Adjustment of the Band Gap Energies of Biostabilized CdS Nanoparticles by Application of Statistical Design of Experiments

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The colloidal synthesis of CdS nanoparticles with the biostabilizers cysteine and glutathione, respectively, at pH values ranging from 4 to 10 is described. For the adjustment of their UV/Vis absorption properties and hence their band gap energies, the Statistical Design of Experiments (DoE) was used. This method allows the simultaneous variation of the synthesis parameters in a systematic manner, and thereby synergistic interaction effects can be obtained. The band gap energies of the quantum dots can be tuned from 3.32 to 4.26 eV by varying kind and concentration of stabilizer, pH value, and concentration of sulfide source. The energy position is significantly dependent on the interaction between the pH value and the concentration of the stabilizer, and the effect of high glutathione concentration is opposite at acidic and alkaline conditions thus leading to band gaps of 4.10 eV at pH = 6 and of 3.64 eV at pH = 10. Examples for the synthesis of semiconductor nanoparticles with predefined spectroscopic properties and preset preparation conditions, e.g., alkaline conditions for the implementation of acid-sensitive dopants, are given.

1. Introduction

During the past decade the synthesis of semiconductor nanoparticles has become a major field of research due to their unique chemical and electronic properties. The quantum confinement provides molecular-like discrete energy levels, and the semiconductor band gap exhibits strong size dependence. The influence of various parameters on the band gap position of colloidal CdS nanoparticles has been widely investigated.[1−12] In most of these studies the classical experimental design was used whereby one parameter is systematically varied while the others are kept constant, thus disregarding possible parameter interactions. In this paper the Statistical Design of Experiments (DoE)[13−15] is used to explore the influence of three synthesis parameters on the band gap energies of CdS nanoparticles, namely, the concentration of the stabilizers cysteine and glutathione, respectively, the concentration of the sulfidation reagent, and the pH value of the sols. We have chosen not to perform exchange of the capping ligands of CdS nanoparticles as described in the literature[16−18] because of the potentially incomplete exchange of the quantum dot surface[19,20] and because of the facile preparation of the biostabilized nanoparticles comprising a one-pot-process and mild synthesis conditions such as room temperature and the use of water as solvent.

The stabilizers applied in this work render the photoluminescent CdS nanoparticles water-soluble and additionally they provide functional groups, i.e., the amino and the carboxyl group. This allows, for example, covalent labeling[21,22] of biological moieties such as antibodies and related molecules of biological interest. Selected samples of cysteine- and glutathione-stabilized nanocrystals have been investigated regarding growth kinetics, size, crystal structure, bond attributes, chemical composition, and absorption as well as emission properties, and these characteristics are described elsewhere.[12,23,24] In this paper the particles are characterized by UV/VIS absorption spectroscopy, and the position of the semiconductor exciton peak corresponds to the band gap energy and therefore to the particle size.[25−28]

We present a systematic investigation of the scope and capability of this preparation method within a wide range of synthesis parameters. As multiparameter DoE varies all synthesis parameters simultaneously in a predefined mode, an appropriate experimental design gives information not only on the influence of particular synthesis parameters but also on synergistic parameter interactions. It can provide predictive tools for the properties of the system under various conditions, and optimal parameter values can be determined to produce CdS colloids with predefined absorption properties.

2. Experimental Section

Synthesis of Colloids. *Reagents.* Cadmium chloride hemipentahydrate A.C.S. (Aldrich), 1,1,1,3,3,3-hexamethyl-disilathiane HMDST (Aldrich), L-cysteine (≥99%, Fluka), glutathione GSH (98%, Sigma), tetramethylammoniumhydroxide TMAH (25 wt % in methanol, Aldrich), and tetrahydrofuran THF_{abs} (≥99.5% with molecular sieve, Fluka) were used without further purification. Deionized water was used with a conductivity of 0.055 μS cm^{-1}. HMDST was used as 0.1 M stock solution in THF_{abs}, and for the other stock solutions the solvent was deionized water. All reactions were carried out under argon using Schlenk technique, and the precursor solutions were thoroughly degassed.

Synthesis of Cysteine-Stabilized CdS. As examples for the syntheses with cysteine as stabilizer, the following synthesis parameters are used: cysteine/Cd^{2+} = 3.0, HMDST/Cd^{2+} = 1.0, and pH = 8 prior to sulfidation. In a three-neck flask 15.0 mL of 0.1 M cysteine stock solution was added to 225 mL of deionized water, and after stirring for 5 min 5.0 mL of 0.1 M stock solution of $CdCl_2 \cdot 2.5\ H_2O$ was added. After 10 min the

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pH value was adjusted to pH = 8 by dropwise addition of TMAH, and the rapid addition of 5.0 mL of 0.1 M stock solution of HMDST resulted in a clear colloidal solution of slightly yellow cysteine-coated CdS nanoparticles. The final cadmium concentration was 2×10^{-3} mol L^{-1}.

