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Effect of acid or alkaline catalyst and of different capping agents on the optical properties of CdS nanoparticles incorporated within a diureasil hybrid matrix

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ABSTRACT

CdS nanoparticles (NPs) were synthesized using colloidal methods and incorporated within a diureasil hybrid matrix. The surface capping of the CdS NPs by 3-mercaptopropyltrimethoxysilane (MPTMS) and 3-aminopropyltrimethoxysilane (APTMS) organic ligands during the incorporation of the NPs within the hybrid matrix has been investigated. The matrix is based on poly(ethylene oxide)/poly(propylene oxide) chains grafted to a siliceous skeleton through urea bonds and was produced by sol–gel process. Both alkaline and acidic catalysis of the sol–gel reaction were used to evaluate the effect of each organic ligand on the optical properties of the CdS NPs. The hybrid materials were characterized by absorption, steady-state and time-resolved photoluminescence spectroscopy and High Resolution Transmission Electron Microscopy (HR-TEM).

The preservation of the optical properties of the CdS NPs within the diureasil hybrids was dependent on the experimental conditions used. Both organic ligands (APTMS and MPTMS) demonstrated to be crucial in avoiding the increase of size distribution and clustering of the NPs within the hybrid matrix. The use of organic ligands was also shown to influence the level of interaction between the hybrid host and the CdS NPs. The CdS NPs showed large Stokes shifts and long average lifetimes, both in colloidal solution and in the xerogels, due to the origin of the PL emission in surface states. The CdS NPs capped with MPTMS have lower PL lifetimes compared to the other xerogel samples but still larger than the CdS NPs in the original colloidal solution. An increase in PL lifetimes of the NPs after their incorporation within the hybrid matrix is related to interaction between the NPs and the hybrid host matrix.

1. Introduction

Nanotechnology, as a science field, is gaining increasing interest among researchers around the world. At nanoscale dimensions materials exhibit very different properties, such as electrical, optical and chemical, when compared to the properties they show on a macroscale. Semiconductor NPs, also called quantum dots (QDs) are an example of such nanomaterials that has attracted tremendous attention in the last two decades. QDs have a typical size between 1 and 20 nm and contain between 100 and 100,000 atoms in each nanoparticle. Examples of QDs are the binary semiconductor compounds consisting of II–VI elements, such as cadmium sulfide (CdS), cadmium selenide (CdSe), zinc sulfide (ZnS), and zinc selenide (ZnSe). In case of CdS the bulk band gap energy is 2.42 eV [1]. The optical and electrical properties of QDs make them excellent candidates for many applications in the optical and electronic fields. In QDs, as the size of the particles decreases the electronic properties change [1]. This is known as a quantum size effect and enables many applications in different areas such as biomarkers [2], solar cells [3] and light emitting diodes [4]. For example, QDs offer tunable emission colors due to the quantum size effect, which can be used in display lighting devices such as QLED using colloidal CdSe quantum dots [4].

Several colloidal methods can be used to synthesize QDs with narrow size distribution. Examples of such synthetic pathways are the reverse micelle technique [5], synthesis using organometallic precursors in coordinating solvents such as TOPO at high temperatures [1] or the aqueous synthesis using mercapto-acids or mercapto-alcohols as stabilizers [6]. However quantum dots produced by colloidal methods tend to photo dissolution and slow degradation when exposed to light [7]. Also the application of the quantum dots requires their immobilization within substrates or

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within solid matrices. An important task is therefore the development of methods to incorporate NPs previously synthesized by colloidal methods into solid matrices. A great amount of research has already been performed to meet this goal. Common methods used to immobilize quantum dots have been developed by using polymers [8], hybrid gels [9], and silica [10]. Recently, the incorporation of semiconductor NPs within hybrid organic–inorganic matrices known as diureasil has also been studied [11–15]. The diureasil hybrid matrix consists of a siliceous backbone covalently grafted to polyether chains through urea bonds [16]. These hybrid solid matrices can be simply produced at room temperature using a well known sol–gel process. The sol–gel process allows the synthesis of amorphous silica gels using mild conditions [17,18]. The method involves the hydrolysis and condensation of monomers having silyl ether functional groups. These sol–gel reactions can be catalyzed by both bases and acids. Hybrid organic–inorganic materials can be synthesized from molecular monomers containing an organic moiety attached to two silyl ether groups. The sol–gel hydrolysis and condensation reactions of these monomers leads to a three-dimensional network made of organic moieties covalently grafted to siliceous domains. It is possible to encapsulate QDs within the sol–gel hybrid matrix if these sol–gel reactions are performed in the presence of the QDs dispersed in a compatible organic solvent.

