NANO LETTERS

2003
Vol. 3, No. 11
1603−1606

Addition, Suppression, and Inhibition in the Electrophoretic Deposition of Nanocrystal Mixture Films for CdSe Nanocrystals with γ-Fe_2O_3 and Au Nanocrystals

Mohammad A. Islam, Yuqi Xia, Michael L. Steigerwald, Ming Yin, Zhen Liu, Stephen O'Brien, Rastislav Levicky, and Irving P. Herman*

Materials Research Science and Engineering Center, Columbia University,
New York, New York 10027

Received August 8, 2003; Revised Manuscript Received September 18, 2003

ABSTRACT

Electrophoretic deposition from mixtures of CdSe and γ-Fe_2O_3 nanocrystals forms identical films on the positive and negative electrodes composed of both types of nanocrystals. In contrast, the electrophoretic deposition from mixtures of CdSe and Au nanocrystals forms films composed of only CdSe nanocrystals, and these films form only on the positive electrode. As the density of charged Au dots is decreased below that of charged CdSe dots, the suppression of CdSe dot film formation on the negative electrode lessens, and films composed of CdSe nanocrystals form on both electrodes.

The importance of films composed of different nanocomponents is being increasingly recognized because they can have intriguing multifunctional properties that can be tailored and tuned. For example, nonmagnetic, semiconductor nanocrystals with an optical band gap determined by dot size, such as CdSe dots, can be mixed with magnetic nanocrystals, such as γ-Fe_2O_3 (maghemite) dots, to form a novel magnetooptic material. Although mixtures of different types of nanocrystals can be formed by dry casting or spin casting, such thick films usually have poor properties, even when cast from a single type of nanocrystal, and are usually very rough. Under carefully controlled conditions, dry casting can form ordered multilayers of nanocrystals composed of one type of nanocrystal,[1] two sizes of the same type of nanocrystals,[2] and two different types of nanocrystals (of different sizes).[2,3]

We recently showed that patterned and unpatterned CdSe nanocrystal films of controlled thickness can be fabricated by electrophoretic deposition from solutions of ~3 nm diameter CdSe nanocrystals capped by TOPO (trioctylphosphine oxide) ligands (CdSe/TOPO) in hexane by using uniform dc electric fields.[4] Identical ~0.5 μm-thick films deposited on both the positive and negative electrodes, which do not redissolve in the hexane solvent. Films composed of dots reprecipitated after synthesis were found to be very smooth, with ~2 nm rms roughness, and films treated with a solution with linker molecules did not dissolve in many reactive solvents.[5] It is shown here that very different types of films result from the electrophoretic deposition process when another type of nanocrystal is added to the CdSe/TOPO dot solution. The added dot can either be incorporated into the film (added γ-Fe_2O_3/oleic acid dots) or not be incorporated into the film and, in fact, suppress or inhibit the deposition of the CdSe dots on one of the electrodes (added Au/dodecanethiol dots).

CdSe nanocrystals of diameter ~3.4 nm capped by TOPO (and TOP, trioctylphosphine) were synthesized by the wet chemical methods of Murray et al.[6] and Peng et al.[7] After the synthesis, the nanocrystals were treated as described in ref 5. γ-Fe_2O_3 nanocrystals with 12 nm diameter and capped by oleic acid were prepared by the wet chemical method of Hyeon et al.[8] Au nanocrystals with 2.3 nm diameter capped by dodecanethiol were prepared following Brust et al.[9]

In the electrophoretic deposition, a pair of parallel plate electrodes (150 nm thick Au-on 10 nm Ti-on Si (100)) of lateral dimension ~2 cm and separated by ~2 mm were submerged in nanocrystal/hexane solution in a beaker, and high dc voltage (530 V) was applied across them in a dark room at room temperature.[4] Alternatively, 100 nm thick ITO-on-glass electrodes were used for transmission and XPS

---

* Corresponding author. E-mail: iph1@columbia.edu.

