STABILIZATION OF CADMIUM SULFIDE NANOPARTICLES USING BLOCK-COPOLYMERS

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Abstract

This study investigated the stabilization of cadmium sulfide (CdS) nanoparticles in aqueous solutions of the triblock copolymer Pluronic P123. The concentration of the added cadmium sulfide varied between 0.002 and 0.02 M. For the synthesis, sodium sulfide and cadmium chloride were both dissolved in aqueous P123 solutions with concentrations of 23 and 30 weight percent (wtp) of polymers. Both solutions were cooled to low temperatures and mixed in a heated sample cell. The stabilization of CdS nanoparticles was successful for both P123 concentrations. The stabilized nanoparticle-polymer solutions were investigated using ultraviolet-visible spectroscopy (UV-Vis) and small- and wide-angle-x-ray-scattering (SAXS/ WAXS). In the absorption spectra measured by UV-Vis spectroscopy, no shift of the absorption edge, depending of the CdS concentration in solution is visible indicating a bulk like behavior. SAXS showed, that the distance between the Pluronic micelles is not changing in the lyotropic liquid crystal (LC) phase by adding CdS, but a significant rise of the scattering intensity was visible. We assume, that the nanoparticles are located in the micellar core. As proved by WAXS, in some cases even crystalline nanoparticles could be produced. This sample system consisting of polymeric micelles and nanoparticles can be seen as a model for studying the formation of nanoparticles because the crystallization process of the nanoparticles was enlarged form a timescale of nanoseconds to minutes.

Keywords: Pluronic, P123, cadmium sulfide, nanoparticles, SAXS, WAXS, UV-Vis, kinematics, stabilization

1. INTRODUCTION

Cadmium sulfide nanoparticles were studied, because of their size-dependent optical and electronic properties. As an II-VI semiconductor it has a wide band gap in the range from $2.45\ eV$ as bulk material to $3.25\ eV$ as a $3\ nm$ small particle [1]. They can be used in catalysis [2], the purification of water [3], as biological labels [4] or as materials for solar cells [5]. One of the most interesting effect of CdS is the size quantization effect or quantum size effects (QSE). At first it was calculated by Burs [6] and also shown by Schmidt et al. [7]. The calculation is based on the lowest Eigenstates of an electron-hole pair, also called Wannier exciton. The lowest 1S exciton of CdS is about 60 Å in diameter [6]. Lowering the diameter of the nanoparticles from 100 to 40 Å, a shift of $0.43\ eV$ towards higher energies will accrue. Thus, the absorbance will be different for different sized nanoparticles. Since CdS is very hydrophobic, it is not possible to synthesize nanoparticles in aqueous solutions without added stabilizers. Various ways to synthesize CdS nanoparticles and quantum dots can be found in literature [4], [8], [9]. A. Rempel et. al. found a way to synthesize CdS nanoparticles in water with EDTA disodium salt ($C_{10}H_{14}N_2O_8Na_2$, Na_2H_2edta) [10]. They found that the nanoparticle size distribution could be described with a normal distribution function with a maximum at $2.6\ nm$ surrounded by an organic shell of around $5\ nm$.

In our opinion, another promising way to stabilize CdS are polymers, which form micelles with hydrophobic cores. With this method, the properties of the polymers can be used - e.g. the formation of liquid crystals - to

modify the structuring of the nanoparticles. A suitable candidate is Pluronic P123, because it is already well investigated and has the required behavior [11]-[14]. At low temperatures (5°C), P123 is present as unimers, elongated chains in an aqueous solution. Reaching the critical mizellization temperature, unimers will form to micelles. In this manner P123 is a promising system to stabilize CdS.

2. SAMPLES AND METHODS

2.1. Samples

Pluronic P123 was purchased from Sigma Aldrich (CAS Number: 9003-11-6) and used as received without any further purification. P123 (PEO_{19}-PPO_{69}-PEO_{19}) is a triblock polyether copolymer consisting of polyethyleneoxid (PEO) and polypropyleneoxide (PPO). Fourier transform infrared studies show that both PEO and PPO chains undergo a dehydration while increasing the temperature. The degree of dehydration is lower for PEO than for PPO [15].

