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Abstract

Thin polymeric films with high concentration of CdTe-nanocrystals are obtained by the self-assembly process of layer-by-layer deposition. Water soluble CdTe particles stabilized by a shell of thioglycolic acid are combined with three different polyelectrolytes: poly(ethylenimine) (PEI), poly(allylamine hydrochloride) (PAH), and poly(diallyldimethylammonium chloride) (PDDA). The film build-up is monitored by means of absorption and fluorescence spectroscopy. The electrostatic adsorption of the particle at the polymer surface is strongly determined by the pH value of the particle solution and the chemical structure of the polymer. Polycations with partially unsaturated nitrogen groups exert strong quenching on the particle fluorescence. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Semiconducting nano particles; Self-assembly; Thin organic films

1. Introduction

Nanometer sized crystals (nanocrystals, nanoparticles, or quantum dots) of II–VI semiconductors have attracted increasing interest for their use in electro-optical applications such as photovoltaic [1,2] or electroluminescence devices [3–6]. The promising advantages of these particles are the high photochemical stability and the size dependent optical properties due to quantum confinement effects [7,8]. Therefore, the color of the fluorescence emission of the particles can be tuned over the whole visible spectrum by variation of the mean size.

However, for any application in thin organic film devices, it is necessary to optimize the volume fraction of particles within a polymer matrix and to understand the polymer/particle interactions. Especially for LED devices, a high density of particles has to be achieved when an insulating polymer is used and electron-transfer from the polymer to (or from) the particle should be possible. Additionally, no fluorescence quenching should occur from the chemical nature of the polymer.

It was demonstrated earlier, that the self-assembly technique of layer-by-layer deposition of oppositely charged polyelectrolytes, as invented by Decher [9] and Decher and Hong [10], is a useful tool to prepare films of polymers and inorganic nanoparticles [3,4,6,11]. To obtain acceptable film quality, the charge density of the polyelectrolyte and the surface charge density of the inorganic particle have to be optimized within their mutual solutions [12] with respect to the pH value. Here, we report on the preparation of thin films from water soluble and highly luminescent thioglycolic acid capped CdTe nanoparticles [13] and different polycations.

2. Experimental

The CdTe particles are prepared in water solution by adding NaHTe solution to $Cd(ClO_4)_2 \cdot 6H_2O$ solution saturated with N_2 in the presence of thioglycolic acid (HS–C–COOH).

NaHTe is generated from the reaction of NaOH and H_2Te, which is obtained from the addition of Al_2Te_3 to HCl. More details are described in Refs. [13,14]. Particles with a mean size of approximately 3 to 5 nm are obtained which consist of a CdTe core covered by a CdS shell due to the binding of the thiol groups to the Cd ions as

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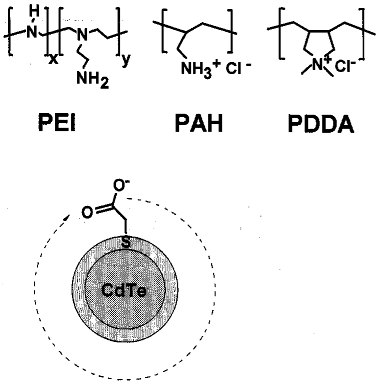

Fig. 1. Principal sketch of the structure of the CdTe particles (not scaled) and the polycations used for film preparation.

indicated in Fig. 1. The carboxyl groups of the thiolactic acid provide a negative surface charge density. If not stated otherwise, the experiments are performed at pH = 6 of the particle solution, adjusted by addition of HCl. The polyelectrolytes are purchased from Aldrich and dissolved in purified water (Millipore). Their chemical structure is shown in Fig. 1. The molecular weight was 750 000 for poly(ethylenimine) (PEI), 50 000–60 000 for poly(allylamine hydrochloride) (PAH), and 200–350 000 for poly(diallyldimethylammonium chloride) (PDDA). The films are prepared on quartz slides which always were initially covered by adsorption of a single layer of PEI. The film preparation was performed following the standard layer-by-layer deposition procedure as invented by Decher and Hong [10]. Each deposition cycle is carried out as follows: dipping into particle solution for 20 min, rinsing with purified water, dipping into polycation solution for 20 min, rinsing with water again; *n* dipping cycles result in *n* 'double layers' of adsorbed material. The concentration of all polyelectrolyte solutions was 10^{-2} mol/l with respect to the monomer concentration. Absorption spectra were recorded in a CARY-5 spectrometer and fluorescence was measured with the help of a Fluorolog 212 spectrometer.

