Electrodeposition of Polymer−Semiconductor Nanocomposite Films

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Hybrid polymer−semiconductor nanostructured films were obtained by co-electrodeposition of poly(vinyl acetate-*co*-crotonic acid) and CdS or CdTe nanoparticles (NPs) stabilized with 1-thioglycerol (TGL) or thioglycolic acid (TGA). Composite films were enriched with negatively charged NPs stabilized with TGA. Relative uptake of these NPs increased with electrodeposition time and increase in NP concentration in solution, while the variation in electric field had little effect on NP electrodeposition. No substantial aggregation or NP growth occurred in the electrodeposition process and during film formation. Electrodeposited films showed higher quality and better properties of NPs compared to the cast films obtained from the same solutions. Electrodeposition of hybrid polymer−semiconductor films on patterned substrates was demonstrated.

Introduction

Hybrid polymer−semiconductor nanostructured materials have potential applications in optical and electronic devices: polymers offer low cost, transparency, processability, and easy functionalization, while semiconductor nanoparticles (NPs) show size-dependent band gap shift, excitonic photoluminescence, electroluminescence, and nonlinear optical properties.[1−3] These materials thus show promising applications in light-emitting diodes, optical limiters and switches, optical fibers, and hard transparent coatings used as protective layers or sensors.

All strategies used for the preparation of polymer films doped with semiconductor nanoparticles involve intimate mixing of NPs with the matrix-forming polymer.[4−8,13] Compatibilization of polymers and semiconductor NPs is achieved via in situ synthesis of semiconductor NPs in a polymer matrix,[9] by mixing solutions of polymer and nanoparticles and film casting,[10,11] and by polymerization of a monomer mixed with nanoparticles.[12,13] These methods have been successfully used to produce nanocomposite films without notable aggregation of the NPs. However, casting or spin-coating of such films on fibers, on patterned surfaces, and, in general, on objects with a complicated shape is a challenge, though new technologies are currently emerging (e.g., the use of masks or ink-jet technology[14]).

Here, we report the use of co-electrodeposition of polymers and semiconductor NPs from aqueous solutions as a method of producing hybrid polymer−semiconductor nanocomposite films. Electrodeposition (ED) of polymers is extensively used in coating technologies. This process has at least two important advantages: it produces coatings with a uniform thickness and it allows one to obtain coatings on surfaces with complex shapes. In addition, electrodeposition of polymers is characterized by a high electrical equivalent weight of a coating[15] (by contrast with electrodeposition of metal alloys). Electrodeposition (ED) of submicrometer- and micrometer-size colloid particles has been thoroughly studied.[16,17] Recently, several groups reported the electrophoretic deposition of semiconductor nanoparticles (quantum dots).[18,19] Nanocrystals of ZnO with dimensions from 3.5 to 5.5 nm were electrodeposited from their 2-propanol solution onto the anode surface, yielding smooth and thin semiconductor NP films.[18] After deposition, the NPs retained their size-dependent optical properties due to the quantum confinement effect. Similarly, CdSe nanocrystals were electrodepodeposited from their hexane solution to form several micrometer-thick films.[19] Electrodeposition oc-