CdS was synthesized with the method of A. Rempel et.al. [10]. There cadmium chloride ($CdCl_2$) and sodium sulfide (Na_2S), each in an aqueous solution with EDTA, have to be mixed to produce nanoparticles. Both were purchased from Sigma Aldrich and used as received (CAS-Numbers: 10108-64-2 and 1313-84-4). Instead of EDTA we used P123 as a stabilizer. Thus, two solutions were prepared. One with water, P123 and $CdCl_2$ (Sol_C) and one with water, P123 and Na_2S (Sol_S). When those two solutions were mixed at the right temperatures and the right concentrations, stable solutions can be realized. We used two concentrations 23 and 30 wtp of P123 and seven concentrations 2, 4, 6, 8, 10, 15 and 20 mM of $CdCl_2$ and Na_2S.

2.2. Methods

In principle, the mixing and stabilization process consists of two steps: cooling the reactants (Sol_C) and (Sol_S) and mixing them in a tempered sample cell. Thus P123 at 30 wtp is forming a liquid crystal, which is gel like, the reactant temperature has to be below the critical crystallization temperature. The reactants were filled in syringes and cooled in a tempered metal block. The liquids were lead through short pips into a Y-connector where they were mixed and the mixed product was lead into a tempered cell after the mixing. This flow through cell was also the sample cell for the SAXS and WAXS measurements and is suitable for vacuum. Before the mixing, the solvents were cooled to 5°C and tempered to 30°C after the mixing to have a defined start for the stabilization of the nanoparticles. For uniformity, the 23 wtp solutions were treated the same way. For the UV-Vis-spectroscopy measurements the sample were premixed in a glass container before transferring them in the designated sample holders.

Small angle x-ray scattering (SAXS) and wide angle x-ray scattering (WAXS) measurements were accomplished at an in-house self-build machine, at the Chair of X-ray Microscopy (University Würzburg), which is optimized for low contrast measurements. The machine is equipped with a rotating anode micro focus x-ray source with a copper target, a paralyzing mirror and slits for a determinable and variable beam shape with a high flux. The sample can be tempered between 2 °C and 70 °C. The sample detector distance (SDD) is variable between 5cm and 3.5 m with a resulting Q-range of 0.005 to 5 $Å^{-1}$. The detector is a Dectris EIGER 1M. The complete system operates in vacuum to minimize scattering and absorption of air. All data sets were reduced with Nika a macro for Igor Pro [16].

Optical absorption spectra were recorded by a FS-5 spectrofluorometer from Edinburgh Instruments, at the Institute of Solid State Chemistry (Ural Branch of the Russian Academy of Sciences, Eekaterinburg) in the UV and visible ranges. The device is equipped with continuous Xe-lamp (450 W) and silicon photodiode for transmission measurements. Quartz cuvettes with a optical light paths of 0.5 mm were used. The reference sample for measurements was an aqueous solution of P123.

3. RESULTS

To choose the right temperatures and conditions for the stabilization and mixing process, pure aqueous solutions of P123 with a concentration of 30 wtp were precisely examined. At 10 °C unimers start to form micelles, which can be seen in the **Figure 1**. The scattering curve of unimers can be described as an exponential decay. At 17°C the micelles can be seen in the scattering curve with a strong form factor. Heating the solution above 20 °C a liquid crystal is formed, which can be seen by the peaks of the red curve. The solution forms a gel. Above 37 °C the slope changes again to a less ordered system. The black curve has no distinct peaks due to the peak broadening. Also the gels start to liquefy again.