Synthesis of Glutathione-Stabilized CdS. As an example for the syntheses with glutathione as stabilizer, the following synthesis parameters are used: $GSH/Cd^{2+} = 4.5$, $HMDST/Cd^{2+} = 0.75$, and pH = 8. To 250 mL of 2×10^{-4} M $CdCl_2$ solution 2.25 mL of 0.1 M glutathione stock solution was added and stirred for 5 min. The pH value was adjusted to 8 using TMAH, and subsequently 0.375 mL of 0.1 M HMDST stock solution was rapidly injected. After 30 min the pH value was raised to 11, and 1.5 mL of 0.1 M $CdCl_2$ stock solution was added to the colloidal solution, thus resulting in CdS nanoparticles with a mixed glutathione/$Cd(OH)_2$ shell. All pH values cited in the text refer to the pH prior to sulfidation.

Absorption spectra were recorded 30 min after synthesis on a Hitachi U-3000 UV/VIS-spectrophotometer.

Statistical Design of Experiments. The mathematical model fitted to the experimental data is a quantitative way of relating the experimental output to the input parameters. It can be represented as a polynom regression, and the applied second-order model with interaction has the general form

$$Y = \sum_{i=1}^{N} b_i X_i + \sum_{i=1}^{N} b_{ii} X_i^2 + \sum_{i,j=1}^{N} b_{ij} X_i X_j \qquad (1)$$

Equation 1 describes the relationship between the response Y, i.e., the band gap position derived from the UV/Vis absorption spectra, and the independent input parameters X_i (with $i = 1, ..., N$). The terms $b_i X_i$ are the linear terms depending on the parameters, $b_{ii} X_i^2$ are the corresponding quadratic terms, and the terms $b_{ij} X_i X_j$ describe the synergistic interactions between the parameters. The statistical analysis of the output data results in values for the coefficients b thus providing a quantitative model for the effects of the input parameters on the experimental output.

The linear terms specifiy the main relationship between the exciton peak in the UV/Vis absorption spectra and a given factor, and in our investigation the factors represent the pH value of the colloidal solution and the relative concentrations of the sulfidation reagent and the stabilizer, respectively. The quadratic terms allow curvature, and in this way a maximum or minimum for experimental conditions can be obtained. For quadratic terms it is a precondition that all of the investigated factors can be applied in a continuous manner and not only in a discrete one. The interaction terms specify the connectivity of the influences of two factors on the output, i.e., the tendency for the combination of the factors to produce a result that is different from the mere sum of their two individual contributions.

For the analysis and evaluation of the data the software Statgraphics Plus 4.1 (Manugistics) was used. For cysteine as well as for glutathione the selected model is adequate for the observed data at the 95% confidence level.

3. Results and Discussion

The stabilizer cysteine has its isoelectric point at pH = 5.02. In Figure 1(a) cysteine is shown in the zwitterion form prevailing at this pH value, where the stabilizer as a whole is uncharged and not soluble in water. Therefore the syntheses were performed at pH = 4.0 and pH = 8.0 providing molecules with either a positive charge or a negative one. The main effects of the three factors were investigated with continuous variation

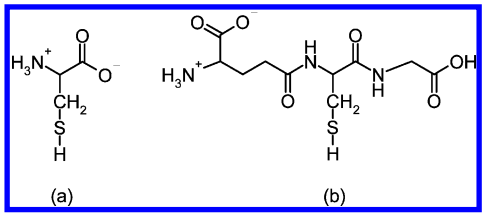

Figure 1. Structural formula of the stabilizers (a) cysteine and (b) glutathione.

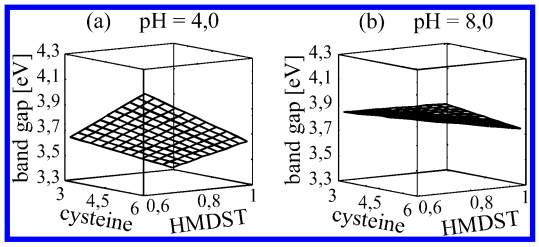

Figure 2. Band gap energies of cysteine-stabilized CdS nanoparticles depending on the concentration of the stabilizer (3.0−6.0 mole equiv/Cd^{2+}) and of sulfidation reagent HMDST (0.6−1.0 mole equiv/Cd^{2+}) for (a) pH = 4 and (b) pH = 8.

of the relative amounts of stabilizer from 3.0 to 6.0 mole equivalents with respect to cadmium and of sulfur source HMDST from 0.6 to 1.0 mole equivalents, and with the two levels of the discontinuous pH value of the colloidal solution.

