

# Homogeneously distributed CdS and CdSe nanoparticles in thin films of mesoporous silica

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## Abstract

A procedure for the preparation of homogeneously distributed cadmium sulfide or cadmium selenide nanoparticles within thin mesoporous silica films was developed. It is based on the use of alkyl (ethylene oxide) surfactant as a structure directing agent and the dip-coating technique for film formation. The films prepared are characterized by low surface roughness and developed mesoporosity. The addition of Cd<sup>2+</sup> ions to the reaction sol prior to the formation of films, followed by the calcination of films at 623 K and treatment with hydrogen sulfide or hydrogen selenide led to the creation of cadmium sulfide or cadmium selenide nanodispersions. The occurrence of the size-quantization effect confirms the location of the particles within the pores and proves the particle size to be consistent with the pore width of the host.

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## 1. Introduction

The formation of host–guest composites of chalcogenide semiconductor nanoparticles, like cadmium (CdS) or lead (PbS) sulfides or cadmium selenide (CdSe), embedded within the micropores or mesopores of inorganic solids has been described up to now only for powders [1–7]. The powders are unfavorable with respect to the potential application in non-linear optics, and, in general, to the optical characterization of the composites [2,8,9]. Since in powders, a large number of individual crystallites cause an intense scattering, the use of the transmission modulus is impeded. Therefore, diffuse reflectance techniques and the Kubelka–Munk formalism [10] have to be employed for measuring the UV/Vis spectra and interpreting the obtained data.

To avoid these drawbacks, two alternatives are possible. First, guest species can be embedded within optically transparent silica monoliths, whose synthesis, however, is rather demanding because of the danger of

crack formation and the difficult homogeneous loading with guests [11,12]. Secondly mesoporous thin films less than 1 μm in thickness on suitable supports are more promising hosts. Ogawa [13] and Brinker and co-workers [14] reported the first sol–gel spin-coating and dip-coating procedures, respectively, to fabricate transparent mesoporous silica films. However, the obtained films were mostly granular and possessed two-dimensional hexagonal structure with pore channels aligned within the substrate plane, which prevents the easy accessibility to the substrate. To solve this problem, Stucky and co-workers developed a general procedure for the formation of continuous, crack-free, highly ordered mesoporous silica films with both two- and three-dimensional symmetries using non-ionic poly(alkylene oxide) tri-block copolymers and low molecular weight alkyl(ethylene oxide) surfactants [15]. Later, the same group presented a method for predictably controlling mesostructures of silica in thin films according to the binary water-Pluronic P123 phase diagram [16]. Such silica films have been loaded with nanoparticles for the first time, in that case consisting of TiO<sub>2</sub> [17].

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Here we report a procedure, which was developed for the homogeneous embedding of CdS and CdSe nanoparticles within the channels of thin mesoporous silica films. Their morphology was determined by profilometry, atomic force microscopy (AFM) and krypton adsorption. X-ray photoelectron spectroscopy (XPS) provided data on the stoichiometry of CdS and CdSe nanoparticles. The absorption behavior of these nanoparticles embedded within the films was determined by UV/Vis spectroscopy.

## 2. Experimental

### 2.1. Chemicals

The following chemicals were used: tetraethylorthosilicate (TEOS), Fluka; Brij 56 ( $C_{16}H_{33}(OCH_2CH_2)_{10}OH$ ), Aldrich; cadmium acetate dihydrate, Aldrich; ethanol, Riedel-de Haen; HCl, Fluka, hydrogen sulfide ( $H_2S$ ), Messer-Griesheim or hydrogen selenide ( $H_2Se$ ), directly prepared from  $Al_2S_3$ , Aldrich, and  $H_2SO_4$ , Fluka.