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(1) Nirmal, M.; Brus, L. *Acc. Chem. Res.* **1999**, *32*, 407−414.
(2) Klimov, V. I. *J. Phys. Chem. B* **2000**, *104*, 6112−6123.
(3) Eychmueller, A. *J. Phys. Chem. B* **2000**, *104*, 6514−6528.
(4) Musiani, M. *Electrochim. Acta* **2000**, *45*, 3397−3402.
(5) Pomogailo, A. D. *Russ. Chem. Rev.* **2000**, *69*, 53−80.
(6) Huczko, A. *Appl. Phys. A* **2000**, *70*, 365−376.
(7) Beck, F.; Abdelmula, E.; Dahlhau, M. *Electrochim. Acta* **2000**, *45*, 3423−3429.
(8) Gangopadhyay, R.; De, A. *Chem. Mater.* **2000**, *12*, 608−622.
(9) Krishnan, M.; White, J. R.; Fox, M. A.; Bard, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 7002−2003.
(10) Lin, Y.; Zhang, J.; Sargent, E. H.; Kumacheva, E. *J. Mater. Sci.* **2004**, *39*, 993−997.
(11) Mattoussi, H.; Radzilowski, L. H.; Dabbousi, B. O.; Fogg, D. E.; Schrock, R. R.; Thomas, E. L.; Rubner, M. F.; Bawendi, M. G. *J. Appl. Phys.* **1999**, *86*, 4390−4399.
(12) Zhang, H.; Zhanchen, C.; Wang, Y.; Zhang, K.; Xiulei, J.; Changli, L.; Yang, B. *Adv. Mater.* **2003**, *15*, 777−780.
(13) Percy, M. J.; Barthet, C.; Lobb, J. C.; Khan, M. A.; Lascelles, S. F.; Vamvakaki, M.; Armes, S. P. *Langmuir* **2000**, *16*, 6913−6920.
(14) De Gans, B. J.; Schubert, U. S. *Macromol. Rapid Commun.* **2003**, *24*, 659−666.
(15) Bikales, N. M. *Polymer Science and Technology, Vol. 2, Water Soluble Polymers*; Plenum Press: New York, 1973.
(16) Zhitomirsky, I. *Adv. Colloid Interface Sci.* **2002** *9*, 279−317.
(17) Vereecken, P. M.; Shao, I.; Searson, P. C. *J. Electrochem. Soc.* **2000**, *147*, 2572−2575.
(18) Wong, E. M.; Searson, P. C. *App. Phys. Lett.* **1999**, *74*, 2939−2941.
(19) Islam, M. A.; Herman, I. P. *App. Phys. Lett.* **2002**, *80*, 3823−3825.

10.1021/cm049446v CCC: $27.50

curred on both the anode and the cathode, which was explained by the presence in the solution of the positively and negatively charged nanoparticles. When dried, films of CdSe NPs featured small cracks. Recently, this method has been improved to yield smoother films with high stability in various solvents.[20]

Co-electrodeposition of polymers and semiconductor NPs can substantially improve the mechanical and some of the optical properties of films. Since electrodeposition of water-soluble polymers and colloid particles is driven by different mechanisms,[21−23] the resulting structure and properties of the nanocomposite films are not obvious. Moreover, it is important to preserve the optical properties of NPs (e.g., their photoluminescence) upon their electrodeposition-driven transfer into a hybrid film. Here, we examined the dependence of composition, morphology, and optical properties of polymer−semiconductor films on ED conditions. We also compared the properties of the electrodeposited and cast films obtained from the same original polymer−semiconductor NP solutions. Finally, we demonstrated the possibility of electrodeposition of hybrid polymer−semiconductor nanocomposite films on patterned conductive surfaces and wires.

Experimental Section

All chemicals were purchased from Aldrich Canada. Poly(vinyl acetate-*co*-crotonic acid) with a molar ratio of crotonic acid/vinyl acetate = 1/9 and M_n=18 750, M_w = 33 560 was added into deionized water (Millipore Milli-Q) to a concentration of 10 wt %. The value of pH of this system was adjusted to pH = 8.0 by triethylamine (ACP Montreal, Canada) to deprotonate the carboxylic groups of the polymer and produce its water-soluble salt.

Semiconductor CdS and CdTe nanocrystals were synthesized in aqueous solutions following the method of Rogach et al.[24] We used 1-thioglycerol (TGL) or thioglycolic acid (TGA) as the capping ligands. In a typical reaction, 4.06 mmol of $Cd(ClO_4)_2 \cdot 6H_2O$ was dissolved in 100 mL of water. Then, 9.7 mmol of the stabilizer (TGL or TGA) was added to this solution under stirring. The value of pH was adjusted to 10.0 by dropwise addition of a 1 M aqueous solution of NaOH. Then, 4.06 mL of 0.5 M Na_2S or NaHTe solution was introduced into the system under stirring to obtain CdS or CdTe NPs. The reaction mixture was refluxed for 8 ± 2 h. The solution of NPs was dialyzed against deionized water for 48 h before its addition to the polymer solution. The electrokinetic potential (ζ-potential) of TGA- and TGL-stabilized nanoparticles was −38.0 and −25.2 mV, respectively, at pH = 7.5 ± 0.5.