10.1021/nl034634q CCC: $25.00

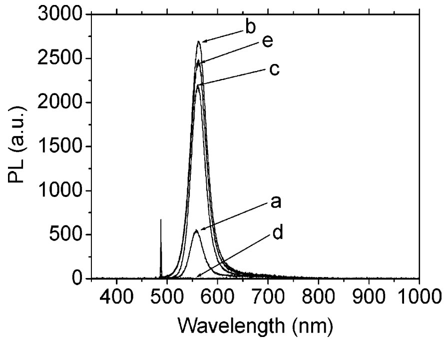

Figure 1. PL of a (a) CdSe nanocrystal solution (3.1×10^{14} dots/cc in each case) and of the electrophoretically deposited films using a (b) CdSe dot solution, formed on the positive electrode; CdSe dot/Au dot (4×10^{13} dots/cc) solution, formed on the (c) positive and (d) negative electrodes; and (e) CdSe dot/γ-Fe_2O_3 dot (5.2×10^{12} dots/cc) solution, formed on the positive electrode, excited by the 488 nm line from an argon-ion laser.

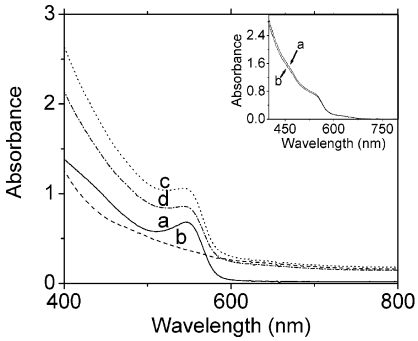

Figure 2. Transmission spectra of (a) CdSe dot (3.1×10^{14} dots/cc) and (b) γ-Fe_2O_3 dot (5.2×10^{12} dots/cc) solutions, and a solution of a mixture of CdSe and γ-Fe_2O_3 dots, initially at these densities (c) before and (d) after deposition (8 mm path length). The inset shows the transmission spectra of the mixed film of CdSe and γ-Fe_2O_3 dots on the (a) positive and (b) negative ITO-on-glass electrodes.

measurements. The film current was monitored during deposition and the films were analyzed after removal from the beaker.

First the electrophoretic deposition from single component solutions of each of these three types of nanocrystals in hexane was investigated. With the CdSe dot solution, identical, smooth films of CdSe nanocrystals formed on both Au electrodes (~2 nm rms roughness for ~515 nm thick films, 3.1×10^{14} dots/cc solution, 20 min), with photoluminescence (PL) showing the film was composed of CdSe dots (Figure 1).[4] Thicker films formed with longer deposition times, limited by the concomitant loss of dots in solution, and underwent fracture for very thick films (thicker than those formed here). With the γ-Fe_2O_3 dot solution, similar films composed of γ-Fe_2O_3 nanocrystals formed on both electrodes. These films were rougher, ~15 nm roughness for 130 nm thick films (5.2×10^{12} dots/cc solution, 20 min), in part due to the larger dot size. (In longer runs, film thickness was limited to ~200 nm, with most of the dots remaining in solution.) For both cases, the fraction of dots deposited was roughly the same when determined by either the film thickness − assuming a dense packing fraction 0.74 of the films by the dots (~18% for CdSe dots and ~8.6% for γ-Fe_2O_3 dots) − or by the loss of dots in solution, as measured by visible/ultraviolet transmission (~26% and ~13% respectively) (initial transmission spectra in Figure 2). This gives a ratio of the time-averaged total deposition rates of γ-Fe_2O_3 and CdSe dots of 0.0080 for these conditions, and of ~0.48 (from the film thickness) for these total rates normalized by the respective initial dot densities. In contrast, deposits were not seen on either electrode with Au dots in hexane, as determined by transmission and X-ray photoelectron spectroscopy (XPS) (for deposition on ITO electrodes). (There have been reports of electrophoretic deposition of Au dots in water.[10])

The initial conductivity σ of these dot solutions was determined from the dc current (Figure 3), by using $\sigma_{\text{measured}} = J/E$, where J is the current density and E is the applied field. This was analyzed using the Einstein−Nernst equation: $\sigma_{\text{calculated}} = n_{\text{charged}}e^2/6\pi\eta R$, where n_{charged} is the density of charged spheres, η is the viscosity of the solvent (3.26×10^{-4} N s/m^2), and R is the hydrodynamic radius of the spheres (2.25 nm for 3.4 nm core diameter CdSe dots with a 1.1 nm TOPO cap, 7.1 nm for 12 nm core diameter γ-Fe_2O_3 dots with a 2.2 nm oleic acid cap, and 1.8 nm for 2.3 nm core diameter Au dots with a 1.3 nm dodecanethiol cap)[11]. By comparing σ_{measured} with $\sigma_{\text{calculated}}$, 0.23% of the CdSe dots, 10.4% of the γ-Fe_2O_3 dots, and 9.4% of the Au dots were initially charged, if there were no other ions in the dot solution.[4,12,13] This gives a ratio of the time-averaged deposition rates of γ-Fe_2O_3 and CdSe dots of 0.0106, when the total rates are normalized by the respective initial charged dot densities. The formation of films with the same thickness on both electrodes for CdSe dots only[4] and γ-Fe_2O_3 dots only, suggests that there are equal densities of positively and negatively charged dots in solution for each.