### 2.2. Preparation of the CdS and CdSe loaded mesoporous thin films

The mesoporous thin films were synthesized according to the procedure reported in Ref. [15] using Brij 56 surfactant as the structure-directing agent. 8.35 g of TEOS were dissolved in 16 g ethanol followed by 4 g of 0.1 M HCl and the sol obtained was heated under reflux for 1 h. After cooling down to room temperature, a solution of 3 g of Brij 56 in 16 g ethanol was added under vigorous stirring. If  $Cd^{2+}$  ions are to be incorporated in the films, 0.56 g of cadmium acetate were additionally added. The mixture was allowed to age at room temperature for 2 h. Subsequently, the viscous sol was used for the preparation of films either on quartz glass or on silicon wafers ( $3 \times 3$  cm in size) by drawing the respective support from the sol with a constant velocity of  $1 \text{ mm s}^{-1}$ . After drying at room temperature for 1 h, the films were calcined in air at 623 K for 2 h (heating rate of  $1 \text{ K min}^{-1}$ ).

Alternatively,  $Cd^{2+}$  ions were introduced into pre-formed silica films by impregnation using a methanol solution of cadmium acetate, which was either dropped onto the film or the film was dipped into it (dipping and withdrawing rates of  $1 \text{ mm s}^{-1}$ ). The cadmium concentration was adjusted in dependence on the film weight and the desired degree of loading, the latter being varied between 1 and 10 wt.% of Cd.  $Cd^{2+}$  ions were transformed into CdS or CdSe nanoparticles by reaction with  $H_2S$  or  $H_2Se$ , respectively. The latter was formed directly by the reaction of adequate amounts of  $Al_2Se_3$  with 0.5 M  $H_2SO_4$ . The films were placed on a glass frit in a glass reactor and flushed with  $H_2S$  or

$H_2Se$  at 303–373 K for approximately 1 h. The stream of  $H_2S$  or  $H_2Se$  was diluted with  $N_2$  and circled around in the reactor system. In order to ensure complete reaction the gases were added in an excess of approximately 100% with respect to the amounts of  $Cd^{2+}$  ions in the films. Prior to and after the reaction, all physisorbed species were removed in vacuum ( $\sim 0.1 \text{ Pa}$ ).

### 2.3. Characterization techniques

The morphology of thin films was determined by profilometry (Veeco DEKTAK 3030ST), atomic force microscopy (AFM, NT-MDT Smena B microscope) and krypton adsorption (Micromeritics ASAP 2010). The roughness factor of the thin films supported on glass sheets was calculated from their BET surface area, determined from Kr adsorption isotherms measured at 77 K. As the films exhibit a very low adsorption capacity but have large space requirements, the use of Kr is unavoidable because of its very low saturation vapor pressure leading to a much smaller ‘dead space’ correction than it is necessary if nitrogen is used as probe gas [18].

The completeness of the film calcination was checked by FT-IR spectroscopy (Biorad FTS-60A). The absorption behavior of CdS and CdSe nanoparticles embedded within the films, which allows to estimate the particle size due to the existence of the size-quantization effect [19,20], was determined by UV/Vis spectroscopy (Varian Cary 4). X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5600) provided data on the stoichiometry of CdS and CdSe nanoparticles.

## 3. Results and discussion

### 3.1. Preparation of mesoporous thin films of $SiO_2$

It was found that homogeneous films cannot be obtained without the presence of a distinct amount of ethanol in the sol for dip-coating. By evaporating different amounts of ethanol in a rotary evaporator, the thickness of the films was varied between 50 and 800 nm. To avoid that the sol used for dip-coating turns too much viscous, at most 20 g of the starting 32 g of ethanol must be removed. From very viscous sols inhomogeneous films or films more than 800 nm in thickness are formed. With such a thick films, the formation of cracks during the calcination cannot be avoided.

The film thickness was determined by profilometry, which enabled to scan an area of approximately  $1 \text{ cm}^2$ . By this technique the height of the step at the film edge is determined with a higher accuracy than by atomic force microscopy, which scans an area of only  $100 \text{ }\mu\text{m}^2$ .