The polyelectrolyte−nanoparticle aqueous solution used for electrodeposition contained 7 wt % of poly(vinyl acetate-*co*-crotonic acid), 8 wt % of 2-propanol (used as plasticizer), and from 84.65 to 84.98 wt % of water. Nanoparticle concentration was varied from 0.02 to 0.35 wt %. A higher concentration of nanoparticles in the aqueous solution led to a decrease in film transparency. Composite coatings were electrodeposited at pH = 8 ± 0.2 onto glass slides (2.5 cm × 0.8 cm × 0.7 mm) coated with indium−tin oxide (ITO) (Delta Technologies, Serial Number CG-41IN-S107). A stainless steel plate (2.5 cm × 0.8 cm × 2.0 mm) was used as a cathode. Prior to deposition, the electrodes were washed with acetone and then with deionized water.

We found that composite coatings had craterlike defects when the current density exceeded 1 mA/cm^2. To suppress the formation of defects, the voltage was increased gradually to achieve the required value within 2−3 min after the beginning of electrodeposition. Then, the deposition process was carried out in a potentiostatic mode. The distance between the electrodes was 5.0 mm; the applied voltage and the deposition time varied from 5 to 20 V and from 5 to 275 min, respectively. After electrodeposition was complete, the coatings were washed with deionized water and heat processed at 100 °C for 30 min.

The thickness of the coating electrodeposited onto the ITO−glass electrode was obtained from the interference pattern in the absorption spectrum of the film using a modified Fabry−Perot equation,[25]

$$L = \frac{\lambda_1 \lambda_2}{(\lambda_1 - \lambda_2)} \frac{1}{2 n_{\mathrm{eff}}}$$

where L is the thickness of the film, λ_1 and λ_2 are the two consecutive maxima in the interference pattern, and n_{eff} is the effective refractive index of the film. An interference pattern was acquired in the spectral range from 450 to 500 nm (at a wavelength longer than the absorption band of the NPs used). Film thickness varied in the range from 5 to 20 μm, depending on the electric field and ED time.

Absorption properties of semiconductor nanoparticles in solutions and in composite films were measured using a Cary-5000 UV−vis−NIR spectrophotometer. Photoluminescence properties of the NPs were examined using a Perkin-Elmer LS-50B luminescence spectrophotometer and a PTI spectrometer. The excitation wavelengths were 375 and 400 nm for CdS and CdTe nanoparticles, respectively.

To examine the cross-sectional morphology of the electrodeposited films, first, a several nanometers thick layer of gold was sputtered on the surface of the epoxy resin coating. Then, a composite polymer−semiconductor film was electrodeposited onto the gold surface, and the second layer of epoxy-resin was applied onto the top of the polymer−semiconductor film. The sandwichlike film was cured at 60 °C for 24 h. Then, ca. 100-nm-thick slices of the composite film were ultramicrotomed from the "sandwich" at room temperature in the direction normal to the film plane. The morphology of the films was studied by transmission electron microscopy (TEM) using a JEOL 1210 electron microscope operating at 75 kV.

The weight ratio (X_f) of the nanoparticles/polymer in electrodeposited films was determined by the atomic absorption (AA) technique (Analyst 100 AAS atomic absorption spectrometer). The relative nanoparticle uptake was determined as the value of X_f/X_S, where X_S is the NPs/polymer weight ratio in the solution.

Hybrid polymer−CdTe films were electrodeposited on patterned substrates. The surface of ITO−glass was patterned with a negative photoresist (SU-8 2000).[26] The composites were electrodeposited at 20 V/cm for 45 min. Fluorescence optical microscopy images were taken using the Olympus BX51 microscope equipped with a CCD camera (Photometrics CoolSnap ES). A filter cube with excitation from 460 to 500 nm and emission from 515 to 560 nm was used.