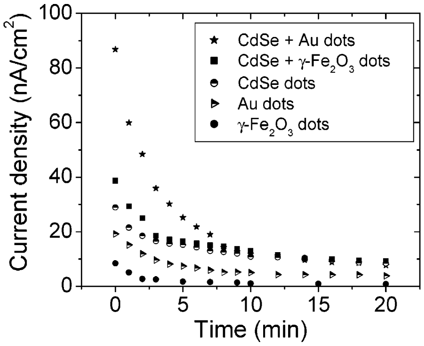

Figure 3. Time dependence of the dc current density during the electrophoretic deposition of CdSe (3.1×10^{14} dots/cc), γ-Fe_2O_3 (5.2×10^{12} dots/cc) and Au (2.4×10^{13} dots/cc) nanocrystals, and of mixtures of CdSe and γ-Fe_2O_3 or Au nanocrystals, with these same densities.

The current decreased with time during each single component deposition (Figure 3) due to the loss of dots in solution from deposition and possible slow thermal recharging of the dots, slow dot diffusion into the electrode region, and the increasing resistance of the deposited film. About 10× more CdSe dots were deposited than elementary charges collected.[4] About 1.03 γ-Fe_2O_3 dots were deposited for each elementary charge collected.

Electrophoretic deposition from a mixture of CdSe and γ-Fe_2O_3 dots, with the same concentrations as above, resulted in films composed of both dots on both electrodes. The mixed films on both electrodes appeared to be identical, 580 nm thick (20 min run, 22 nm rms roughness), with the same visible/ultraviolet transmission spectra (Figure 2 inset). The current during electrophoretic deposition for the mixture was the sum of those for the individual dot solutions (Figure 3). Energy dispersive analysis (EDX) determined a Cd/Se/Fe ratio of about 1.0:0.96:1.28 in these films. Changes in the visible/ultraviolet transmission spectra of the dot solutions during deposition (Figure 2) suggested ~19% of the CdSe dots and ~19% of the γ-Fe_2O_3 dots deposited in 20 min. With an estimated ~415 Cd and ~415 Se atoms per CdSe dot and 33,000 Fe atoms per γ-Fe_2O_3 dot, this suggests a Cd/Se/Fe ratio of about 1.0:1.0:1.33 in the films. If the rates of deposition of each dot in the mixed film were the same as for the single component films, one would expect a ratio of 1.0:1.0:0.64 from the thickness measurements and 1.0: 1.0:0.67 from the transmission experiments, or smaller Fe/ Cd ratios than measured for the mixed dot film. Part of this difference may be due to large uncertainties in the calculation due to packing fractions, errors in the dot dimensions and number of atoms in the dots, and uncertainties in the absorption measurements. Some of it could arise from a depressed time-averaged rate of CdSe dot deposition (19%/ 26% = 0.73×) and/or enhanced time-averaged rate of γ-Fe_2O_3 dot deposition (19%/13% = 1.46×) for the mixture, which could be related to the different resistances of the deposited films.

The mixed film thickness (580 nm) is a bit smaller than the sum of the single component film thicknesses (515 nm for CdSe dots + 130 nm for γ-Fe_2O_3 dots = 645 nm). This would not be inconsistent with the same dot deposition rates in the single component and mixed dot films if there were denser packing, with some of the smaller CdSe dots fitting in the interstitial regions between the larger γ-Fe_2O_3 dots. It is also consistent with the somewhat changed time-averaged deposition rates in the mixed dot films (0.73 × 515 nm for CdSe dots + 1.46 × 130 nm for γ-Fe_2O_3 dots = 566 nm).

In summary, the films formed from the CdSe dot/γ-Fe_2O_3 dot mixture consist of mixtures of these nanocrystals in very rough proportion to that expected for the deposition of each dot individually, and as such the deposition is additive.

