular poly-(3-hexyl thiophene)-2,5 dyl (P3HT) Sigma Aldrich (99.99%) and poly(3,4-ethylene dioxythiophene) doped with polystyrenesulfonic acid (PEDOT:PSS) Sigma Aldrich (99.99%) were used for casting of different layers towards development of solar cell structures.

2.2. Synthesis of TGA capped CdSe nanoparticles

CdSe nanoparticles were synthesised with the following procedure: Cadmium chloride (1 mM) was dissolved in the deionised water and the ligand thioglycolic acid (5 mM) was added with it. A white turbidity of the solution arises which confirms the formation of cadmium thiolate complex. This turbidity was eliminated when the pH of the solution was adjusted into 10.5 using 0.1 M NaOH solution. Then trisodium citrate dihydrate was added into the solution. The entire mixture was taken in the three necked flask and the solution was stirred under the nitrogen atmosphere. With this, sodium selenite (0.5 mM) and excess of sodium borohydride were added gradually and heated upto 90 °C. The appearance of yellow coloured solution which turned into red orange colour on prolonged refluxing indicates the formation of CdSe nanoparticles. The entire solution was refluxed under the nitrogen atmosphere to get the desired size.

2.3. Phase transfer of the CdSe nanoparticles

Aqueous synthesised CdSe nanoparticles were transformed into organic phase using Gaponik's method [18]. Briefly, 1-dodecanethiol was mixed with equal amount of the aqueous CdSe nanoparticles in solution. A measured quantity of acetone was added and the entire mixture was shaken well with mild heating. The transformation of the CdSe nanoparticles from aqueous phase to organic phase was observed after some time due to partial ligand exchange of the thioglycolic acid by 1-dodecanethiol. The organic phase was separated and precipitated with the addition of methanol and the resultant precipitate was redispersed in chloroform for further studies. The schematic diagram of this phase transfer process is given in Fig. 1. The particles were found to be stable in the organic phase. As prepared 1-DDT capped nanoparticles were mixed with chloroform and P3HT polymer. The entire solution was stirred for 12 h for complete mixing of P3HT and CdSe nanoparticles.

The ITO coated glass substrate was pre-treated with various solvents including acetone, isopropanol, methanol and dried in vaccum. Finally, aqueous dispersion of PEDOT:PSS was applied on the ITO layer for 1000 rpm through spin coating. Then the substrate was allowed to anneal at 80 °C for 15 min. The prepared CdSe/P3HT blend in chloroform was then coated on the substrate at 1500 rpm. The substrate was again heated at 100 °C for 10 min. The final structure ITO/PEDOT:PSS/CdSe–P3HT was analysed for further characterisation.

2.4. Characterisation instruments

UV–visible absorption spectra of the particles were analysed with ELICO SL-159 UV–Visible conventional spectrophotometer in the range of 200–800 nm. Photoluminescence spectra were recorded using JASCO FP-6300 spectrofluorometer at the excitation wavelength 400 nm. HRTEM images were observed with an electron microscope (Tecnai G2 model T-30 s-twin) using an accelerating voltage of 300 kV. SEM images were recorded using Carl Zeiss MA15/EVO 18 Scanning Electron Microscope. AFM

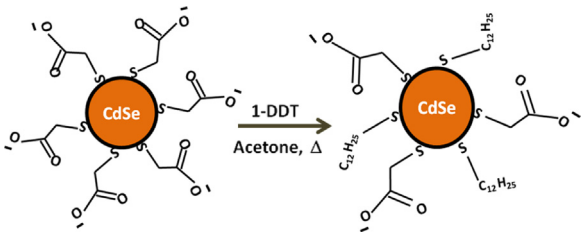

Fig. 1. Phase transfer process of the CdSe nanoparticles.