Conference Paper

Synthesis and Efficient Phase Transfer of CdSe Nanoparticles for Hybrid Solar Cell Applications

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Colloidal cadmium selenide (CdSe) nanoparticles capped by a short chain thiol ligand thioglycolic acid (TGA) were prepared in aqueous medium at 100°C using sodium selenite as the selenium source. The prepared particles were efficiently transferred into organic phases through the partial ligand exchange process using 1-dodecanethiol (1-DDT). The FT-IR spectrum analysis shows the existence of the ligands on the surface of the nanoparticles in aqueous and organic phase through their characteristic modes. TEM analysis of the prepared samples reveals the size and crystalline nature of the particles. EDX analysis indicates the presence of respective elements in the resultant powdered sample. The possible mechanism of the phase transfer process was analysed. The resultant phase-transferred particles can efficiently be blended with a low band gap semiconducting polymer in a common solvent for active layer in hybrid solar cell fabrication. The results are discussed in detail.

1. Introduction

II–VI group semiconductor nanoparticles have attracted much attention in recent years for solar cells due to their size tunable optical properties, absorption of light in the visible region, and so forth [1]. Among them, CdSe nanoparticles have shown potential applications due to their high quantum yield, the tunable emission spectrum wavelength, and so forth. So far, organometallic precursors-based syntheses are widely reported which need high temperature, pyrophoric nature and extremely toxic one [2]. The aqueous-based synthesis of CdSe nanoparticles is, hence, much attracted. But in application purpose, the major hindrance of aqueous synthesized particles is the setback in terms of solubility in organic solvents. This makes them keeping away from their usage in solar cells. But, by applying phase transfer chemistry, it is possible to replace the ligands on the surface of the nanoparticles thereby making them into photovoltaics and other applications. Phase transfer of semiconductor nanoparticles was reported using various types of ligands [3]. Here, in the present work, aqueous synthesis of CdSe

nanoparticles is reported using air stable selenium source, sodium selenite. The synthesized particles were transferred into organic phase using 1-dodecanethiol through partial ligand exchange strategy. The synthesized and phase-transferred nanoparticles were studied using various characterization techniques.

2. Experiment

2.1. Chemicals. Cadmium chloride (CdCl_2), sodium selenite (Na_2SeO_3), trisodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$), sodium borohydride (NaBH_4), sodium hydroxide (NaOH), thioglycolic acid (TGA), 1-dodecanethiol (1-DDT), and acetone ($\text{C}_7\text{H}_6\text{O}$) are used.

2.2. Synthesis of CdSe Nanoparticles. Cadmium chloride was dissolved in water and with this thioglycolic acid (TGA) added in dropwise under vigorous stirring. Trisodium citrate dihydrate, sodium selenite, and sodium borohydride were added with this mixture successively. The entire mixture was

FIGURE 1: Absorption spectra of the CdSe nanoparticles in water and in chloroform with 1-DDT.

taken in the three-necked flask and allowed into heat under the nitrogen atmosphere. The temperature was followed as 100°C. The appearance of yellow color of the solution represents the formation of the CdSe nanoparticles in the solution. The solution was strongly refluxed to get different sizes at different time intervals. The overall reaction of the formation of CdSe nanoparticles can be summarized as

The synthesized particles were precipitated by adding isopropanol by strong stirring. The particles were separated through centrifugation and dried in vacuum.

2.3. Phase Transfer of CdSe Nanoparticles. Aqueous synthesized cadmium selenide nanoparticles were transferred into organic medium through the method proposed by Gaponik et al. [4]. In brief, about 50 ml of the synthesized particles were taken in the beaker and equal volume of the 1-dodecanethiol was added and with this about 70 ml of acetone was added. This mixture was allowed into mild heating with constant stirring. After about 10 minutes, the transfer of CdSe nanoparticles from aqueous to 1-DDT medium was achieved. This organic phase was carefully separated out and mixed with chloroform. Then methanol was added dropwise under stirring which made the particles as powder form settled under bottom of the vessel. The particles were finally separated out and redispersed in chloroform. These particles are described as organically soluble CdSe nanoparticles (OS-CdSe).

FIGURE 2: Existence of CdSe nanoparticles in water (a) and in 1-dodecanethiol (b).

3. Results and Discussion

UV-visible spectrum of the synthesized particles and phase-transferred nanoparticles is given in Figure 1. The spectrum clearly shows that the particles have the approximately similar absorption edge in two phases. The slight variation in their spectra may be due to their change of medium. The photographic representation of the synthesized and phase-transferred particles is shown in Figure 2.

It was observed that when 1-dodecanethiol was added into the aqueous synthesized particles, a clear distinct boundary between the two phases appeared due to the hydrophobic nature of 1-DDT. The change of the particles from aqueous to organic phase may be due to the bulky nature of 1-DDT which replaces the short chain thioglycolic acid on the surface of the CdSe nanoparticles. Even though the replacement of TGA was done effectively, it was observed that only partial exchange of the ligand TGA was done by the long chain ligand 1-DDT [4].

The particles were more stable in 1-DDT phase as like in aqueous phase. The transfer of the nanoparticles from aqueous to organic phase depends upon volume of the 1-DDT, amount of acetone, and the temperature used for the transformation process. The HRTEM image of the phase transferred particles has very good size distribution as shown in Figure 3. The particles have the size around 5 nm. Since the particles were synthesized in aqueous medium, most of the particles were found in agglomerated form. The EDX analysis of the prepared phase-transferred powdered sample was also given in Figure 3. It is shown clearly that the particle contains their respective elements. The presence of sulphur in the spectrum is attributed from the attachment of the ligand thiol on the surface of the nanoparticles. The FTIR spectrum of TGA-capped CdSe nanoparticles, OS-CdSe, is shown in Figure 4. It is clear that the ligands are attached with the particles on its surface. The variation of the stretching frequencies in the phase-transferred CdSe nanoparticles from TGA-capped nanoparticles shows that

FIGURE 3: HRTEM image and EDX spectrum of CdSe nanoparticles.

TABLE 1: IR frequencies of TGA-CdSe and OS-CdSe.

TGA-CdSe		OS-CdSe	
Wave number (cm ⁻¹)	Type of vibration	Wave number (cm ⁻¹)	Type of vibration
3426	(-OH)	2923	(ν_{as} -CH ₂ -)
1560	(ν_{as} COO-)	2854	(ν_s -CH ₂ -)
1046	(ν C-O)	1450	(δ_{as} -CH ₃)
683	(ν C-S)	718	(ν C-S)

the confirmation of the attachment of the 1-DDT ligand on the surface [5, 6].

The various stretching frequencies associated with the TGA-capped CdSe and OS-CdSe are given in Table 1.

4. Conclusion

Colloidal cadmium selenide (CdSe) nanoparticles were synthesized in aqueous medium and transferred into organic medium through efficient phase transfer process. The transferred particles can be used as the good electron acceptors in

FIGURE 4: FT-IR spectrum of TGA@CdSe and OS-CdSe.

active layer with organic polymer in the presence of suitable organic solvent to fabricate hybrid solar cell.

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