3. Results and discussion

In Fig. 2, the absorption and fluorescence spectra of four CdTe/polymer double layers are shown using three different polycations, PEI, PAH, and PDDA, respectively. In all cases, the films were prepared from fractions of the same CdTe solution with pH adjusted to 6. The absorbance in the spectral range shown here is entirely caused by the particle absorption and therefore reflects the amount of CdTe particles in the film. It can be seen that the largest amount of particles is adsorbed when PEI is used as polycation, while approximately 10 times less material is adsorbed when PAH is used. Similar amount is adsorbed for the case of PDDA as for PEI. However, the fluorescence emission of the particle/PDDA is much more efficient than for the other polymers. This behavior was observed reproducible in a series of experiments.

Obviously, PEI and PAH cause quenching of the particle photoluminescence. Although the reason for this quenching effect is not fully understood at the present time, it seems reasonable to assume that it is caused by primary and secondary amine groups of the PAH or PEI. It is well known that such groups can act as efficient fluorescence quenchers for organic dye molecules by charge transfer of a free electron from the nitrogen to the chromophore [15]. This process is inhibited if the nitrogen is fourfold coordinated, as it is the case for the ammonium groups of PDDA, or for the protonated nitrogen groups of PEI and PAH. Therefore, one has to assume that the polycations PEI and PAH are not fully protonated within the film structure. It is likely that an adsorbed polycation layer becomes partially deprotonated when dipped into the alkaline particle solution. To investigate this effect, we have prepared multilayers using CdTe particle solutions of different pH. In Fig. 3, the absorption and fluorescence spectra of four double layers CdTe/PEI prepared at three different pH values are shown. Less particles are adsorbed at higher pH value of the solution. A similar behavior was observed for all three polyelectrolytes.

Since the adsorption is driven by electrostatic interaction between the species adsorbed at the substrate and the oppositely charged species in the solution, one has to consider the influence of the pH on both parts. The surface charge of the CdTe particles is given by the caboxylic groups of the thiglycolic acid shell. These groups are

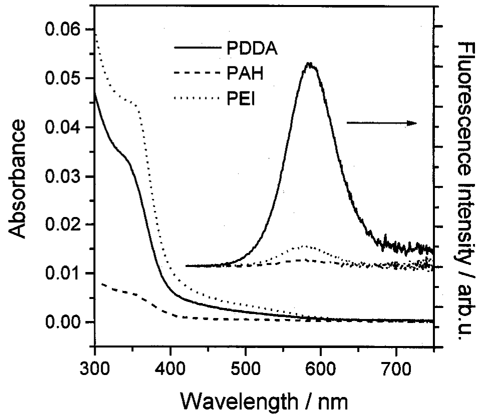

Fig. 2. Absorption and fluorescence spectrum of four double layers of CdTe/polycation, prepared at a pH of 6 of particle solution. Fluorescence excitation was at 400 nm.

highly dissociated at high pH values (alkaline range) and, thus, one would expect increasing attractive interaction with increasing pH, resulting in increasing adsorption of particles. On the other hand, the polycations become less charged in the alkaline range. Therefore, the surface charge density of the last adsorbed polymer layer can be reduced, when it is immersed into CdTe solution of high pH, which leads to reduction of particle adsorption. With respect to this, the amount of adsorbed material would be optimized if the pH value was as low as possible. However, the stability of the colloidal CdTe solution decreases significantly in the acidic range. Therefore, an optimum value of pH = 6 was found for all three polycations investigated here.

In this case, a linear growth of absorbance with the number of dipping cycles was observed. As an example, the spectra recorded after each adsorbed double layer of CdTe and PEI are shown in Fig. 4. The linear growth can be seen from the insert, where the absorption at 350 and 500 nm is plotted against the number of double layers. The photoluminescence quantum yield at room temperature of the particles in CdTe/PDDA samples was determined to be 5%. The latter value has to be compared to the 20% Q.Y. determined in the aqueous solution of the particles [13].