Results and Discussion

In the first step, we examined polymer co-electrodeposition with negatively charged NPs stabilized with TGA and with neutral or weakly negatively charged NPs stabilized with TGL.[27] (In a strongly basic medium, the negative charge of the TGL-stabilized NPs can originate

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(20) Islam, M. A.; Xia, Y.; Telesca, D. A.; Steigerwald, M. L.; Herman, I. P. *Chem. Mater.* **2004**, *16*, 49−54.

(21) (a) Koelmans, H.; Overbeek, J. T. G. *Discuss. Faraday Soc.* **1954**, *18*, 52−63. (b) Hamaker, H. G.; Verway, E. V. W. *Trans. Faraday Soc.* **1940**, *36*, 180−185.

(22) Shane, M.; Talbot, J.; Schreiber, R.; Ross, C.; Sluzky, E.; Hesse, K. *J. Colloid Interface Sci.* **1994**, *165*, 325−333.

(23) Shane, M.; Talbot, J.; Kinney, B.; Sluzky, E.; Hesse, K. *J. Colloid Interface Sci.* **1994**, *165*, 334−340.

(24) Rogach, A. L.; Katsikas, L.; Kornowski, A.; Dangsheng, S.; Eychmueller, A.; Weller, H. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 1772−1778.

(25) Reculusa, S.; Ravain, S. *Chem. Mater.* **2003**, *15*, 598−605.

(26) MICROCHEM Instruction manual. URL: http://www.microchem.com/products/pdf/SU8_2002−2025.pdf

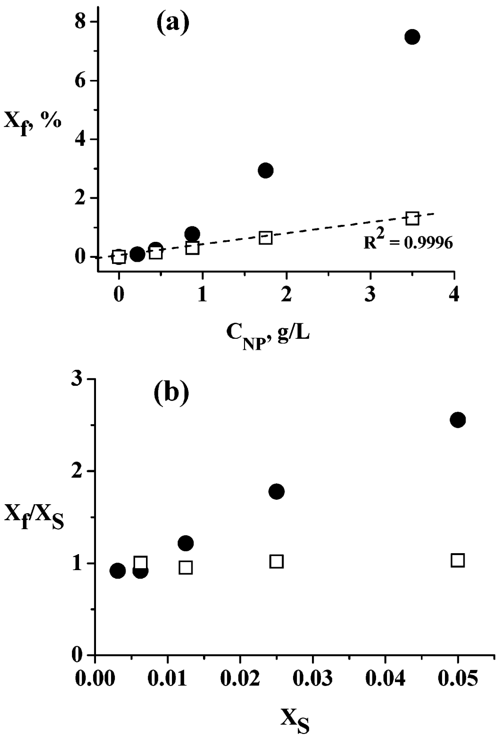

Figure 1. (a) Variation in the weight ratio CdS nanoparticles/polymer in the electrodeposited film versus NP concentration in solution and (b) variation in the relative uptake (see text) with the weight ratio CdS nanoparticles/polymer in solution for nanoparticles stabilized with TGL (hollow squares) and TGA (filled circles). Electrodeposition time and applied electric field were 30 min and 20 V/cm, respectively.

from the deprotonation of the alcohol groups of the stabilizer).[28]

Figure 1 shows the dependence of NP concentration in the composite film as a function of CdS concentration in solution. In Figure 1a, the uptake of CdS nanocrystals stabilized with TGL (hollow squares) increased linearly with the increase in concentration of NPs in the electrodeposition chamber. The relative uptake of these nanoparticles (Figure 1b, hollow squares), however, did not change with the ratio of the NP/polymer in solution. These results indicated that NPs stabilized with TGL were trapped in the composite film by the polymer loosing its solubility in the acidic near-to-electrode zone. Such codeposition was not charge-specific and, in principle, could be conducted by codeposition of polymers with NPs that are neutral or even charged similarly to the electrode to be coated.