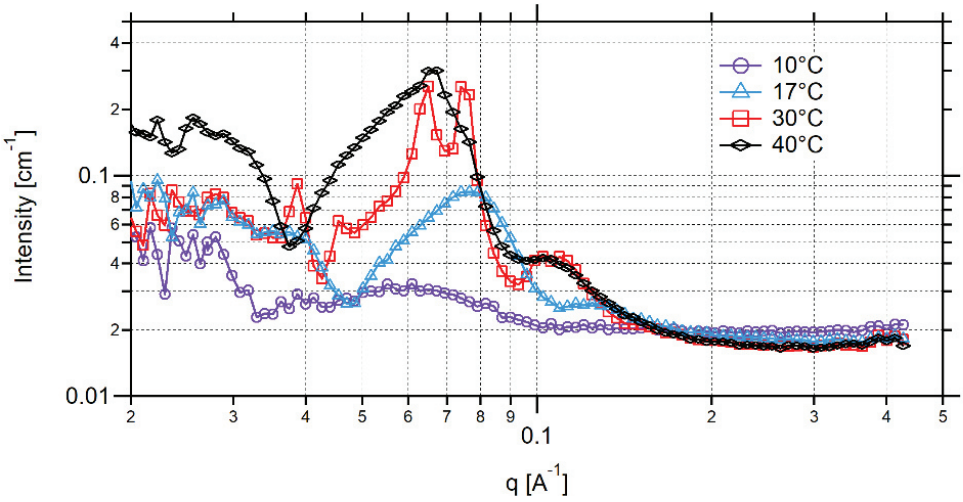

Figure 1 SAXS measurements of Pluronic P123 with a concentration of 30 wtp at different temperatures. Each measurement was integrated for 2h.

The two reactants solutions (see 2.1) were cooled down to 5 °C and mixed in a heated capillary at 30 °C. CdS was stabilized with this method, proved in **Figure 2**. On the left side (**Figure 2a**) various CdS concentrations are shown starting from 0.002M on the right up to 0.02M on the left. The gels have a light yellow color at low concentrations changing to orange for higher concentrations, which are stable for days. In **Figure 2b** shows pure CdS in water mixed in a capillary. An orange separated phase arises due to the high hydrophobicity of CdS.

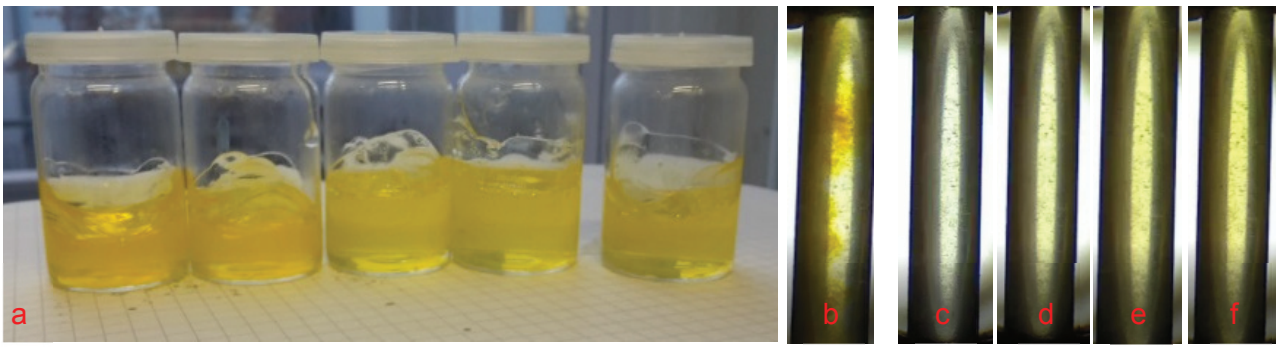

Figure 2 Exaples of stabilized CdS nanoparticles from 0.002M rigth and 0.02M left (a). The capilliry of the sample cell is shown in (b-f), where (b) is filled CdS in pure water, and (c-f) shows the stabilization of CdS with P123 rigth after the mixing of both solutions (c) until five minutes after the mixing (f).

Figures 2c-f depict the formation process of a 0.005M CdS solution at different times. Until a stable color settles, 5 minutes passed. No phase separation is visible. P123 with an CdS concertation of 0.005 and 0.01M

were analyzed with SAXS and WAXS. The SAXS scattering pattern are shown in **Figure 3**. The peaks corresponding to the LC structure for pure P123 and with added CdS do not shift (see **Table 1**). The peaks were fitted with a gaussian function. By adding CdS to P123, a significant higher scattering intensity is visible. Aqueous solutions of P123 with a concentration of 23 wtp were also used to produce CdS nanoparticles and measured with SAXS. Those samples show the same color as CdS in a 30 wtp solution of P123, but 23 wtp do not form lyotropic LC. Those samples were able to stabilize CdS, but have been still liquid. To study the optical properties and thus to draw conclusions about the nanoparticle sizes UV-Vis Spectroscopy measurements of different CdS concentrations were conducted (see **Figure 4a**). The absorbance increases with raising the concentration of CdS. The region between 450 and 500 nm is interesting to determine the bandgap of the CdS nanoparticles. For this purpose an analysis of the absorption spectra was carried out using current concepts of semiconductor physics developed for bulk materials [17]. According to Tauc theory the spectra indicate a direct optical transition [18]. Using the spectral curves, the absorption edge or band gap is specified as the intersection of the first linear segment of the absorption curve with the x-axis [18]. The resulting bandgap does not change within the error with changing concentration of CdS (see **Figure 4b**). For both concentrations of CdS also WAXS measurements were conducted, to characterize the crystallinity of the produced CdS nanoparticles. For 0.005M, no reflexes were visible. However, for a concentration of 0.01M CdS stabilized in 30wtp P123 very narrow single reflexes are visible and can be assigned to circles (see **Figure 5**). The reflexes are marked with white rings.