Preliminary X-ray reflectivity measurements demonstrate that the linear increase in absorption is in accordance with a linear growth of film thickness. However, the increase in thickness per dipping cycle is less than the mean diameter of the particles. This is an indication that the particles do not form a closed packing monolayer. A similar effect was observed earlier for CdSe particles [6]. Nevertheless, the method of alternating adsorption of particles and polymers allows the control of film thickness in the range of the particle diameter.

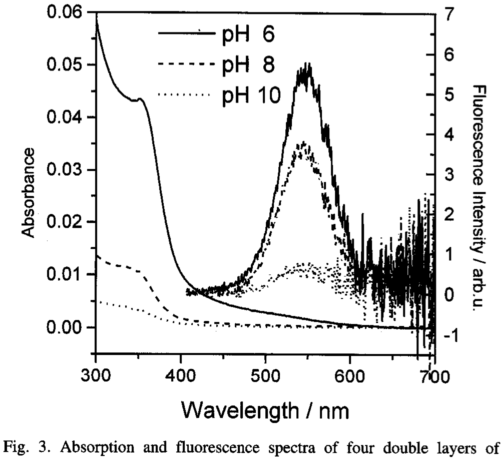

Fig. 3. Absorption and fluorescence spectra of four double layers of CdTe/PDDA prepared from particle solutions with different pH value.

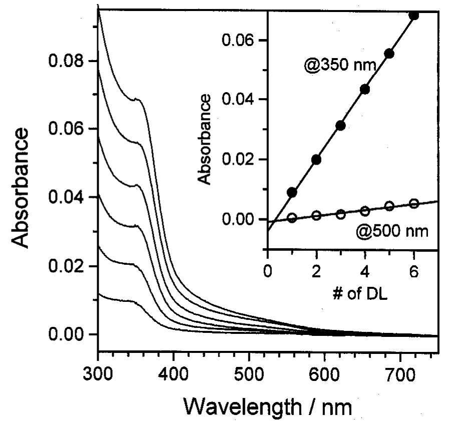

Fig. 4. Absorption spectra of CdTe/PEI measured after each dipping cycle n, for $n = 1, \ldots, 6$. Insert: absorbance at maximum of the shoulder (350 nm) and near the absorption edge (500 nm).

4. Conclusions

It was demonstrated that highly luminescent films can be prepared by the layer-by-layer adsorption technique using thioglycolic acid capped CdTe nanoparticles in combination with PDDA polycations. The adsorption properties as well as the fluorescence yield strongly depend on the coordination of the nitrogen atom within the chemical structure of the polymers and on the pH of the particle solution. The strong fluorescence quenching observed for PEI and PAH indicates that an electron transfer to (or from) the particles may occur from deprotonated nitrogen groups of the polymers. The high fluorescence quantum yield of the particles observed in the film makes them promising for electro-optical applications. This is confirmed by preliminary electroluminescence results obtained from CdTe/PDDA films [16].

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References

[1] Y. Wang, N. Herron, Chem. Phys. Lett. 200 (1992) 71.
[2] N.A. Kotov, I. Dekany, J.H. Fendler, J. Phys. Chem. 99 (1995) 13065.
[3] H. Mattoussi et al., J. Appl. Phys. 83 (1998) 7965.
[4] V. Colvin, M.C. Schlamp, A. Alivisatos, Nature 370 (1994) 354.
[5] M. Gao, B. Richter, S. Kirstein, Adv. Mater. 9 (1997) 802.
[6] M. Gao, B. Richter, S. Kirstein, H. Möhwald, J. Phys. Chem. B 102 (1998) 4096.
[7] L. Brus, J. Chem. Phys. 80 (1984) 4403.
[8] A. Henglein, Ber. Bunsenges. Phys. Chem. 99 (1995) 903.
[9] G. Decher, Science 277 (1997) 1232.
[10] G. Decher, J.-D. Hong, Thin Solid Films 210/211 (1992) 831.
[11] J. Schmitt et al., Adv. Mater. 9 (1997) 61.
[12] D. Yo, S. Shiratori, M. Rubner, Macromolecules 31 (1998) 4309.
[13] M. Gao et al., J. Phys. Chem. B 102 (1998) 8360.
[14] A. Rogach et al., Ber. Bunsenges. Phys. Chem. 100 (1996) 1772.
[15] J. Lakowicz, Principles of Fluorescence Spectroscopy, Plenum, New York, 1983.
[16] M. Gao et al., Manuscript in preparation.