In contrast, the fraction of CdS NPs stabilized with TGA abruptly increased when their concentration in the electrodeposition chamber was increased (Figure 1a, solid circles). In Figure 1b, the relative uptake of these NPs by the film increased almost linearly with CdS/polymer weight ratio in the chamber. For $X_S > 0.015$, the electrodeposited films were enriched with CdS NPs; that is, the NP/polymer weight ratio was higher than in the solution. On the basis of these results, we conclude that the formation of the composite films occurred via the competition between the electrodeposition of NPs and the polymer. We also note that the transparency of the composite films was reduced when the relative uptake of CdS NPs exceeded 2.5. Similar results were obtained for the co-electrodeposition of CdTe NPs.

Figure 2a,b shows typical TEM images of hybrid electrodeposited films. Image analysis yielded an average size of ca. 3 nm for the individual CdS and CdTe NPs, similar to their dimensions in polymer solutions. Imaging of the composite films with a relative uptake of nanoparticles $X_f/X_S > 2.5$ indicated that the decrease in film transparency resulted from the formation of NP clusters (and hence light scattering). The size of clusters varied from 20 to 100 nm. Nevertheless, as shown in the inset to Figure 2a, individual CdS NPs in these aggregates were separated from each other by the well-resolved gaps.

Figure 2c shows UV–vis spectra of CdS NPs stabilized with TGL and TGA in polymer solutions and in electrodeposited films (dotted and solid lines, respectively). A blue shift in absorption of TGL-stabilized NPs (λ_{abs} = 373 nm) compared to TGA-stabilized NPs (λ_{abs} = 403 nm), both in solutions, was observed and attributed to the smaller size of the former nanoparticles. More importantly, no red shift in absorption was observed for both types of NPs following their co-electrodeposition with the polymer. This result suggested that NP properties during electrodeposition and film formation were well-preserved. In contrast to CdS nanocrystals, absorption of electrodeposited CdTe NPs stabilized with TGA was blue-shifted from 561 to 554 nm compared to their absorption in aqueous solution. The reason for this effect is discussed later.

We used CdS nanoparticles stabilized with TGA to study the effect of electrodeposition time and the electric field on NP deposition. Figure 3a shows a gradual increase in concentration of CdS NPs in the composite film when electrodeposition time increased, with a maximum NP/polymer weight ratio of 7.5 wt %. Electrodeposition of NPs was governed by the increase in concentration of electrolyte (due to electrolysis of water) in the near-to-electrode zone causing coagulation of nanoparticles[21a] and/or by electrocoagulation of NPs delivered to the electrode surface by the electric field.[21b] In both mechanisms, an increase in time favored particle deposition on the electrode. A weak increase in NP concentration after 10 min of deposition (Figure 3a) was caused by the retardation time required to accumulate a critical concentration of electrolyte and NPs in the near-to-electrode zone to cause nanoparticle coagulation.

In contrast, an increase in electrodeposition voltage for the deposition time of 30 min showed insignificant effect on NP weight fraction in polymer films: in Figure 3b in the potentiostatic mode, an increase in the electric field from 10 to 40 V/cm did not notably change NP concentration in the film, which remained at 0.7 ± 0.05. This effect was not expected, since both electrochemical and accumulative mechanisms[21] predict that an increase in electric field leads to more efficient deposition from particle dispersions. Nanoparticle uptake by the film was presumably not enhanced because of the competition between polymer and NP electrodeposition.

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(27) Gaponik, N.; Talapin, D. V.; Rogach, A. L.; Hoppe, K.; Shevchenko, E. V.; Kornowski, A.; Eychmueller, A.; Weller, H. *J. Phys. Chem. B* **2002**, *106*, 7177–7185.

(28) Rogach, A. L.; Kotov, N. A.; Koktysh, D. S.; Susha, A. S.; Caruso, F. *Colloid Surf., A: Physicochem. Eng. Aspects* **2002**, *202*, 135–144.

