



White-light photoluminescence and photoactivation in cadmium sulfide embedded in mesoporous silicon dioxide templates studied by confocal laser scanning microscopy

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ABSTRACT

SBA-15 and SBA-16 silica templates have been infiltrated with CdS by means of nanocasting using a hybrid precursor. The morphology and structure of both the SiO₂@CdS nanocomposites and the silica-free CdS replicas have been characterized. The three-dimensional nanocrystalline CdS networks embedded in SBA-15 and SBA-16 silica templates exhibit broad photoluminescence (PL) spectra over the entire visible range, together with enhanced PL intensity compared to silica-free CdS replicas. These effects result from the role silica plays in passivating the surface of the CdS mesostructures. Furthermore, photoactivation is eventually observed during continuous illumination because of both structural and chemical surface modifications. Owing to this combination of properties, these materials could be appealing for solid-state lighting, where ultra-bright near-white PL emission is indispensable.

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1. Introduction

Wide band gap II–VI semiconductor nanoparticles, also termed “quantum dots (QDs)” (e.g., CdS, CdSe, ZnSe, etc.), have received considerable attention in recent years owing to their unique size-dependent optical properties that result from the quantum confinement of electron–hole pairs in the three spatial dimensions. As the nanocrystal size is reduced, the band gap increases and, consequently, a blue-shift of the photoluminescence (PL) emission is observed. This makes it possible to tune the emission color of QDs [1,2]. These materials have been proposed for a wide variety of technological applications, including biological labeling, electronic devices, optically-driven lasers and waveguides, hydrogen production, solar cells, quantum computing and solid state lighting (SSL), among others [1,3–6].

SSL devices based on QDs incorporated into light emitting diodes (LEDs) are more efficient than conventional incandescent and fluorescent lamps in aspects like mechanical stability against vibration and shock, overall life-time and, most importantly, overall power consumption [7]. Indeed, incandescent light is highly inefficient because about 90% of the energy input is emitted as heat. Hence, switching from conventional light sources to SSL would represent a massive energy saving of more than 50% [6,8]. Both organic [9] and inorganic [10] materials have been proposed for highly-efficient SSL. In terms of optical properties, SSL needs a broad-band luminescence in the wavelength interval ranging from 400 nm to 750 nm. This broad spectrum can, in principle, be obtained by simply mixing QD nanoparticles with narrow emission bands at the red, green and blue wavelengths [11], but this is not very efficient due to self-absorption effects. Alternatively, white-light emission has been reported for the so-called “magic sized” CdSe QDs, which consist of uncoated nanoparticles of about 1.5 nm in diameter [6]. To achieve the desired effects, precise control of the CdS particle size was required using specific pyrolysis techniques.

One of the drawbacks of CdS comes from the acute toxicity of Cd, which precludes its use in biomedicine and other applications. In addition, the presence of structural defects at the surface of QDs

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typically causes non-radiative decay of excitons and a concomitant loss of PL. For these reasons, organic ligands are commonly used to coat and passivate the surface of QDs [12,13]. However, these ligands make the QDs hydrophobic, while most biological applications require water-soluble systems. Alternatively, QDs can be embedded into silica colloids or inside silica mesostructures, which are biocompatible [14–16]. Coating QDs with silica or inorganic semiconductors with a large bandgap also leads to effective surface passivation and enhances the PL intensity [17,18].

Furthermore, the PL intensity can sometimes be enhanced by illuminating the QDs with UV or visible light. This phenomenon is known as photoactivation [14,19–23], and can be fostered in the presence of certain liquids or gases that facilitate passivating the QD surface in a reversible or irreversible manner. Photoactivation competes with an opposing effect called photobleaching, which is the decrease in the PL intensity due to photon-induced chemical damage and concomitant increase of non-radiative decay [24].

Besides nanoparticles, one-dimensional semiconductor nanostructures with variable geometry (e.g., nanowires, nanotubes, nanobelts and nanohelices) also maintain the interesting luminescent properties that arise from quantum confinement effects [25–27]. When arranged in the form of 2D or 3D periodic structures (for example, in ordered mesoporous frameworks), these materials can be regarded as a negative replica of an array of regularly-spaced QDs. Therefore, these arrangements are often referred to as “quantum antidots” [28,29]. Similar to QDs, it should be possible to tune the band gap of quantum antidots to meet specific technological demands [29]. Actually, some functionalities of QDs that depend on the overall surface area (e.g., photocatalysis, photovoltaic activity and electrochemical properties) would presumably be enhanced in mesoporous quantum antidots [25,30].