With cysteine as stabilizer, the absorption spectra show reasonably sharp exciton peaks at pH = 8 and broad shoulders at pH = 4. In these cases the position of the band gap was determined by the minimum of the second derivation of the absorbance. In Figure 2 the band gap energies derived from the UV/Vis absorption spectra are shown, depending on the cysteine/Cd^{2+} ratio and the HMDST/Cd^{2+} ratio for (a) pH = 4 and (b) pH = 8.

At pH = 4 the amino group and the carboxylate group are protonated and thus the stabilizer is positively charged. The obtained semiconductor nanoparticles have band gaps in the range of 3.32 eV to 4.10 eV with significant dependencies on the concentrations of both stabilizer and sulfidation reagent. The smallest particles having the highest band gap energy can be synthesized with 6.0 mole equivalents of cysteine and 0.6 mole equivalents of HMDST with respect to cadmium, and the largest particles are obtained with the ratio cysteine/Cd^{2+} = 3.0 and HMDST/Cd^{2+} = 1.0. This corresponds to the expected effects of stabilizer and sulfidation agent, i.e., the formation of smaller particles with higher concentration of stabilizer and lower concentration of sulfide source. The band gap difference of 0.780 eV obtained in acidic solution is remarkably large.

At pH = 8 the amino group is uncharged and the carboxyl group is deprotonated. As can be seen in Figure 2(b), the range of the energetic position of the exciton peak is rather small, varying from 3.74 to 3.90 eV according to minor influences of the relative concentrations of cysteine and HMDST. Interestingly, the largest particles are formed with the highest amount of stabilizer, namely, with 6.0 mole equivalents of cysteine, and 1.0 mole equivalent of HMDST, while the smallest particles are formed with 6.0 mole equivalents of cysteine and 0.6 mole equivalents of HMDST. Thus, at pH = 8 the effect of cysteine concentration is negligible in contrast to the findings at pH = 4, and the influence of the HMDST concentration is less pronounced. The analysis provides planar surfaces since the pH value is not continuous but rather has two levels due to the isoelectric point of cysteine.

Summarizing, for cysteine-stabilized CdS nanoparticles the position of the band gap is significantly influenced by each of

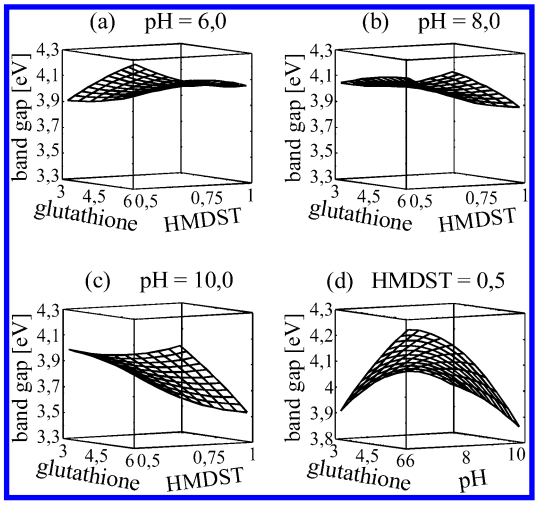

Figure 3. (a)−(c) Band gap energies of glutathione-stabilized CdS nanoparticles depending on the concentration of the stabilizer (3.0−6.0 mole equiv/Cd^{2+}) and of sulfidation reagent HMDST (0.5 − 1.0 mole equiv/Cd^{2+}) for (a) pH = 6, (b) pH = 8, and (c) pH = 10. (d) Band gap energies of glutathione-stabilized CdS nanoparticles depending on the concentration of the stabilizer (3.0−6.0 mole equiv/Cd^{2+}) and of pH value (6.0−10.0) for a HMDST/Cd^{2+} ratio of 0.5.

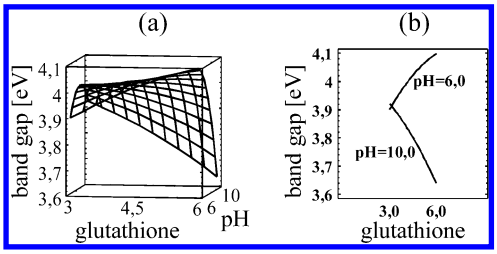

Figure 4. Significant interaction effect between the stabilizer glutathione and the pH of the colloidal solution; (a) surface plot and (b) interaction plot, both with HMDST/Cd^{2+} = 0.75.

the three main factors as well as the interaction effects between pH and stabilizer and between pH and sulfidation reagent.