Although AFM failed in the measurement of the film

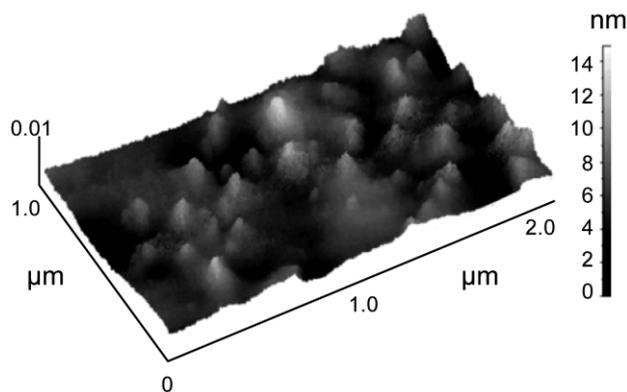


Fig. 1. Atomic force micrograph of a 300-nm thick mesoporous SiO<sub>2</sub> film.

thickness, it is really useful in order to determine the film morphology. Fig. 1 shows a typical AFM micrograph of a 300-nm thick film, supported on a Si wafer. Compared with the film thickness of 300 nm, its roughness within the measured area of 2 μm<sup>2</sup> was very small achieving only ±7 nm. Scanning over wide parts of the film (approx. 300×300 μm) proved that this value was typical for the whole film.

X-ray diffraction provided relatively sharp reflections at  $2\theta=1.4$  and  $1.6^\circ$ , which is in agreement with data in Ref. [15]. Additional data on the mesoporosity of the films were obtained by the analysis of gas adsorption isotherms, which are rather demanding to measure due to the low quantity of adsorbing material. Fig. 2 shows the Kr adsorption isotherm on a mesoporous SiO<sub>2</sub> film of 500 nm thickness deposited on a glass sheet in comparison with the N<sub>2</sub> adsorption isotherm on corresponding powder, prepared from the same sol by slow evaporation of the solvent and subsequent calcination at 773 K. For the film a roughness factor of approximately 40 was determined, which, taking into account the low surface roughness of ±7 nm, determined by AFM, clearly demonstrates the presence of mesoporosity in

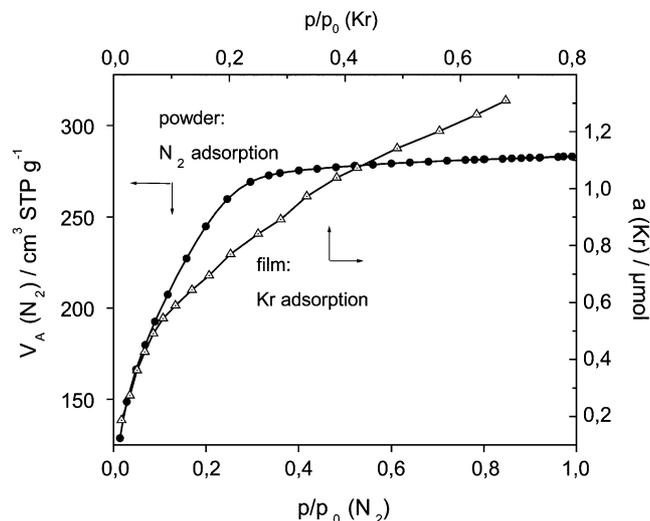


Fig. 2. Kr adsorption isotherm on a CdSe-loaded mesoporous SiO<sub>2</sub> film (a) and N<sub>2</sub> adsorption isotherm on the corresponding powder (b).

the film. This conclusion was confirmed by N<sub>2</sub> adsorption data obtained on the corresponding powder, exhibiting the BET surface area of 915 cm<sup>2</sup>/g and the mesopore volume of 0.432 cm<sup>3</sup>/g. The obtained films are optically transparent (Fig. 3a).