In contrast, electrophoresis using mixtures of CdSe dots (3.1×10^{14} dots/cc) and Au dots (2.4×10^{13} dots/cc) in hexane produced films only on the positive electrode; this was seen for both Au and ITO film electrodes. PL analysis showed the presence of CdSe nanocrystals in these films (Figure 1). EDX, probing the entire film thickness, and XPS, probing only near the surface, showed the presence of Cd and Se, but no Au, for films deposited on the positive ITO electrodes, so this film seemed to be composed of only CdSe/ TOPO dots.

Figure 4 shows that when the density of Au dots in solution was decreased the thickness of the film on the positive electrode did not change. Moreover, no film formed on the negative electrode, as detectable by PL (Figure 1) and EDX, until the initial density of Au dots decreased below 1.5% of that of the CdSe dots. As this density approached zero, the thickness of the film on the negative electrode approached that on the positive electrode. Again, the PL spectra suggested that this film was composed of CdSe dots. This transition to film formation on the negative electrode occurred for a total Au dot density ~1.2%× the total CdSe dot density. Assuming that all of the current was due to nanocrystals (and not other ions), the density of *charged* Au dots was ~0.5× that of *charged* CdSe dots at this transition, and so within the uncertainties they were roughly equal.

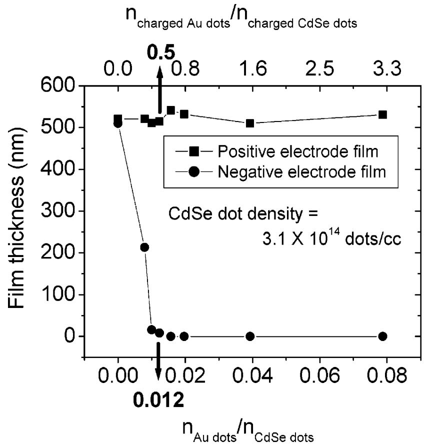

Figure 4. Thickness of the CdSe dot film as a function of Au dot density with constant CdSe dot density, expressed as the ratios of the Au dot and CdSe dot densities, and of the charged Au dot and charged CdSe dot densities. The arrows denote the onset of CdSe dot formation on the negative electrode.

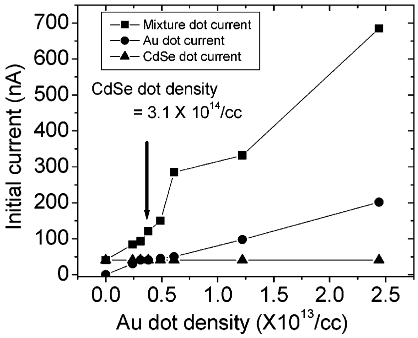

Figure 5. The initial dc current during electrophoretic deposition from mixtures of CdSe and Au dots as a function of Au dot density for constant CdSe dot density. The arrow corresponds to the transition region densities marked by the arrows in Figure 4.

The initial current during electrophoretic deposition for this mixture was much greater than the sum for the individual dots, as seen in Figure 5, which shows the current as the Au dot density was changed. Similar results were seen as the CdSe dot density was changed (not shown).

Nanocrystal charging, transport of dots to the film surface, transfer of charge from the dot to and through the film, and adhesion of the neutralized dot to the growing film are all important in electrophoretic film formation. Each of these can be influenced by the core of the nanocrystal and by the capping ligands on the core and those that dissolve in the solution.

A fraction of the CdSe dots are charged in hexane. When charged CdSe dots hit the electrodes, there is charge transfer and dot adhesion resulting from direct chemical bonding between the dot and the electrode surface − since dots do not stick with no electric field. Because the TOPO ligands are monodentate (as are oleic acid and dodecanethiol) they cannot bind to both the dot and the surface and be the agents of adhesion, and so some of the ligands must be removed for dots to stick. Adhesion of both CdSe/TOPO and γ-Fe_2O_3/oleic acid dots occurs when bare spots on the dots encounter the electrode surface. The dissociation of TOPO or oleic acid from the dot surface may be mediated by the collision of the charged dot with the electrode, but there is no direct evidence for this. (Some bare spots may also result from the reprecipitation of the dots after synthesis.[5])

Au dots might not deposit on either electrode because the thiol ligand is bound so strongly to the Au surface that no bare spots on the dot can be formed. The Au−S bond is quite strong, so its homolytic cleavage to give two neutral species is unlikely. Heterolytic cleavage to give a positive Au dot and negative thiolate anion is also unlikely, since it would require the solvation of an isolated thiolate anion in hexane. (This latter process is not unexpected in an aqueous environment.)