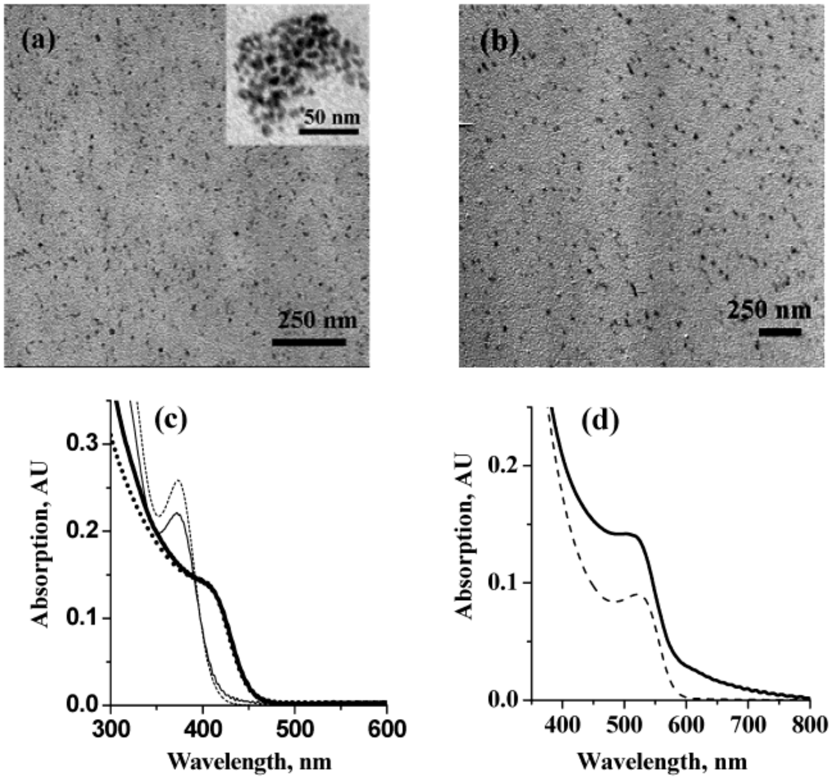

Figure 2. (a) Low resolution and high resolution (inset) (scale bar 50 nm) typical TEM images of CdS−polymer composite films deposited. (b) TEM image of CdTe−polymer composite film deposited. (c) Absorption spectra of TGL-stabilized CdS NPs in solution (thin dashed line) and in nanocomposite (thin solid line), and TGA-stabilized CdS NPs in solution (thick dashed line) and in electrodeposited film (thick solid line). $X_f = 3$ wt %. (d) Absorption spectra of CdTe NPs in solution (dashed line) and in composite film (solid line). Electrodeposition was conducted at 20 V/cm for 30 min and $X_S = 0.014$.

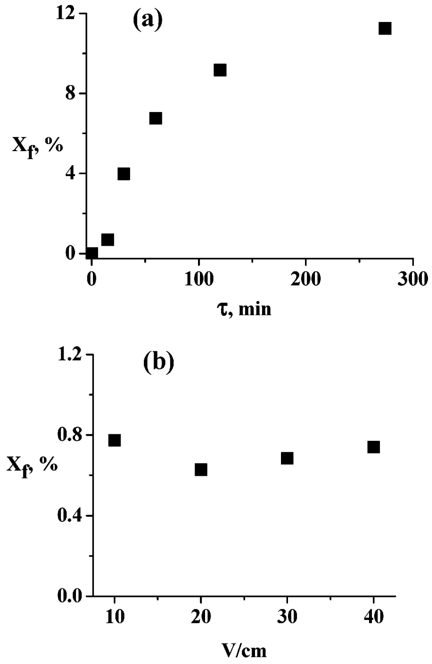

Figure 3. Variation in NP weight fraction in composite film versus (a) electrodeposition time (electric field is 20 V/cm) and (b) electric field (deposition time is 30 min). CdS NPs were stabilized with TGA; $X_S = 0.014$.

An increase in electric field resulted in a higher concentration of H^+ ions next to the anode surface affecting coagulation of both poly(vinyl acetate-*co*-crotonic acid) and CdS nanoparticles.