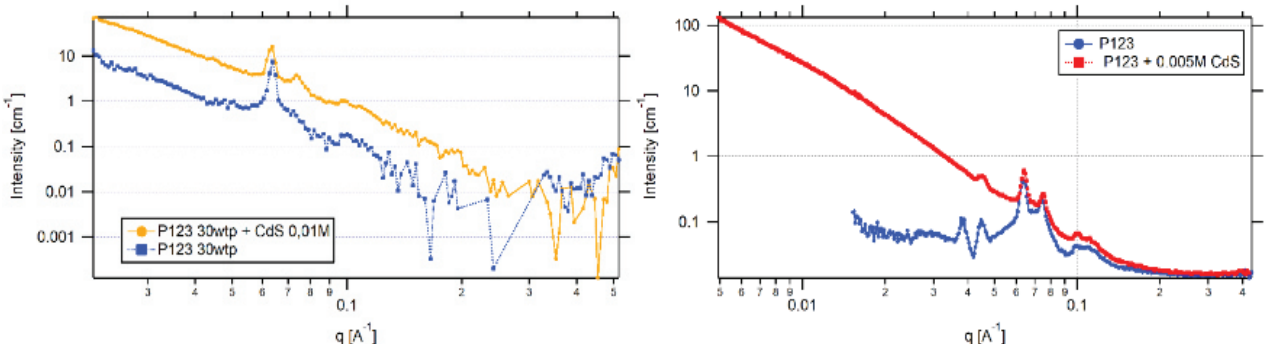

Figure 3 SAXS measurements of pure P123 and with added CdS with concentrations of 0.005M on the left and 0.01M on the right. Note that on the left side water was not subtracted, where water is subtracted from both data sets in the right graph.

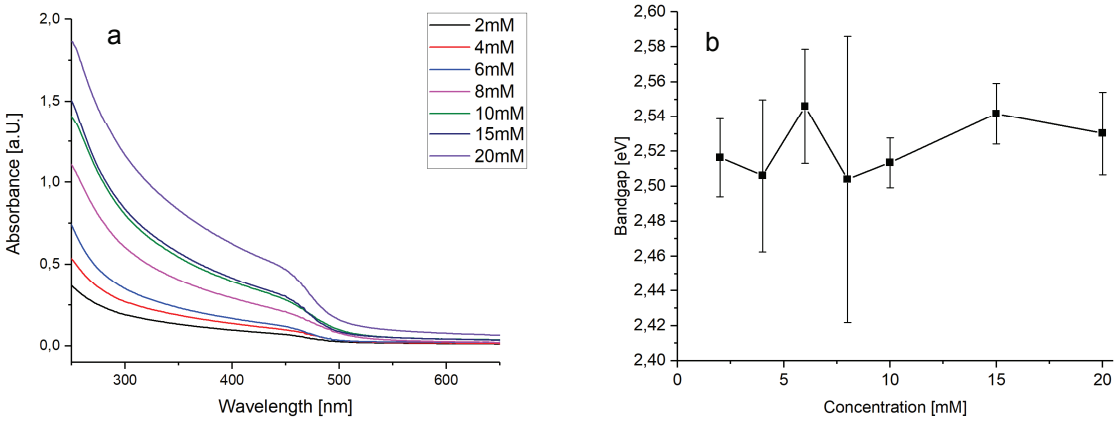

Figure 4 UV-Vis measurments of 30 wtp P123 and different concentrations of CdS on the left (a) and the calculated bandgaps with Tauc theory [20] on the right (b).

