Nanorainbows: Graded Semiconductor Films from Quantum Dots

Arif A. Mamedov,† Artem Belov,† Michael Giersig,‡
Nataliya N. Mamedova,† and Nicholas A. Kotov*,†

ChemistryDepartment, Oklahoma State University
Stillwater, Oklahoma, 74078
Hahn-Meitner-Institut, Abteilung Physikalische Chemie
Glienickerstrasse 100, D-15109, Berlin, Germany

Received March 21, 2001
Revised Manuscript Received May 20, 2001

Layer-by-layer assembly (LBL)[1] enables effective processing of semiconductor, metal, or metal oxide nanoparticle (NP) dispersions into functional advanced materials, which retain distinctive optical, magnetic and electrical qualities of size-quantized state of matter.[2,3] In an optimized LBL deposition, when the UV−vis absorption density linearly increases with the number of deposition cycles, the packing and thickness of NPs is reproduced from layer to layer. For LBL pairs with strong both electrostatic and van der Waals interactions between NPs and polyelectrolytes,[3,4] there is little (if any) restructuring of the NP layer during the polyelectrolyte deposition.[3] After coating with polyelectrolyte, the NPs become virtually immobile in the densely packed multilayer stack. The tight packing of NPs makes possible the design of materials with intentional inhomogeneity by depositing LBL bilayers in a certain sequence. The order of the layers can be used as a powerful tool for optimizing diverse functional properties of layered nanostructured materials from biological to electronic.[2a,5]

In this communication, we show the possibility of the LBL production of one-dimensionally graded semiconducting films. The latter demonstrate exceptional capabilities as photodetectors, bipolar transistors, waveguides, light-emitting, nonlinear optical, magnetooptical, and high-speed devices.[6] This type of materials also reveals new phenomena in charge injection, charge carrier dynamics, and light-trapping.[7] However, graded semiconductors are difficult to make, and expensive, complex, and hazardous techniques, such as molecular beam epitaxy and plasma-enhanced chemical vapor deposition, are required for their preparation.[6,7] Taking advantage of the simplicity and universality of the LBL assembly, one can build graded semiconducting material by laying water soluble NPs on a substrate in a sequence from smaller to bigger sizes. Because of the strong size-dependence of the NP conduction and valence band energies, a layer sequence with a gradual change of NP diameters creates an intrinsic ramp of hole and electron potential.

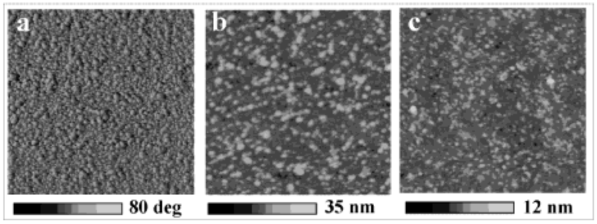

Figure 1. $1\ \mu m \times 1\ \mu m$ AFM phase (a) and topography (b,c) images of PDDA/CdTe (a, b) and PDDA/CdTe/PDDA (c). As evidenced by image (a), CdTe forms dense films in both dark and bright areas of (b) and (c).

The model graded films were prepared from highly luminescent CdTe NPs (quantum yield 15−20%) stabilized by thioglycolic acid with a partner polyelectrolyte poly(diallyldimethylammonium chloride), MW 400,000−500,000, (PDDA). CdTe NPs of different diameters were synthesized according to the published procedure.[8] The synthesized CdTe NPs had high affinity to PDDA and easily formed densely packed layers (Figure 1a), which differed them from films made by the Langmuir−Blodgett technique.[5c] Besides the reduction of film roughness (apparently due to preferential polyelectrolyte adsorption between NPs), the morphology of the layers did not change significantly after the deposition of the PDDA layer on top of CdTe (Figure 1b,c), which indicated that the original closely packed structure was retained.