The addition of Au/dodecanethiol dots to CdSe/TOPO dots in hexane inhibits the formation of a film of CdSe/TOPO dots on the negative electrode because Au dots either (1) inhibit the transfer of charge of positive CdSe/TOPO dots at the electrode, (2) inhibit the sticking of these dots, or, most likely, (3) greatly decrease the density of positive CdSe/TOPO dots by charge exchange. Positive CdSe/TOPO dots may react with neutral or negative Au dots, generating neutral or positive Au dots, in a very efficient process occurring in solution. There would then be only negative CdSe/TOPO dots and deposition of CdSe/TOPO dots only on the positive electrode. (Note that a CdSe dot film on the negative electrode forms only when the density of charged Au dots is decreased below that of charged CdSe dots.)

To assess the effect of ligands in solution that may have left the dots, free ligands were added to the dot solutions (with densities corresponding to those of the capping ligands for the dot densities used here). Adding either oleic acid or dodecanethiol to the CdSe dot solution produced electrophoretic CdSe dot films on both electrodes that were rough and very clumpy. Rough films with no indication of electrode selectivity were also formed when current was run first with only the dodecanethiol in hexane and then continued after the CdSe/TOPO dots were added. Adding free TOPO to the CdSe/TOPO dot solution, oleic acid to the γ-Fe_2O_3/oleic acid dot solution, and dodecanethiol to the Au/dodecanethiol dot solution did not change the initial current.

Exploratory experiments of electrophoretic deposition using mixtures of γ-Fe_2O_3 and Au nanocrystals and mixtures of CdSe, γ-Fe_2O_3 and Au nanocrystals were conducted with ITO electrodes and the above densities, using XPS, transmission and PL spectroscopy for analysis. In both cases no film formed on the negative electrodes. Films of only γ-Fe_2O_3 dots and mixed films of only CdSe and γ-Fe_2O_3 dots, respectively, formed on the positive electrodes. These observations of inhibition by the Au dots are consistent with those for CdSe and Au dot mixtures and will be explored in more detail in future studies.

In conclusion, the electrophoretic formation of films composed of two types of nanocrystals can produce high quality films with new and controllable functionality, such as mixed CdSe/γ-Fe_2O_3 nanocrystal films with potentially interesting optical and magnetic properties. However, this additivity is not universal. The inhibition of electrophoretic deposition, caused by the addition of Au dots to a solution of CdSe dots, leads to selective deposition of CdSe nanocrystals on only the positive electrode, in contrast to the deposition on both electrodes with only CdSe dots. Tailored control with partial suppression of film formation on the negative electrode is possible by controlling the density of Au dots. Such additive, suppressive, and inhibitive effects should characterize the electrophoretic deposition of many types of mixed nanocrystal films.

Acknowledgment. The authors thank Shengguo Jia, Amanda Willis, and Nicholas Turro for advice and other help in the experiments. This work was primarily supported by the MRSEC program of the National Science Foundation, under Award No. DMR-0213574, and in part by the EMSI Program of the National Science Foundation and the U.S. Department of Energy under Award Number NSF CHE-9810367.

References

(1) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335.
(2) Brust, M.; Kiely, C. J. *Colloids Surf. A* **2002**, *202*, 175.
(3) Redl, F. X.; Cho, K.-S.; Murray, C. B.; O'Brien, S. *Nature* **2003**, *423*, 968.
(4) Islam, M. A.; Herman, I. P. *Appl. Phys. Lett.* **2002**, *80*, 3823.
(5) Islam, M. A.; Xia, X.; Telesca, D. A.; Steigerwald, M. L.; Herman, I. P. *Chem. Mater.* **2003**, accepted for publication.
(6) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.
(7) Peng, X.; Wickham, J.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1998**, *120*, 5343.
(8) Hyeon T.; Lee, S. S.; Park, J.; Chung, Y.; Na, H. B. *J. Am. Chem. Soc.* **2001**, *123*, 12798.
(9) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, *1994*, 801.
(10) Giersig, M.; Mulvaney, P. *Langmuir* **1993**, *9*, 3408.
(11) Murray, C. B. Ph.D. Thesis, MIT, 1993.
(12) Blanton, S. A.; Leheny, R. L.; Hines, M. A.; Guyot-Sionnest, P. *Phys. Rev. Lett.* **1997**, *79*, 865.
(13) Wong, E. M.; Searson, P. C. *Chem. Mater.* **1999**, *11*, 1959.

NL034634Q