### 3.2. Formation of mesoporous thin films of SiO<sub>2</sub> with incorporated CdS or CdSe nanoparticles

Since it is not possible to introduce a sufficient amount of cations into the non-charged mesoporous SiO<sub>2</sub> films by ion-exchange, a post-synthesis loading with Cd<sup>2+</sup> can only be achieved by impregnation with a suitable cadmium salt, such as acetate. This procedure, however, led to inhomogeneous distributions of Cd<sup>2+</sup> cations within the film and of CdS or CdSe nanoparticles formed by subsequent precipitation with H<sub>2</sub>S or H<sub>2</sub>Se. Fig. 3b shows a film CdSe-loaded by dropping a

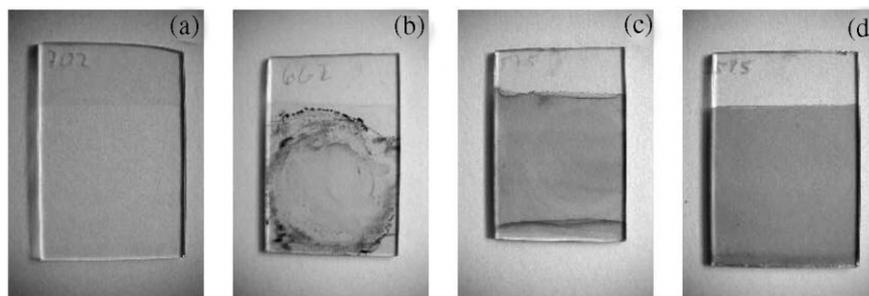


Fig. 3. Images of parent and CdSe-loaded mesoporous SiO<sub>2</sub> films. Unloaded 300 nm thick parent film (a), film with CdSe particles, introduction of Cd<sup>2+</sup> ions by impregnation with a droplet of a cadmium acetate solution (b), film with CdSe particles, introduction of Cd<sup>2+</sup> ions by dip-coating with a cadmium acetate solution (c) and film with homogeneously distributed CdSe nanoparticles, introduction of Cd<sup>2+</sup> ions to the synthesis sol (d).

methanol solution of cadmium acetate onto it, drying and, finally, precipitating CdSe nanoparticles with H<sub>2</sub>Se. The CdSe particles are observable as dark spots concentrated mainly at the edge of the film. If the impregnation was carried out by dip-coating, a more homogeneous distribution was achieved (Fig. 3c), but the concentration of the salt could hardly be controlled. This serious drawback can be circumvented by adding cadmium acetate directly to the sol used for film formation. After the treatment with H<sub>2</sub>Se thus prepared films turned color into orange without any local color variations (Fig. 3d). Except for the intense color, the introduction of Cd<sup>2+</sup> and precipitation of CdSe did not lead to any other changes in the film properties.

The content of Cd and Se in differently prepared films was determined by X-ray photoelectron spectroscopy (Table 1). The three films prepared by adding cadmium acetate to the sol before dip-coating, differ in temperature of calcination applied prior to the treatment with H<sub>2</sub>Se. In the film calcined at 773 K almost no Cd was detected. Consequently, highly dispersed Cd must have evaporated from the sample during calcination at that high temperature. It is well known that the vapor pressure of Cd oxide, presumably formed as an intermediate due to calcination, is drastically increased if the diameter of the oxide particles is restricted to only a few nanometers [21].

Thus, a decrease in the calcination temperature was necessary. In-situ IR spectroscopy of films treated in an O<sub>2</sub>/Ar gas flow (1:4 mixture, flow rate of 10 l h<sup>-1</sup>) at 373–723 K proved that treatment at 623 K was sufficient to remove surfactant molecules from the as-made film (Fig. 4). At 373 K, signals of the CH valence vibrations at ~2900 cm<sup>-1</sup> and the CH<sub>2</sub> and CH<sub>3</sub> distortion vibrations at ~1400 cm<sup>-1</sup> were clearly observable, all the vibrations resulting from the surfactant. At 423 K, an additional band at 1735 cm<sup>-1</sup> appeared, which was assigned to carbonyl species and indicated the start of an oxidative destruction of the surfactant molecules. With increasing temperature the intensity of the carbonyl band increased whereas those of the CH vibrations decreased. Above 523 K also the carbonyl band decreased in intensity and at 623 K completely disappeared. At 623 K, a distinct band at 2300 cm<sup>-1</sup> indicating the presence of CO<sub>2</sub> was clearly observed, which vanished after 30 min and the IR spectrum