The graded NP films were assembled by using four different CdTe dispersions with luminescence maxima at 495−505, 530−545, 570−585, and 605−620 nm which display respectively green, yellow, orange, and red luminescence (Figure 2a) and which will be referred to accordingly. Layer-by-layer assembly was carried out on glass and plastic substrates and typically 5−10 CdTe NP bilayers of each of four luminescent colors were deposited.[9]

The assembly started from the smallest NPs ("green") and proceeded to the biggest ones ("red") according to the visible light spectral sequence (rainbow). With the addition of new layers from bigger NPs, the luminescence of the assembly shifted toward the red part of the spectrum while also becoming broader (Figure 2b). Finally, the luminescence spectrum of the stack of all four NP diameters had a plateau appearance reflecting almost equal emission intensity in a wide range of wavelengths. As compared

---

† Oklahoma State University.

‡ Hahn-Meitner-Institut.

(1) Decher, G. *Science* **1997**, *277*, 1232−1237; Decher, G.; Hong, J. D. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 1430−1434.

(2) (a) Kotov, N. A.; Dekany, I.; Fendler, J. H. *J. Phys. Chem.* **1995**, *99*, 13065−13069. (b) Aliev, F.; Correa-Duarte, M.; Mamedov, A.; Ostrander, J. W.; Giersig, M.; Liz-Marzan, L.; Kotov, N. *Adv. Mater.* **1999**, *11*, 1006−1010. (c) Schrof, W.; Rozouvan, S.; Vankeuren, E.; Horn, D.; Schmitt, J.; Decher, G. *Adv. Mater.* **1998**, *10*, 338−341. (d) Caruso, F.; Caruso, R. A.; Mohnwald, H. *Science* **1998**, *282*, 1111−1114. (e) Gao, M.; Lesser, C.; Kirstein, S.; Mohwald, H.; Rogach, A. L.; Weller, H. *J. Appl. Phys.* **2000**, *87*, 2297−2302.

(3) Ostrander, J. W.; Mamedov, A. A.; Kotov, N. A. *J. Am. Chem. Soc.* **2001**, *123*, 1101−1110.

(4) Kotov, N. A. *Nanostruct. Mater.* **1999**, *12*, 789−796; Hammond, P. T. *Curr. Opin. Colloid Interface Sci.* **2000**, *4*(6), 430. Dubas, S. T.; Schlenoff, J. B. *Macromolecules* **1999**, *32*, 8153−8160.

(5) (a) Ho, P. K. H.; Kim, J.-S.; Burroughes, J. H.; Becker, H.; Li, S. F. Y.; Brown, T. M.; Cacialli, F.; Friend, R. *Nature* **2000**, *404*, 481−484. Wu, A.; Yoo, D.; Lee, J.-K.; Rubner, M. F. *J. Am. Chem. Soc.* **1999**, *121*, 4883−4891; Eckle, M.; Decher, G. *Nano Lett.* **2001**, *1*(1), 45−49. (b) Onda, M.; Lvov, Y.; Ariga, K.; Kunitake, T. *J. Ferment. Bioeng.* **1996**, *82*(5), 502−506. Caruso, F.; Furlong, D. N.; Ariga, K.; Ichinose, I.; Kunitake, T. *Langmuir* **1998**, *14*(16), 4559−4565; Baur, J. W.; Rubner, M. F.; Reynolds, J. R.; Kim, S. *Langmuir* **1999**, *15*(19), 6460−6469; Joly, S.; Kane, R.; Radzilowski, L.; Wang, T.; Wu, A.; Cohen, R. E.; Thomas, E. L.; Rubner, M. F. *Langmuir* **2000**, *16*(3), 1354−1359; Narvaez, A.; Suarez, G.; Popescu, I. C.; Katakis, I.; Dominguez, E. *Biosens. Bioelectron.* **2000**, *15*(1−2), 43−52; Kaschak, D. M.; Lean, J. T.; Waraksa, C. C.; Saupe, G. B.; Usami, H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1999**, *121*, 3435−3445; Kaschak, D. M.; Johnson, S. A.; Hooks, D. E.; Kim, H.-N.; Ward, M. D. Mallouk, T. E. *J. Am. Chem. Soc.* **1998**, *120*, 10887. (c) Samokhvalov, A.; Berfeld, M.; Lahav, M.; Naaman, R.; Rabani, E. *J. Phys. Chem. B* **2000**, *104*(36), 8631−8634.