Table 1 Positions of the structure peaks of pure P123 with a concentration of 30 wtp and added Cds

Composition	1. Peak [1/Å]	2. Peak [1/Å]
P123	0.063730 ± 0.000046	0.07402 ± 0.00027
P123 + CdS	0.063980 ± 0.000016	0.07492 ± 0.00023

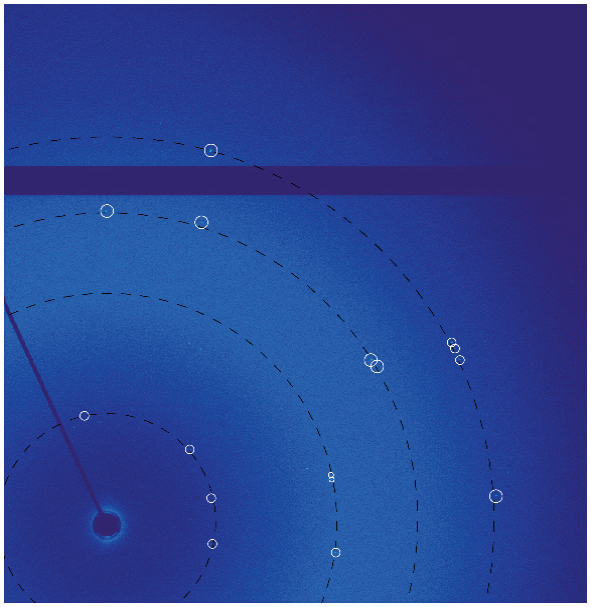

Figure 5 WAXS measurement of 0.01M CdS stabililized with 30wtp P123. Reflexes, which are located on rings were marked with white rings

4. DISCUSSION

Having in mind that CdS and PPO of P123 are distinct hydrophobic (see 2.1), we assume, that the stabilization process is driven by a hydrophobic-hydrophobic interaction. The SAXS data for pure 30wtp P123 and for added CdS show, that the inter micellar distance, represented by the peaks, does not change. This is an indication that there was no change in the size of the micelles. The succinct raise of the intensity is caused by an amplification of the scattering contrast due to the presence of CdS. According to this interpretation, the CdS could be found either in the micelle or between the micelles stabilized by the lyotropic LC. Since the liquid 23wtp P123 solutions were able to stabilize CdS and no precipitation of CdS was visible, the latter option must be dismissed. Considering that the shell of the micelle is usually more hydrated then the core, we assume that the CdS is stabilized inside the micellar core. Furthermore, this confirms the hydrophobic-hydrophobic interaction. It was not possible to determine the size of the CdS nanoparticles with SAXS. In this regard, UV-Vis measurements were conducted to draw conclusions about the size of the nanoparticles. The measurements showed that CdS nanoparticles display the same behavior as bulk CdS, with a bandgap of $E_G = 2.45\ eV$. By varying the concentration of CdS, no correlation to the quantum size effect could be determined. The reason for this could be that the number of nanoparticles larger than 60Å in diameter is much higher than for particles with smaller diameters showing a quantum size effect. This indicates a broad size distribution. However, note that the mixing procedure of UV-Vis and SAXS was not identical, due to experimental requirements. WAXS analyzes the crystallinity of the CdS nanoparticles. The optical absorption spectra prompt the formation of a CdS phase. WAXS measurements of 0.01M CdS in 30wtp P123 showed sharp single crystal reflexes. Although the exact crystal structure cannot be determined out of the date, it clearly shows that the crystallinity is temperature dependent. By controlling the temperature, it is possible to influence the

micellization and formation of LC. Thus, it is possible to control the kinematics of the crystallization process of cadmium sulfide. Additionally the timescale for the crystallization is enlarged from the timescale of nanoseconds [19] towards minutes, which is a deceleration of seven orders of magnitude in time.

5. CONCLUSION

It is possible to stabilize hydrophobic CdS nanoparticles with Pluronic P123. The structure of 30wtp P123´s lyotropic LCs does not change upon adding CdS, but it's scattering intensity rises significantly. Also CdS could be stabilized with a liquid P123 solution, proving that the nanoparticles are located inside the micelles. Due to the lower hydration level of core compared to the shell, the nanoparticles should be stabilized by the core, which confirms a hydrophobic-hydrophobic interaction. UV-Vis measurements yield mostly nanoparticles bigger than 60Å, because of a bulk-like behavior of the nanoparticle's bandgap. With WAXS it was proved, that it is possible to produce crystalline CdS nanoparticles. First investigations of the kinematical process show an enlargement of the crystallization timescales form nanoseconds to minutes.

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