We note that an electrodeposition voltage higher than 22.5 ± 2.5 V led to the craterlike holes in the film. The number of such defects, however, was a function of NP concentration in solution.

To explain the dependence of NP uptake on time, we note that although both the polymer and the NPs are negatively charged, their electrodeposition occurs via different mechanisms. Rapid polyelectrolyte deposition on the electrode surface occurs because of the loss in polymer solubility in the acidic near-to-electrode zone. Electrodeposition of NPs occurs via the electrocoagulation process, which is substantially slower than polymer deposition. The competition between these processes led to the increase in NP uptake with time.

We further examined the optical properties of the composite films by measuring the photoluminescence (PL) of NPs in hybrid films and comparing them with the PL of the same NPs in polymer solution. The composite films were obtained by co-electrodepositing the polymer and CdTe NPs capped with TGA. In Figure 4 the PL peak of CdTe NPs in the electrodeposited film became broader and it was blue-shifted compared to PL wavelength for the NPs in solution (=554 and 561 nm, respectively). Broadening and the blue shift of PL of CdTe NPs in nanocomposite films was explained by the oxidation of the surface of nanoparticles.[29] This process resulted in a decrease of the average size of nanoparticles. We also note that the second PL peak at $\lambda = 700$ nm appeared for CdTe NPs in the composite film, attributed to the radiative recombination of electrons

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(29) Alivisatos, A. P. J. *Phys. Chem.* **1996**, *100*, 13226−13239.

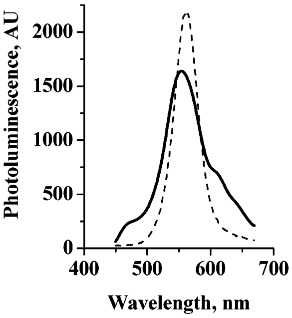

Figure 4. Photoluminescence spectra of TGA-stabilized CdTe nanoparticles in solution (- - -) and electrodeposited composite films (—). Electric field is 20 V/cm, deposition time is 30 min, and $X_S = 0.014$.

and holes in surface defects of the NPs: in water the surface of NPs was passivated, while when water was removed the surface of CdTe nanocrystals oxidized, giving rise to trap emission.[30]

We also compared the optical properties of composite films obtained by electrodeposition and casting and found the former to have several advantages. Visual inspection of cast films revealed their inferior transparency in comparison with electrodeposited films (though NP concentration in electrodeposited films was slightly higher). TEM imaging revealed that the loss in transparency of cast films originated from the formation of large NP clusters that were formed during water evaporation. In addition, transparency of cast films was reduced due to light scattering by the pores formed during water evaporation. In contrast, because of electroosmosis, electrodeposited films contained a low amount of water and thus showed no evidence of such pores. Figure 5a,b shows absorption and PL spectra of CdTe NPs embedded in cast and electrodeposited films (dotted and solid lines, respectively). Absorption and PL shoulders were blue-shifted for the NPs in cast films, possibly due to the diffusion of oxygen through the film pores, which facilitated faster NP oxidation.[29]

We accomplished selective (site-specific) electrodeposition by codepositing CdTe NPs and poly(vinyl acetate-*co*-crotonic acid) onto the patterned anode surface. ITO-coated glass was patterned in two ways. First, the entire surface was insulated with a ca. 1.0 μm-thick photoresist, leaving a small area (the letters “U of T”) conductive. Figure 6a shows a fluorescent microscopy image of the patterned film obtained by co-electrodeposition of CdTe NPs and polymer. The thickness of bright lines is 40 μm, close to that in a photoresist. In the second experiment, the surface of ITO-coated glass was left conductive while a small fragment (the letters “U of T”) was insulated. In Figure 6b the surface of the anode is coated with a hybrid fluorescent film (bright background), whereas the insulated area remains dark. Furthermore, Figure 6c shows an optical fluorescence micrograph of a 100-μm-thick copper wire coated with an electrodeposited CdTe—polymer film. The film thickness of ca. 10 μm and fluorescence intensity were uniform through the entire wire length of 6 cm.