(6) Capasso, F. *NATO Adv. Study Inst. Ser., Ser. B* **1988**, *180*, 659−682. Newman, A. K.; Liu, J. M. *J. Appl. Phys.* **1997**, *82*, 4637−4646. Lee, J. H.; Li, S. S.; Tidrow, M. Z.; Liu, W. K.; Bacher, K. *Appl. Phys. Lett.* **1999**, *75*, 3207−3209. Aigouy, L.; Mathet, V.; Liaci, F.; Gil, B.; Briot, O.; Briot, N.; Cloitre, T.; Averous, M.; Aulombard, R. L. *Phys. Rev. B: Condens. Matter* **1996**, *53*, 4708−4721.

(7) Sokolovskii, B. S. *Phys. Status Solidi A* **1997**, *163*, 425−432; Aichmayr, G.; Martin, M. D.; van der Meulen, H.; Pascual, C.; Vina, L.; Calleja, J. M.; Schafer, F.; Reithmaier, J. P.; Forchel, A. *Appl. Phys. Lett.* **2000**, *76*, 3540−3542; Vlaev, S.; Velasco, V. R.; Garcia-Moliner, F. *Phys. Rev. B: Condens. Matter* **1994**, *49*, 11222−11229; Geller, M. R. *Phys. Rev. Lett.* **1997**, *78*, 110−113; Chattopadhyaya, S. K.; Mathur, V. K. *Phys. Rev. [Sect.] B* **1971**, *3(3)* 3390−3399; Fujiwara, H.; Koh, J.; Wronski, C. R.; Collins, R. W.; Burnham, J. S. *Appl. Phys. Lett.* **1998**, *72*, 2993−2995; Tomasiunas, R.; Pelant, I.; Honerlage, B.; Levy, R.; Cloitre, T.; Aulombard, R. L. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1998**, *57*, 13077−13085

(8) Rogach, A. L.; Katsikas, L.; Kornowski, A.; Su, D. S.; Eychmuller, A.; Weller, H. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 1772−1778.

(9) High-luminescence quantum yield is not a rigid requirement for the further studies of graded semiconductors from NPs; however, it is a useful property that enables convenient probing of the film structure.

10.1021/ja015857q CCC: $20.00

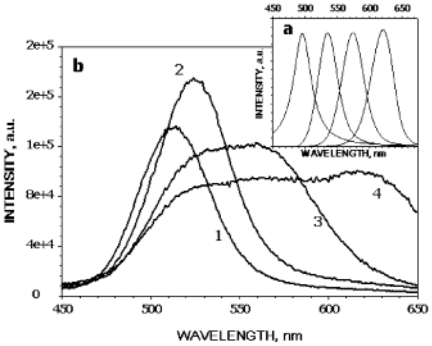

Figure 2. Luminescence spectra of (a) exemplary CdTe NPs used in this work and (b) thin films obtained after the sequential deposition of five bilayers of (1) “green”, (2) “yellow” (3) “orange”, and (4) “red” CdTe.

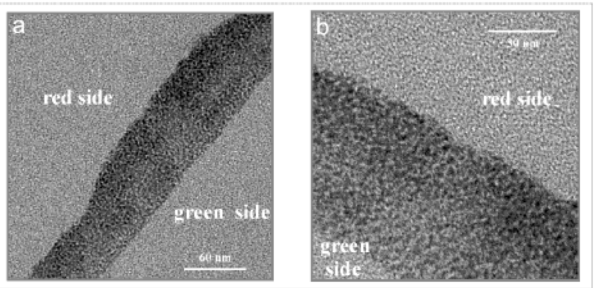

Figure 3. Transmission electron microscopy images of cross-sections of a graded film made from five bilayers of “green”, “yellow”, and “red” (total 15) NPs with different magnification.”

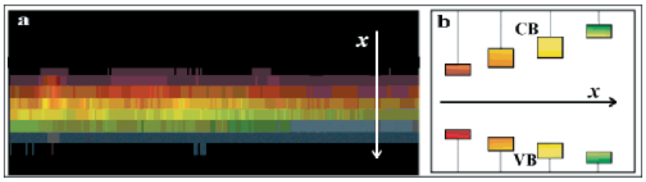

Figure 4. (a) Cross-sectional confocal microscopy image of the graded LBL film of CdTe NPs made of 10 bilayers of “green”, “yellow”, “orange”, and “red” NPs (total 40). Small NPs are assembled in the lower part (green and yellow luminescence), while bigger NPs are assembled on top of them (orange and red luminescence). The total thickness of the film was estimated to be 220 ± 20 nm by the same technique. (b) Schematic arrangement of the conduction (CB) and valence (VB) energy levels of the film in (a). The axes in (a) and (b) show the property gradient.