The stabilizer glutathione, shown in Figure 1(b), has a low isoelectric point due to the second carboxyl group. The second-order model described above was applied with three continuous factors, and the pH value was varyied from 6 to 10, the GSH/Cd^{2+} ratio from 3.0 to 6.0, and the HMDST/Cd^{2+} ratio from 0.5 to 1.0. In Figure 3 (a)−(c) the energetic positions of the exciton peak are shown for different pH values. The parameters significantly influencing the position of the exciton peak are the pH value of the colloidal solution and the interaction between pH and the concentration of glutathione.

The smallest nanoparticles with the highest band gap energy of 4.26 eV are formed at pH = 6, with 6.0 mole equivalents of glutathione and 0.5 mole equivalents of HMDST. The largest glutathione-stabilized CdS particles have a band gap of 3.53 eV, and they are obtained at pH = 10 with 6.0 mole equivalents of glutathione and 1.0 mole equivalent of HMDST. For pH = 6 and pH = 8, respectively, the range of band gap differences comprises 0.37 and 0.27 eV, respectively, whereas for pH = 10 the adjustment range spans 0.46 eV. It can be seen in Figure 3 (a)−(c) that the concentration of the sulfide reagent HMDST affects the particle sizes, especially at pH = 10, and that at pH values of 6 and 8 the semiconductor nanoparticles have comparatively higher band gap energies than at pH = 10.

In Figure 4 the significant interaction effect between glutathione and pH is shown. The interaction is calculated for the mean value of the noninvolved factor, in our case for HMDST/Cd^{2+} = 0.75, and the effect describes a change in the response due to the combination of two factors where the influence of one factor depends on the level of the other factor. It can be seen in Figure 4 that the effect of the stabilizer concentration is reverse at acidic and alkaline conditions: the ratio glutathione/Cd^{2+} = 6 generates band gaps of 4.10 eV at pH = 6 and of 3.64 eV at pH = 10. Or, the other way around: for lower glutathione concentrations the pH value of the colloidal solution marginally affects the position of the exciton peak, whereas with increasing stabilizer concentration the pH value becomes increasingly relevant.

The results potentially can be explained in terms of the charge of the stabilizer and the coordination number of cadmium and sulfur atoms on the surface of the nanoparticles. It was shown for glutathione-stabilized CdS nanoparticles that sulfur located on the surface has a coordination number of two or three while sulfur located within the core of the particle is 4-fold (tetrahedral) coordinated.[24] This coordinatively unsaturated surface sulfur should form bonds to positively charged species. On the other hand, possibly not fully passivated surface cadmium atoms could bind to negatively charged species. The amino acid cysteine and particularly the tripeptide glutathione have amino and carboxyl groups with a variety of charge conditions, depending on the pH value of the solution. Thus the data reflect different pH-dependent bond situations leading to different efficiencies of the stabilizer in regulating the growth and subsequently the band gap energy of the semiconductor nanoparticles.

Utilizing the potential of DoE, specified synthesis parameters can be preset, and the remaining parameters can be figured out. For example, let us assume that nanocrystals with a band gap energy of 3.9 eV should be produced. It might be necessary, maybe for the implementation of acid-sensitive doping atoms, to synthesize in neutral or weakly alkaline medium, for example at pH = 8. Hence it can be calculated that the values of other parameters are glutathione/Cd^{2+} = 6.0 and HMDST/Cd^{2+} = 0.9. If the same exciton peak position should be achieved by using 0.5 HMDST/Cd^{2+} then the corresponding values are pH = 9.9 and glutathione/Cd^{2+} = 5.7 or, alternatively, pH = 6.0 and glutathione/Cd^{2+} = 3.0. These examples are illustrated in Figure 3(b) und (d).

4. Conclusions

In this paper the synthesis of biostabilized CdS colloids was presented, and an application of DoE to the adjustment of their sizes was given.

With the stabilizers cysteine and glutathione, respectively, colloidal nanoparticles could be obtained within a pH range from 4 to 10. The band gap energy of cysteine-stabilized nanoparticles ranges from 3.32 to 4.10 eV, and the position is significantly influenced by the three factors of pH value, concentration of stabilizer, and concentration of sulfide source as well as by the interaction between pH and cysteine and the interaction between pH and sulfide source. Information on these synergistic parameter interactions can be obtained only by the simultaneous variation of parameter values as provided by DoE.

The glutathione-stabilized nanoparticles have band gap energies varying from 3.53 to 4.26 eV, the latter being formed at pH = 6, with the ratios stabilizer/Cd^{2+} = 6.0 and sulfide/Cd^{2+} = 0.5. The energy position is significantly influenced by the pH value and the interaction between pH and concentration of glutathione. The explanation for the results could be the dependency of the stabilizer's charge on the pH thus leading to different bond situations on the surface of the CdS nanoparticles resulting in different stabilization properties.

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