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Photonic materials prepared through the entrapment of quantum dots into silica

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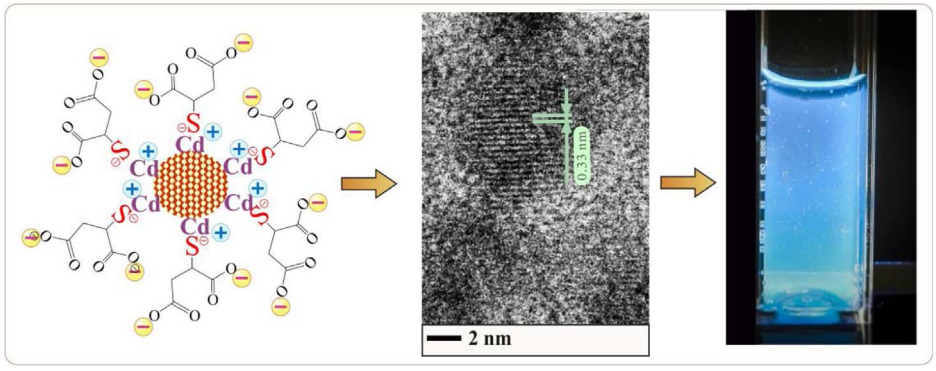
GRAPHICAL ABSTRACT



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ABSTRACT

Silica, which is appropriate as a matrix for developing photonic materials because of its optical transparency and mechanical strength, served here to entrap quantum dots (Qdots) by method of sol-gel chemistry. CdS was initially synthesized in aqueous solution. As ligand, mercaptosuccinic acid was used for Qdot stabilization. Entrapped CdS held its photoluminescence properties in full measure. Synthesized Qdots were characterized in solution and silica matrix by TEM, SAXS, UV–vis and fluorescence spectroscopy. It was found that irradiation by laser resulted in a red shift of photoluminescence and an increase of the light absorbance. The effect is reversible. Dependence of optical properties of Qdots on the irradiation opens a way for developing photonic materials with regulated properties.

1. Introduction

Silica is one of the basic materials in photonics for current developments of active components for all-optical signal processing [1–3]. It is frequently used in the fused form. However, fused silica does not meet with some ever-increasing requirements for applications, such as color tunability, large active areas and mechanical flexibility, being further costly [4,5]. The most convenient technique for silica fabrication including optical material is the sol-gel processing. It can be performed at low temperature that enables one to entrap even relatively unstable organic substances into inorganic matrix, thus developing homogeneous hybrid nanocomposites of various compositions and

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functionalities [6–12]. We could use it for developing photonic materials by entrapping dyes [13,14], gold nanoparticles [15,16] and quantum dots [17].

Sol-gel processing is frequently performed by using tetraethoxysilane, TEOS, as the common precursor [6,18]. Its hydrolysis leads to the production of ethanol. Alcohol appearance in the reaction media can cause the precipitation of quantum dots that is used for the purification in their synthesis [19,20]. This problem was eliminated in [17] by employing a silica precursor tetrakis(2-hydroxyethyl)orthosilicate (THEOS) with ethylene glycol residues. It is compatible better than TEOS with many classes of water-soluble substances such as surfactants, polysaccharides and proteins [7,21–25].

Quantum dots (Qdots) made of nanometer-sized crystalline particles of semiconductors are of great interest for developing photonic materials. They possess bright fluorescence and high efficiency, sharp and rather symmetrical peak of emission, long term photostability (reduced photobleaching) and temperature insensitivity [26–29]. The mentioned advantages make Qdots promising for applications in optoelectronic devices including light-emitting diodes and lasers, solar concentrators and cells, photodetectors and sensors. Their outstanding feature is a high dependence of optoelectronic properties on the size and surrounding. This is explained by the quantum nature of photoluminescence. It is emitted at discrete wavelengths because of the spatial restriction for an exciton (electron-hole pair) generated by photon absorbed when its Bohr radius is greater in size than the nanoparticles. Even a small change in their dimension results in a notable shift of photoluminescence wavelength. This provides a way for the regulation of the emission wavelength by tuning the Qdot size.

Optoelectronic properties depend on the Qdot crystallinity and defectiveness which makes itself evident mainly at the surface [27–31]. Healing of defects is gained through the passivation. Organic and/or inorganic shells are formed, resulting in core/shell structure of Qdots. Efficient passivation of surface defects is observed in case of inorganic shell having higher band gap than semiconductor's core [26,27,30,32]. This causes a significant improvement of photoluminescence quantum efficiency. Similar passivating effect takes place in a case of Qdots embedded into silica matrix [33,34].

