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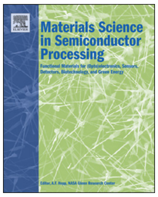

Green synthesis of yellow emitting PMMA–CdSe/ZnS quantum dots nanophosphors

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ABSTRACT

We herein report the fabrication of highly fluorescent yellow emitting nanophosphors using CdSe/ZnS quantum dots (QDs) dispersed in polymethyl methacrylate (PMMA). The QDs were synthesised via a simple, non-phosphine and one pot synthetic method in the absence of an inert atmosphere. The as-prepared nanocrystallites were characterised by Fourier transform infrared spectroscopy (FTIR), ultraviolet–visible (UV–vis) and photoluminescence spectroscopy, energy-dispersive spectroscopy (EDS), Raman spectroscopy, transmission electron microscopy (TEM) and high resolution TEM (HRTEM) microscopy. Optical analysis confirmed that the as-synthesised CdSe/ZnS QDs were of high quality with sharp absorption peaks, bright luminescence, narrow emission width and high PL quantum yield (up to 74%). The electron microscope images showed that the QDs are small and spherical in shape with narrow size distributions while the HRTEM micrograph confirmed the high crystallinity of the material. The Raman analysis of the QDs revealed the formation of core–shell structure and the energy dispersive spectroscopy confirmed the presence of the corresponding elements (i.e., Cd, Se, Zn and S). The dispersion of the core–shell QDs in PMMA matrix led to the red-shifting of the emission position from 393 nm in the neat PMMA to 592 nm in the nanocomposite. The fabricated highly fluorescent yellow emitting PMMA–CdSe/ZnS core–shell QDs polymer nanocomposite film display excellent optical properties without loss of luminescence. Furthermore, the as-synthesised organic soluble CdSe/ZnS QDs were successfully converted into highly water soluble QDs after ligand exchange with mercaptoundecanoic acid (MUA) without the loss of their emission properties. The simplicity of the method and the quality of the

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as-synthesised nanocomposite make it a promising material for the large scale fabrication of diverse optical devices.

1. Introduction

Semiconductor nanocrystallites, due to their quantum confinement effect, possess unique physical and optical properties, which have attracted tremendous attention from researchers in the last two decades. The interest in fluorescent semiconducting nanocrystals has increased due to their enormous applications in absorption filters [1–2], chemical sensors [3], light emitting diodes [4–7], photovoltaic devices and biotechnology [8–10]. Core–shell composite quantum dots exhibit novel properties making them attractive from both experimental and practical points of view. Over-coating nanocrystallites with higher band gap inorganic materials allows passivation of the surface non radiative recombination sites thereby increasing the quantum yield of the nanocrystals. Previous studies have shown that particles passivated with inorganic shell structures are more robust than organically passivated ones and have greater tolerance to processing conditions necessary for incorporation into solid state structures [11–15].

Recently, works on the surface modification of QDs with the aim of improving their luminescence efficiency, photostability [16,17] and reliable processing chemistry [18,19] have been reported. Over-coating of nanocrystals (NCs) with another wide band gap semiconductor is a well-established method. In CdSe/ZnS core–shell NCs, a type I core–shell material, the band gap of the core lies energetically within the band gap of the shell material and the photo-generated electrons and holes are mainly confined inside the CdSe [20]. Such core/shell NCs have widespread applications in biological and biomedical research due to better stability and processibility [21,22]. In the majority of the reported methods, the precursors and solvents used are highly toxic, these solvents can further increase the toxicity of the final product. Recent developments in using greener materials like 1-octadecene, paraffin, hexadecylamine, etc. as alternative to toxic reagents like TOPO, TOP, dimethyl cadmium and so on, has opened a new area for wider application of nanomaterials.

Highly luminescent nanocrystals with narrow emission width may be grown in hydrophobic inorganic surfactants which are insoluble in water, however; such surfactants are not compatible for some applications that require hydrophilic conditions. An alternative to this is the synthesis in aqueous solutions [23,24]. However, this usually produces polydispersed nanocrystals with a broad trapped state emission. This drawback limits some of their applications. One of the strategies to solubilise high quality nanocrystals in aqueous solvents is by ligand exchange of the nanocrystal surface with a thiol-terminated aliphatic compound having a primary carboxyl group [22–27]. Most of the water soluble NCs produced via ligand exchange usually have low (or lose their) luminescent properties after surface modification. In the case of thiol-terminated aliphatic carboxylic acids, the bond holding the primer to the nanocrystal is dynamic, and sometimes leads to low stability of the nanocrystals in water. Hence, the syntheses of highly stable water soluble QDs with high fluorescent emission is still an area of ongoing research.

One application of these ingenious materials is in the solid state lighting devices. This device requires photoluminescent materials which have the capability of converting incident wavelengths to light energy. When such materials are optically excited by UV or blue light sources, they produce fluorescence in the visible spectral range with high photoluminescence efficiency and narrow emission profiles. QDs are promising colour conversion phosphors in this respect. The advantages of using QDs over other colour conversion materials are broad excitation wavelength, high photostability and narrow emission width. In addition, QDs fluoresce very pure colours and these colours can be simultaneously excited by a single excitation source [28,29]. To realise flexible colour conversion or emitting devices, it is desirable to synthesise composite materials consisting of photochemically and thermally stable semiconductor QD materials as the colour emission centres and to synthesise transparent flexible polymers as the embedding matrix materials.

In this paper, we report a simple method to synthesise oleic acid coated, highly fluorescent CdSe/ZnS core–shell semiconductor QDs by using environmental friendly reagents via a non- phosphine method in the absence of any inert atmosphere. The as-synthesised organic soluble CdSe/ZnS QDs were successfully converted to highly water soluble materials after ligand exchange with mercaptoundecanoic acid (MUA) without the loss of their emission properties. By dispersing the as-synthesised QDs in PMMA polymer matrix, highly luminescent yellow emitting polymer composite thin films were fabricated.

2. Experimental procedures

2.1. Materials

Cadmium oxide (CdO, 99.5%) was purchased from Loba-chemie. Selenium powder (Se, 99.9%) and mercaptoundecanoic acid were obtained from Sigma Aldrich. Zinc acetate dihydrate $Zn(CH_3COO)_2 \cdot 2H_2O$, was from Analytical Reagents while anhydrous zinc sulphide (ZnS), sodium sulphide pentahydrate, oleic acid (OA), and toluene were purchased from Merck. Paraffin liquid (chemical grade with boiling point higher than 300 °C), was from Nice Chemicals. The polymer used was poly(methyl methacrylate) PMMA (MW=15,000) supplied by Himedia, Bangalore.

2.2. Preparation of CdSe/ZnS core–shell quantum dots

The preparation of organically soluble CdSe/ZnS core–shell was based on the modification of our previously