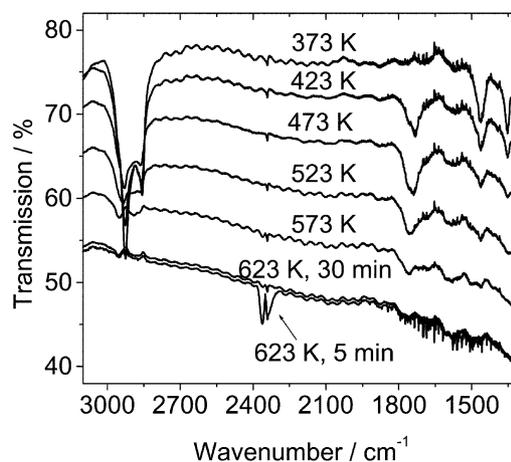


Fig. 4. FTIR spectra of a mesoporous SiO<sub>2</sub> film taken in-situ during its calcination in air.

showed no longer any indication of the presence of organic species. To sum up, calcination of the film in a flow of oxygen or air at 623 K for 2 h is sufficient to remove the surfactant quantitatively. Further, after calcination at temperatures ranging from 453 to 623 K the Cd content in the films was found to be almost invariable (Table 1).

Data on the stoichiometry of the formed CdSe particles showed that approximately 50% of the Cd<sup>2+</sup> ions reacted to CdSe, probably due to the incorporation of a considerable portion of Cd<sup>2+</sup> ions within the silica walls during the gelation and condensation process, rendering them inaccessible for H<sub>2</sub>Se. The relatively low Se content in the impregnated sample (Table 1) might be due to the precipitation of large Cd-acetate crystals on the external surface of the film or even on the glass substrate, only their shell reacting with H<sub>2</sub>Se.

In all the samples containing non-negligible Cd concentration binding energies of the Se3d<sub>5/2</sub> electrons between 54.7 and 55.0 eV were found (Table 1 and Fig. 5b). This is in good agreement with literature data for CdSe [22]. With the film calcined at 773 K an orange-red color appeared after treatment with H<sub>2</sub>Se and a considerable concentration of Se was found. However, the binding energy of the Se3d<sub>5/2</sub> electrons was increased to 55.4 eV (Fig. 5a), which is typical for

Table 1

Binding energies of Cd3d<sub>5/2</sub> and Se 3d<sub>5/2</sub> electrons and elemental concentration of Cd and Se in mesoporous SiO<sub>2</sub> films with embedded CdSe

Introduction of Cd	Calcination prior to H <sub>2</sub> Se treatment, T/K	Binding energy Cd3d <sub>5/2</sub> /eV	Cd/at.%	Binding energy Se3d <sub>5/2</sub> /eV	Se/at.%
To sol	773	405.8±0.2	0.1±0.05	55.4±0.2	6.1±0.1
To sol	623	405.7±0.2	2.1±0.1	54.7±0.2	0.9±0.1
To sol	453	405.5±0.2	2.4±0.1	55.0±0.2	0.4±0.1
By impregnation	623	405.5±0.2	12.7±0.1	55.0±0.2	4.0±0.1