Formation of stable Qdots is one of the main challenges in their synthesis [29–32,35]. There is a permanent growth and merging nanoparticles after their preparation that is well-known from the first publication [36]. As a precautionary measure against the dimension and properties change, stabilizing organic agents are added. They are capped Qdots, forming a shell. This slows down the processes of growing and merging, providing a kinetic stability [37]. Silica matrix has an efficient stabilizing effect because of its rigidity. As additional advantage of the entrapment of Qdots into silica, there is a substantial decrease of the leakage of toxic metal cations like cadmium [28,38].

Silica form robust matrix but nevertheless there are good potentialities for tuning structure and properties of Qdots. The first photoluminescent nanoparticles with quantum effects were synthesized in glass, not in a solution [39]. Their dimensions were regulated despite the solid media that allowed revealing the size dependence of the photoluminescence. Sol-gel derived silica has few decisive advantages over the glasses: low-temperature wet synthesis and post-processing, uniform multicomponent composition including organics, easy-manipulating porosity, less rigid matrix [6,7,18,40]. It can be prepared as a monolith or shell surrounding Qdots and any shape. Because silica is porous and softer than glass, nanocrystallite growth and annealing, which is regulated by thermal diffusion process, proceeds at much low temperature [28,33,41–43].

Well-known phenomenon of Qdots is a change of their optoelectronic properties by UV-lightening. Enhancement of photoluminescence for powdered ZnS doped with Mn^{2+} was first described in Ref. [44]. Further studying of various teams showed that this is a common feature of Qdots. Enhanced photoluminescence was observed for various types of them when they were taken as a powder [30,44], monolayer on various substrates [45,46], embedded into polymer films [47] and dispersed in solutions [48,49]. The phenomenon depends on many factors that makes it difficult to reveal its real mechanism [27].

Optoelectronic properties of Qdots entrapped into silica are sensitive to lightening as well. However, there are differences. Enhancement of photoluminescence is usually accompanied by shifting the fluorescence peak into the blue region [27]. In the case of nanocrystallites in silica matrix, the shift did not take place [46] or occurred in the red region [50,51]. It gives an indication of difference in the mechanism of phenomenon.

Here we are considering silica nanocomposites with entrapped nanocrystalline cadmium sulphide. Their remarkable property is that fluorescent intensity increase is accompanied by Stokes shift of emission peak. It is regulated by exposition dose and polarization that makes possible all-optical devices.

2. Materials and methods

2.1. Materials

2.1.1. Substances

Cadmium acetate (pure grade) was supplied by Labtekh (Russia), sodium sulfide and sodium hydroxide (analytical grade), by Reakhim. Mercaptosuccinic acid and tetraethoxysilane were purchased from Aldrich. All chemicals were used as received without any additional purification. Distilled water was used for solutions. Tetrakis(2-hydroxyethyl)orthosilicate (THEOS) was prepared according to synthetic procedures described previously in Ref. [21].

2.1.2. Synthesis of Qdots

Synthesis of nanocrystalline CdS was followed modified procedure suggested in Ref. [52]. In brief, solutions of cadmium acetate and mercaptosuccinic acid initially prepared were mixed. After stirring at a magnetic stirrer in ca.10 min, NaOH was admixed to shift the pH to 10. Sodium sulfide solution was added into the vigorously stirred reaction mixture that was then left under the intense stirring until the next day. The formation of Qdots was monitored by lightening a luminescent lamp. Their fluorescent color from light blue to red was regulated by the molar ratio of reagents. To purify synthesized Qdots, they were separated at centrifuge after the precipitation by 96% ethanol. Centrifuging of washed precipitate was repeated a few times.

2.1.3. Qdot entrapment into silica matrix

Purified nanocrystalline CdS was redispersed to have 0.3 wt% in deionized water. Different amount of THEOS was admixed in order for varying the precursor concentration in solutions. Mixture was shaken by hand and then stirred intensely for several minutes until a homogeneous mixture was prepared. It was left for gellification. The concentration the higher, the time the shorter.

2.2. Methods

2.2.1. Spectroscopy

UV–vis spectra in a range of 250–800 nm were obtained by means of a UV-2250 spectrophotometer (Shimadzu, Japan). Fluorescence was studied by using an RF-5301PC spectrofluorimeter (Shimadzu, Japan) or a high-speed spectrometer Andor iStar. Bands were deconvoluted into subcomponents using Gaussian functions by adjusting the contour of calculated integral band to the recorded experimental band using OrigiLab OriginPro 8.

2.2.2. Electron microscopy

High-resolution transmission electron microscope (TEM) JEM-2010 (Jeol, Japan) served to examine the structure of Qdots. Samples for observation were prepared by dispersing nanocrystallites in alcohol under the action of an ultrasonic disperser. A droplet of the solution was