Quantum dots can exhibit optical and electrical properties that are dependent upon the ligands used to stabilize their surface. Several types of ligands, such as thiols, tri-n-octyl phosphine (TOP), tri-n-octylphosphine oxide (TOPO) and oleic acid, may be used to stabilize and functionalize the quantum dots in order to avoid aggregation or to increase photostability. The use of ligands or capping agents in quantum dots may also be necessary to increase solvent compatibility or favor their dispersion within certain media such as solid matrices. 3-mercaptopropyltrimethoxysi lane (MPTMS) has been used to increase the dispersion of quantum dots within solid matrices produced by sol–gel [19]. Organic ligands can change the optical properties of quantum dots. For example, CdSe quantum dots capped with TOP/TOPO showed a red shift in fluorescence emission wavelength after ligand exchange with pyridine and exposed to UV light [20]. During the process of transferring the colloidal NPs into a solid matrix the NP surface must be changed, which in turn can lead to unwanted changes of the original optical properties of the NPs. In previous papers MPTMS has been used as capping agent to increase the dispersion of CdS NPs within a diureasil hybrid matrix [12,15]. The CdS NPs capped with MPTMS showed a decrease in their PL emission intensity when compared to CdS NPs capped with other ligands. This prompted us to try other type of ligands that, maintaining the good dispersion of the CdS within the hybrid matrix, could at the same time avoid the decrease of the PL emission intensity of the CdS NPs. In this paper, besides the use of MPTMS, we also used 3-aminopropyltrimethoxysilane (APTMS). Like MPTMS, APTMS has a silyl ether group that undergoes the same sol–gel hydrolysis and condensation reactions of the diureasil precursor and of the MPTMS and may, therefore, be used to anchor the CdS NPs to the inorganic skeleton of the hybrid matrix. Besides the mercapto group, amino groups have also great affinity toward cadmium atoms at the surface of the NPs. QDs have demonstrated high affinity for primary amines [21] and the ability of the terminal $-NH_2$ group of APTMS to bind to QDs has been used to produce amine-capped fluorescent upconverting crystals for the adsorption of QDs [22]. The APTMS has also been used for dispersing CdSe, CdSe/CdS and CdSe/ZnS NPs synthesized in TOPO within hybrid ZrO_2–SiO_2 matrix produced by sol–gel [23,24]. Besides the use of different ligands, the influence of the catalyst used in the sol–gel process was also studied to determine how the acidic or alkaline conditions used in the sol–gel process influence the action of ligands.

2. Experimental

2.1. Chemicals

The functionalized polyether O, O-bis (2-aminopropyl)-block-polypropylene glycol-polyethylene glycol-block-polypropylene glycol-500 (Jeffamine ED-600) was purchased from Fluka. 3-isocyanatepropyltriethoxysilane (ICPTES, 95%), 3-aminopropyltrimethoxysilane (APTMS, 98%), 3-mercaptopropyltrimethoxysilane (MPTMS, 95%), sodium sulfide nonahydrate (98%) and 4-fluorothiophenol (FPhSH, 98%) were purchased from Aldrich. Other reagents used: dioctyl sodium sulfosuccinate (AOT, 98%), from Fisher Chemical, tetrahydrofuran (THF, ACROS), triethylamine (TEA, 99%, ACROS), 2,2,4-trimethylpentane (isooctane, Fluka), cadmium nitrate tetrahydrate (extra pure, Riedel – deHaen) and a concentrated ammonia solution (25% w/w, Pronalab). The water used in the preparation of solutions was of high purity ($R > 18\ M\Omega\ cm$) and was obtained using a Millipore purification system. Jeffamine ED-600 was dried under a dynamic vacuum before use. The other reagents were used without any further purification.

2.2. Preparation of CdS nanoparticles

The CdS NPs were synthesized through colloidal methods by using the reverse micelles technique, following a protocol reported previously [12]. The molar ratio between water and surfactant AOT, w ($w = [H_2O]/[AOT]$), of the micellar solution was kept at $w = 6$ by adding certain amounts of aqueous solutions of sodium sulfide and cadmium nitrate. For the preparation of the colloidal solution of CdS NPs, 1080 μL of 0.1 M aqueous sodium sulfide solution was added to 100 ml of isooctane solution of AOT with 0.1 M concentration. An equal volume of 0.1 M aqueous cadmium nitrate solution was added separately to another 100 ml of isooctane solution of AOT of the same concentration. After 10 min, the micellar solution containing sodium sulfide was added to the micellar solution containing cadmium nitrate. The resulting solution acquired a yellowish color due to the CdS NPs formed. The solution was vigorously stirred for about two hours. FPhSH (100 μL, 0.94 mmol, 5 times the original cadmium concentration) was added to the colloidal solution, which caused the immediate flocculation of the CdS NPs, followed by the addition of TEA (130 μL, 0.94 mmol, 5 times the original cadmium concentration). The precipitates of CdS NPs formed were isolated by centrifugation and washed with isooctane. The NPs were subsequently dispersed in THF.

2.3. Preparation of doped diureasil xerogels

Several diureasil xerogels doped with CdS NPs were prepared using different experimental conditions. The preparation of the doped xerogels was based on a previously published protocol [13]. The diureasil precursor was obtained by mixing Jeffamine – ED-600 (562 mg, 0.936 mmol) and ICPTES (495 μL, 1.87 mmol) in a closed vessel with the stoichiometric amount of 1:2. This mixture was stirred for about 30 min and resulted in the formation of the diureasil precursor consisting of a PEO/POP chain with two triethoxysilane terminal groups. For the preparation of each of the diureasil xerogels, 1 mL of solution of CdS NPs dispersed in THF and capped with FPhSH was added to 1 g of diureasil precursor. This was followed by the addition of 30 μL (0.162 mmol) of MPTMS to two of the samples (samples **AMPS** and **BMPS**). To other two samples, 30 μL (0.128 mmol) of APTMS was added (samples **AAPS** and **BAPS**). In preparation of the remaining two samples (samples **AURS** and **BURS**) no further reagents were added after the addition of the NPs. The reaction mixtures were kept stirring for ten minutes,