So far, reports on mesoporous 2D or 3D CdS structures have been rather scarce [31–39]. In fact, although there is extensive literature on the synthesis of CdS nanoparticles with a narrow size distribution, the rational design of mesoporous 3D CdS architectures is still in its infancy. The first report on the preparation of mesoporous CdS (2D hexagonal superlattices) dates from 1996, when the soft-templating method was used to prepare these materials from an organic phase consisting of tubules of self-assembled amphiphiles [31]. CdS superlattices have also been obtained by direct templating in a lyotropic organic liquid crystal [32]. Similarly, CdS aerogels with thick walls have been produced by assembling nanoparticles [33]. In turn, mesoporous CdS with disordered pore arrangements have been obtained using template-free ultrasonic mediated precipitation [34]. All these processing routes suffer from the drawback that either they render non-crystalline CdS structures with poor optical properties, or the pore distribution is rather inhomogeneous both in size and lateral spacing.

Interest in the use of hosts to accommodate CdS within their pore networks started with zeolites two decades ago, triggered by the early works of Herron and Stucky [35,36]. Later, the use of mesoporous silicas to accommodate CdS in their interior and the possibility to selectively etch away the SiO₂ to obtain self-supported CdS replicas has attracted attention. Nevertheless, there are still very few works on the nanocasting synthesis of 3D mesoporous CdS using silica mesostructures as a hard template [37]. Since SiO₂ can stand calcination at relatively high temperatures, the degree of crystallinity in nanocast CdS is usually higher than in soft-templating routes, and therefore better optical performance is attained. However, due to the low yield and poor pore filling, it is a challenge to form truly ordered mesostructured networks and only isolated dispersed nanoparticles are generally obtained inside the mesopores of the hard templates [38–41]. In most cases the CdS nanoparticles have been introduced in mesoporous silica via reverse micellar systems [42,43].

Higher filling of mesoporous silica hosts with CdS has been achieved by using a special lab-made hybrid precursor, cadmium thioglycolate (Cd₁₀S₁₆C₃₂H₈₀N₄O₂₈) [44], or by one-step impregnation method to replicate mesoporous CdS using thiourea [45]. Hexagonally-packed arrays of CdS and Cd_{1-x}Mn_xS nanowires have also been synthesized from Cd alkyl xanthate and a mixture of Cd and Mn acetates, respectively, using mesoporous silica as a hard template [46,47]. In all these studies, either the SBA-15 or the MCM-41 silica mesostructures were the matrices utilized. Hence, the geometry of the semiconductor obtained was essentially limited to interconnected nanowires. Furthermore, these previous works mainly focused on the synthesis and structural characterization of the obtained replicas, while the possible benefits for the PL properties of hosting 3D quantum antidots inside the pores of mesoporous silica were largely overlooked.

In this work we report on the synthesis of CdS quantum antidots inside the pores of SBA-15 (hexagonally-arranged cylindrical pores) and SBA-16 (interconnected spherical cages) mesoporous silica templates, using cadmium thioglycolate as precursor. Although the confocal laser scanning microscope (CLSM) is mostly (and traditionally) used in the biology field, it is here applied to study the PL properties of the synthesized materials to simultaneously explore its potential in material science [48,49]. On comparing the PL spectra of SiO₂@CdS composites and SiO₂-free CdS mesoporous frameworks, it rapidly emerges that the synthesized materials exhibit an interesting range of photoemission properties. The extremely different responses encountered in absorption, PL emission, and photoactivation experiments are linked to both the presence/absence of the silica hosts and the type of mesostructure arrangement (SBA-15 and SBA-16). In particular, the presence of the SiO₂ template results in a pronounced enhancement of the PL and broad white-light emission spectra.

2. Materials and methods

2.1. Synthesis of cadmium thioglycolate, [Cd₁₀(SCH₂CH₂OH)₁₆](NO₃)₄, precursor

The cadmium thioglycolate precursor was synthesized following the procedure described in [50]. In brief, 6.12 g of Cd(NO₃)₂ was dissolved in 100 mL of dry THF in a 250 mL round-bottomed flask under argon atmosphere. While stirring, 3.12 g of mercaptoethanol dissolved in 50 mL of dry THF was injected with a syringe through a silicon rubber septum into the flask at room temperature. When the addition was complete, the mixture was stirred at reflux for 24 h ($T \sim 65^\circ\text{C}$) by which time a white precipitate appeared. The reaction mixture was then first cooled to room temperature, left in the fridge overnight, and finally the whitish precipitate was filtered off. The solid was washed several times with excess amounts of diethyl ether, and the resultant white powder was collected and dried under vacuum.

2.2. Synthesis of silica templates

SBA-15 silica was synthesized by dissolving 6.0 g Pluronic P123 copolymer in 225 g diluted HCl (1.35 M). 12.5 g of tetraethyl orthosilicate (TEOS, from Sigma-Aldrich), which served as the silicon source, was then added and the solution stirred for 24 h at a constant temperature (about 37 °C) [51]. The hydrothermal treatment was carried out at 90 °C in a sealed plastic container for 24 h. The solid obtained was filtered, washed copiously with water and finally calcined at 550 °C for 5 h to remove the organics. A scan rate of 1 °C min⁻¹ was used to raise the temperature from room temperature to 550 °C. SBA-16 silica was synthesized under similar conditions by using Pluronic F127 (EO₁₀₆PO₂₀EO₁₀₆) as the surfactant. In

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