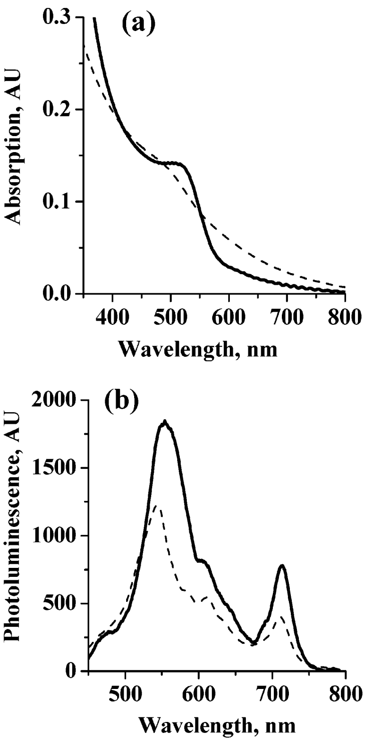

Figure 5. Absorption (a) and photoluminescence spectra (b) of TGA-stabilized CdTe nanocrystals in electrodeposited (—) and cast films (- - -). The same NC solution was used for casting and electrodeposition at $X_S = 0.014$. Electric field is 20 V/cm and time is 30 min.

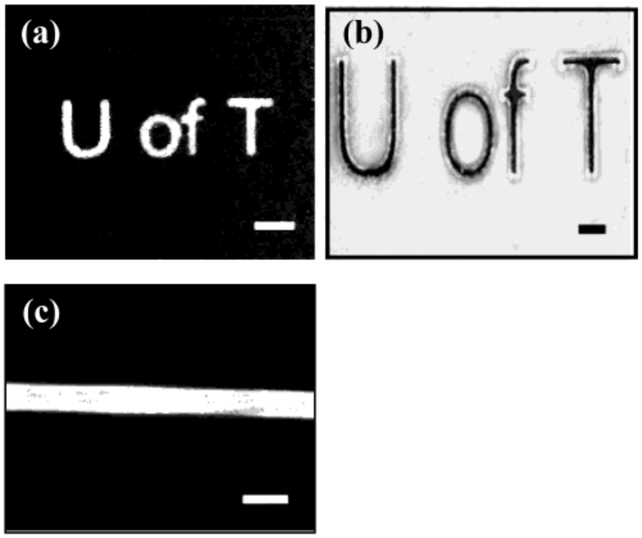

Figure 6. Fluorescence optical microscopy images of nanostructured films obtained by co-electrodeposition of CdTe NPs and poly(vinyl acetate-*co*-crotonic acid) on patterned ITO-coated glass: (a) the surface of anode was insulated with a photoresist leaving the letters “U of T” conductive; (b) the letters “U of T” were insulated leaving the surface of anode conductive. Image c is taken from the surface of a 100 μm-thick copper wire coated with electrodeposited CdTe—polymer film. Electrodeposition conditions: electric field 20 V/cm, time 40 min, and $X_S = 0.014$. Scale bar is 200 μm.

In summary, nanostructured films were obtained by co-electrodeposition of semiconductor NPs and poly(vinyl acetate-*co*-crotonic acid) from their aqueous solutions. Relative uptake of negatively charged nanoparticles increased with electrodeposition time and increase in NP concentration in solution. Composite electrodeposited films were enriched with NPs. No evidence was observed on the variation of NP uptake with change in

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(30) Wuister, S. F.; Swart, I.; Dreil, F.; Hichey, S. G.; Donega, C. *Nano Lett.* **2003**, *3*, 503—507.

electrodeposition voltage. TEM images and comparison of absorption spectra of NPs in solutions and in films indicate that no aggregation or particle growth occurred during electrodeposition and film formation. In comparison with cast films, electrodeposited films showed higher quality and better properties of NPs. Finally, we demonstrated electrodeposition of hybrid semiconductor films on patterned substrates.

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