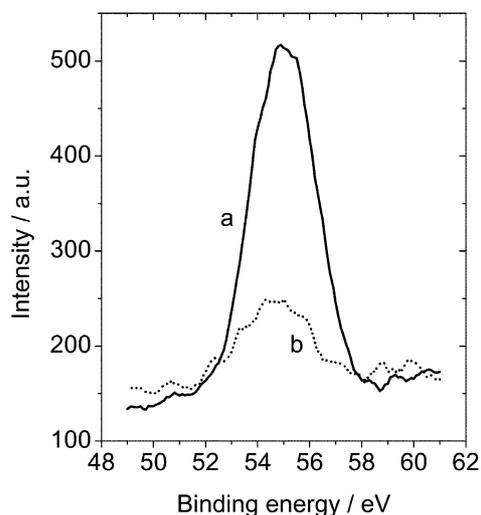


Fig. 5. Se  $3d_{5/2}$  XPS signals of CdSe loaded mesoporous  $\text{SiO}_2$  films after the  $\text{H}_2\text{Se}$  treatment of  $\text{Cd}^{2+}$ -containing films calcined at 773 K (a) and 623 K (b).

elemental selenium [23]. This observation indicates the silica film tends to catalyze the decomposition of  $\text{H}_2\text{Se}$ .

### 3.3. Optical properties of CdS and CdSe nanoparticles in mesoporous thin films of $\text{SiO}_2$

The color of CdS and CdSe loaded films, formed after addition of  $\text{Cd}^{2+}$  ions to the sol, showed no local variations, being pale yellow or and orange, respectively. These colors indicate the occurrence of the size-quantization effects since they are brighter than that of the bulk materials, which are yellow–orange (absorption edge at around  $\lambda=520$  nm) and grey–red (712 nm), respectively. In the prepared films the observed absorption increased considerably at approximately  $\lambda=500$  nm (CdS) and  $\lambda=590$  nm (CdSe), and the first excitonic shoulders were deduced from the second derivation of the spectra at  $\lambda=483$  nm (CdS) and  $\lambda=557$  nm (CdSe) (Fig. 6). According to the tight-binding model for the estimation of semiconductor nanoparticle sizes from altered opto-electronic features [19], mean diameter of approximately 2.5 nm were calculated for both CdS and CdSe nanoparticles, corresponding well to the widths of the host pores (approx. 2 nm). This consistency confirms that CdS and CdSe particles were formed within the pores, where they are protected against further growth even if the samples are heated to 373 K.

## 4. Conclusions

A procedure for the preparation of homogeneously distributed CdS or CdSe nanoparticles within thin mesoporous silica films has been developed, which consists of the following steps: (i) the formation of a sol by acid catalyzed hydrolysis and polymerization of tetra-

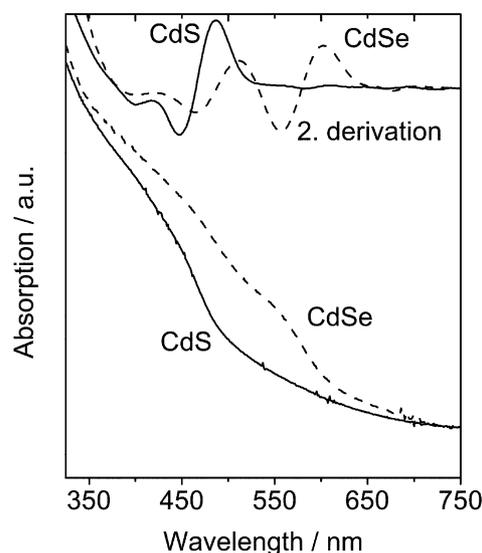


Fig. 6. UV/Vis spectra of CdS and CdSe nanoparticles in mesoporous  $\text{SiO}_2$  films.

ethoxysilane under the directing influence of an alkyl(ethylene oxide) surfactant, such as Brij 56, (ii) addition of suitable cadmium salts, such as acetate, to the sol, (iii) the formation of a thin film by dip-coating, (iv) the formation of mesoporosity by quantitative removal of the surfactant due to calcination at 623 K and (v) the treatment with  $\text{H}_2\text{S}$  or  $\text{H}_2\text{Se}$ , which leads to the creation of CdS or CdSe nanoparticles.

The occurrence of the optical size-quantization effect for the nanoparticles confirms that the particles are located within the pores and that their size is consistent with the pore width of the host.

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