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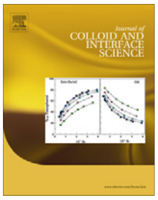

One-pot synthesis of ultra-small cerium oxide nanodots exhibiting multi-colored fluorescence

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ABSTRACT

CeO_2 nanodots of diameter 2 nm have been synthesized by the thermolysis of cerium acetate in diphenylether in the presence of an oleic acid surfactant. The surfactant coating enabled them to be easily dispersible in nonpolar solvents. The CeO_2 dots exhibited size dependant optical properties such as a red shift in absorption and band gap. As a result, the surfactant coated CeO_2 nanocrystals emit photons in the visible region with broad photoluminescence spectra resulting in multi-colored fluorescence, which originates from defects associated with CeO_2 nanocrystals approaching molecular dimensions.

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1. Introduction

The fascination with nanotechnology emerges from the unique physiochemical properties due to the reduction in size [1]. Small nanocrystals often show unusual size- and shape-dependent optical properties as they confine their electrons resulting in quantum effects manifested as novel optical properties. Nanotechnology has succeeded in molding these distinct properties into commercial applications in many devices. Semiconductor nanocrystals, usually called quantum dots (QDs) are fluorescent, allow emission, color tuning, and have great scientific and technological potential for bioimaging [2], solar cells [3] and color display units [4]. Such materials are also being used as alternatives for conventional organic chromophores which are prone to photo bleaching [5]. However, most of the quantum dots are based on Cd, In and As, which are highly toxic, carcinogenic and hazardous for environment [6]. On other hand, rare-earth oxide based fluorescent nanoparticles show negligible toxicity and are easily surface functionalized [7]. Surface passivation using hydrophobic moieties facilitates the facile incorporation of fluorescent nanocrystals in polymer matrices as a possible novel strategy for applications like spectral barcoding, monitoring polymeric scaffolds using fluorescent markers [8,9]. Nanosized cerium dioxide (or ceria) is an extensively studied system for a variety of applications. However, its optical properties are yet to be thoroughly explored. There are few published reports on the optical properties of ceria nanocrystals which mention weak blue–green emission [10]. To the best of our knowledge, there is only one published report on undoped CeO_2-based nanostructures exhibiting fluorescence on surface functionalization with dodecyl sulfates [11].

A large number of techniques have been reported to synthesize nanosized CeO_2 particles with good control of size and properties. The smallest CeO_2 crystals synthesized thus far were 1.8 nm by Yu et al. via a hydrothermal method in the presence of a double hydrophilic block copolymer [12]. In other reports, Inoue et al. adopted a solvothermal method to synthesize colloidal dispersion of 2 nm ceria nanoparticles [13] and Masui et al. produced 2.6 nm zero-dimensional CeO_2 nanostructures using reverse micelles [14]. However, all of these methods produced nanoparticles with hydrophilic surfaces. Oleic acid capped hydrophobic CeO_2 nanocrystals can easily be embedded into organic and polymer matrices [15]. The synthesis of 2.2 nm lipophilic ceria nanoparticles has been reported by Taniguchi et al. [16] and nanorods with diameter 2 nm were also produced by Ahinyaz et al. [17]. However, their optical properties have not previously been systematically studied.

Recent reports suggest that synthesis via an organic route may be preferable to aqueous methods for the preparation of stable nanofluids in apolar solvents, due to the greater control of particle size and polydispersity. Numerous methods such as hydrothermal [18], alcothermal [13], thermal decomposition [19], and aqueous precipitation [8] have previously been adopted for the synthesis of organophilic CeO_2 nanoparticles with good control of size. Among these, hydrothermal and alcothermal methods demand high pressure and/or temperature equipment which invites

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additional costs, safety measures and processing time. Although aqueous precipitation methods are simple, greener and inexpensive, they require multiple processing steps. Solvothermal decomposition on the other hand is a simple, one step method to synthesize monodispersed nanoparticles with narrow size distribution [20]. In this paper, we report a facile synthetic strategy for producing 2 nm ultrasmall CeO_2 nanocrystals from a cerium acetate precursor by thermal decomposition in diphenyl ether. The particles produced stable, transparent dispersions in nonpolar solvents and they show multi-colored fluorescence, making them applicable as fluorescent probes.

2. Experimental

Cerium nitrate hexahydrate (99.9%) was purchased from Indian Rare Earths, India, sodium acetate (extra pure) was obtained from Merck, India, diphenyl ether (99%) and oleyl amine (70%) were procured from Sigma Aldrich, oleic acid (90%) from Alfa Aesar, UK. Common solvents such as acetone, ethyl alcohol and toluene (analytical grade) were procured from Merck, India. All the chemicals were used as received without further purification.

2.1. Synthesis of cerium acetate

Cerium nitrate (0.05 mol) was dissolved in 25 ml 6 M sodium acetate solution. To this 25 ml ethanol was added and stirred well. A 50 ml portion of cyclohexane was added and the mixture was kept at 70 °C overnight. The organic layer, containing cerium acetate was separated and the solvent was removed by evaporation. The precipitated cerium acetate powder was washed several times with acetone and dried.