to the original spectra of CdTe NPs, some prevalence of the red emission (red-shift) should be attributed to the excitation energy transfer from smaller NPs to bigger ones.[10]

To evaluate the internal structure of the gradient CdTe film, it was assembled on a flexible cellulose acetate substrate as described in ref 11. A cross-sectional slice of the NP stack was analyzed by transmission electron microscopy (TEM). The asymmetry of the film could be seen in the difference of electron diffracting power of the “red” and “green” sides of the assembly (Figure 3a,b). The layers of bigger NPs appear noticeably darker in the TEM image due to the greater percentage of heavier elements on this side of the multiplayer stack (Figure 3a,b). As expected, the high-resolution TEM images of single NPs in the network of the polyelectrolyte matrix (identified as areas of CdTe crystallinity) were observed to be different, being 2−3 nm in the “green” and “yellow” parts and 5−6 nm in the “red” side of the assembly (Supporting Information), which correlates well with emission wavelengths of the particles (Figure 2a).

The graded nature of the prepared NP film was also established by confocal optical microscopy. The sample was assembled on a glass slide, and a series of luminescence images was obtained at a different focus depth inside the assembly. The images were processed by Leica TCS NT confocal microscope software, and a cross-sectional image without physical sectioning of the film was obtained (Figure 4). The image clearly shows the gradual change of the luminescence emission wavelength from green in the bottom to red on the top of the stack and the corresponding increase of the NP diameters. The schematic dependence of the valence and conduction band energies on the position along the axes normal to surface of the film is given in Figure 4b. There was a certain degree of interpenetration of the nanoparticle layers, which is reflected by the overlap of the energy distribution in each layer.

The combination of size quantization and gradient nature of the material opens a possibility for new optical and electrical effects as well as for the optimization of existing applications of NP thin films based on charge transfer. The benefits of the graded media and ordered LBL assemblies were already demonstrated by the markedly better light-emitting performance when the homogeneous media in polymer light-emitting diodes was replaced with spatially organized one.[5a] At the same time, one needs to point out that the physical distance, for which programmed change in properties in the LBL films can be obtained, is greater than in vacuum epitaxial methods.[12] Its lower limit is set by the intrinsic roughness of the LBL layers and the average diameter species (Figure 1) being deposited in from cycle to cycle. For PDDA/CdTe multilayers, the characteristic distances of graded properties should exceed ca.100 nm, that is, be several times greater than height variations in individual layers or nanoparticle diameters. Importantly, this limitation does not prevent the NP layers to be organized on a scale smaller than the wavelength of the visible light. One can engineer polarizability, refractive index and other parameters on the molecular level in such assemblies, so that the overall interaction of electromagnetic wave with the film will be significantly different than in the traditional optically uniform material, which is likely to lead to unique photonic and electronic devices.

Acknowledgment. Partial financial support of this project from NSF-CAREER (CHE-9876265), AFOSR (F49620-99-C-0072), OCAST/OARS, Nomadics, Inc., and OSU Censor Center is gratefuly acknowledged. We also thank Dr. A. Rogach (Hamburg University) for the help in synthesis of CdTe nanoparticles.

Supporting Information Available: Description of the LBL assembly of CdTe NPs. Cross-sectional HR-TEM images (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA015857Q

---

(10) Kagan, C. R.; Murray, C. B.; Nirmal, M.; Bawendi, M. G. *Phys. Rev. Lett.* **1996**, *76*, 1517−1520. Kagan, C. R.; Murray, C. B.; Bawendi, M. G. *Phys. Rev. B: Condens. Matter* **1996**, *54*, 8633−8643.

(11) Mamedov, A.; Ostrander, J.; Aliev, F.; Kotov, N. A. *Langmuir* **2000**, *16*, 3941−3949. Mamedov, A. A.; Kotov, N. A. *Langmuir* **2000**, *16*, 5530−5533.

(12) Keller, S. W.; Kim, H.-N.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*(19), 8817−8818.