2.2. Synthesis of cerium oxide nanodots

In a typical synthesis, 1.6 g of the freshly synthesized cerium acetate (0.005 mol) was dissolved in 100 ml diphenyl ether in a round bottom flask. To this, 0.02 mol oleic acid (OA) and 0.023 mol oleylamine were added and the reaction mixture was refluxed at its natural boiling point (~260 °C) for 1 h. After cooling, acetone was added to precipitate the OA coated CeO_2 nanoparticles. CeO_2 precipitate was washed thoroughly with acetone and dried. This material will be denoted as OANP in the remaining text. The dried material (OANP) could be well dispersed in toluene resulting in a transparent dark brown suspension. As a control experiment, uncoated ceria nanoparticles were also synthesized using the same procedure without the use of surfactant and will be referred to as UCNP.

2.3. Instrumental techniques

The X-ray diffraction (XRD) patterns of the samples were obtained using a Philips X'PERT PRO diffractometer with Ni-filtered Cu $K\alpha_1$ radiation (λ = 1.5406 Å) using 30 mA current at 40 kV. Powder samples were scanned in the continuous scan angle range 5–100° (2θ) at a scanning speed of 2°/min with a step size 0.04°. The crystal dimensions and lattice strains were calculated from the line broadening of (1 1 1) peak using the well known Scherrer equation [21] and the Stokes–Wilson formula [22,23]. The morphology and average size of the nanocrystals were investigated by high resolution transmission electron microscopy (HR-TEM) using a FEI Tecnai 30 G^2 S–Twin microscope operated at 300 kV and equipped with a Gatan CCD camera. Size measurements for the cerium oxide suspension were carried out at 25 °C by photon correlation spectroscopy (PCS) on a Zetasizer 3000 HSA, Malvern Instruments, Worcestershire, UK using a 60 mW He–Ne laser producing 633 nm wavelength with General Purpose algorithm with Dispersion Technology Software (v. 1.61) at 90° detection angle. The absorption spectra of the samples were obtained using a UV–visible 2401 PC spectrophotometer (Shimadzu, Japan) in the wavelength range 200–800 nm. The photoluminescence (PL) spectrum of the powdered sample without surfactant was done using a Spex–Fluorolog FL 22 spectrofluorometer equipped with a 450 W Xe lamp as an excitation source. The PL spectrum of the surfactant coated nanoparticle suspension in toluene was taken at room temperature using a Cary Eclipse spectrofluorometer (Varian, Australia). Fluorescent images of the samples were taken using a Leica DMI6000B inverted microscope with a 100 W Hg arc lamp as the excitation source. The oxidation states in the samples were derived using X-ray photoelectron spectroscopy (XPS) using VG Microtech MultiLab ESCA 3000 at a base pressure of 10^{-9} Torr using the Mg $K\alpha$ radiation (1253.6 eV, line width 0.7 eV) generated at a power of 200 W. Fourier transformed (FT) Raman spectra of the samples were recorded at room temperature using a FT-Raman spectrometer RFS (Bruker) with excitation by a 150 mW Nd:YAG laser operating at 1064 nm wavelength.

3. Results and discussion

The thermal decomposition of a metal precursor in a high boiling organic solvent in presence of a suitable surfactant is an efficient one pot method for the synthesis of monodisperse nanoparticles. Studies have indicated that a metal-oleate complex is both the intermediate and the precursor for the decomposition process when such reactions are carried out in presence of OA surfactant [19,24]. The thermal decomposition process is reported to be accompanied by the formation of free radicals [24] which can undergo various reactions such as recombination, decay into smaller fragments, or propagate the decomposition by reacting with other carboxylate complexes. Detailed and stoichiometric description of this process has not yet been established. During the heating up process, the cerium acetate precursor decomposes to generate Ce^{3+} ions in solution. When the Ce^{3+} ion concentration exceeds its supersaturation limit, the oleate ion in the solution is believed to form a complex with Ce^{3+} and precipitate, in order to reduce the Ce^{3+} ion concentration [25]. Subsequently, the decomposition of an oleate complex in an oxygen atmosphere leads to the formation of CeO_2 nanoparticles (NPs) with negatively charged oleate ions adsorbed on the surface and the core of the metal oxide remaining positively charged.

The powder X-ray diffraction patterns of the OANP and UCNP as well as their particle size measurement data using (PCS) are illustrated in Fig. 1. All detectable XRD peaks in both materials were indexed to pure cubic CeO_2 with the space group: $Fm\,\bar{3}\,m$ (according to JCPDS card No. 34-0394) and lattice constant, a = 0.54570 nm in OANP and 0.54357 nm for UCNP displaying lattice expansion in both [21]. The crystal dimensions (D_{XRD}) for OANP and UCNP were estimated using the Debye–Scherrer formula as 0.7 and 1.9 nm respectively. The XRD peaks at ~28.3°, 47°, 56.3° and 76.7° could be assigned to the (1 1 1), (2 2 0), (3 1 1), and (3 3 1) planes of CeO_2. OANP showed a lattice expansion of 0.86% which is nearly twice that of UCNP (0.47%) assuming a = 0.541 nm for bulk ceria (JCPDS card No. 34-0394). The widths of all the X-ray peaks in OANP are broader than the corresponding peaks in UCNP. The calculated crystal lattice strain [22,23] was 4.5% for CeO_2 crystals in UCNP, whereas in OANP (11.4%) it was higher by the same order of magnitude to lattice expansion due to the presence of defects. The particle sizes of CeO_2 NPs in suspension, measured by photon correlation spectroscopy (PCS), are shown in Fig. 1b. Stable dispersions of OANP in toluene and UCNP in water were used for these size measurements. The capped particles were completely

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