

## Spin-Coating Electrostatic Self-Assembly: Fabrication Method for CdSe Nanoparticle Monolayer

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The precise positioning of functionally distinct nanoparticles (NPs) in integration of organic and inorganic materials into hybrid optoelectronic structures appears to be an essential prerequisite for the realization of the high-performance electronic and optical devices.<sup>1</sup> Numerous attempts have been made to fabricate uniform 2D NP monolayers with using diverse techniques such as self-assembly technique,<sup>2</sup> electrophoretic deposition,<sup>3</sup> Langmuir-Blodgett technique,<sup>4</sup> electrostatic interaction,<sup>5</sup> and DNA hybridization.<sup>6</sup> In general, immobilization by means of solution-dipped self-assembly is accomplished *via* surface modification of substrate with functional groups that provide an attractive interaction with deposited nanoparticles. Functional groups such as thiol, pyridil, amino, and carboxy can all be used to immobilize metal NPs on various oxide surfaces. The electrostatic attraction between oppositely charged entities has also been exploited for the immobilization of negatively charged gold NPs on poly(ethyleneimine)-modified substrate.<sup>7</sup> To date, however, there has been no recognizable breakthrough in the preparation of large laterally extended NP monolayers for the development of applications such as metal nanoparticle memory<sup>8</sup> and nanoparticle-based LED device.<sup>1</sup>

The spin coating electrostatic self-assembly (SCESA) method<sup>9</sup> was successfully shown to allow rapid fabrication of a well-ordered structure of multilayer thin films, and to realize a variety of multilayer heterostructures on a solid substrate. Here, this method is adopted to immobilize ~6 nm diameter carboxylic acid-derivatized CdSe nanoparticle in a single layer on an amino-terminated self-assembled monolayer. The morphology of the spin-assembled NP monolayer (*i.e.*, surface roughness and domain feature), as revealed by atomic force microscope (AFM), was compared with that of a sample prepared by solution-dip electrostatic self-assembly (ESA) method.<sup>10</sup>

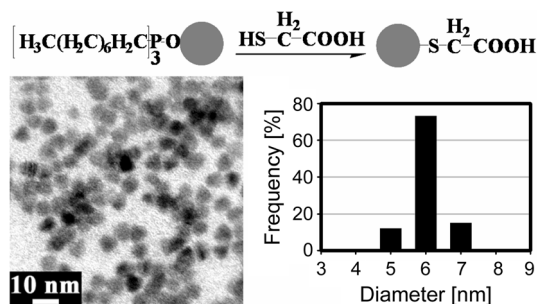
CdSe NPs were synthesized based on the Peng's preparation method.<sup>11</sup> CdSe NPs are synthesized with hydrophobic organic capping agents such as TOPO/TDPA, which in general limits their interaction with specialized materials particularly in an aqueous environment. For the charged CdSe NPs, the hydrophobic capping ligands were exchanged with a thiol-containing organic acid, *i.e.* mercaptoacetic acid (MAA), as described elsewhere.<sup>12</sup> The MAA-modified NPs at a concentration of (10 mg/mL) do not aggregate and remain stable in an aqueous 0.1 M TRIS buffer solution (pH = 9) over several months, indicating that the MAA layer

coats the entire surface of each individual particle.

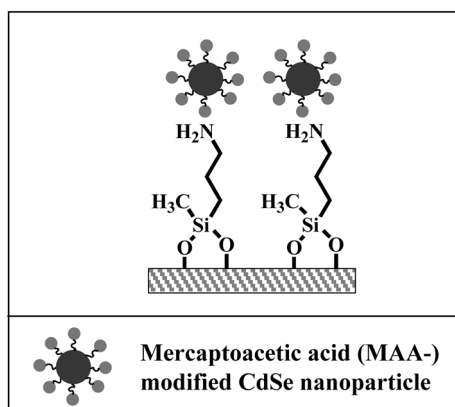
The size of the modified NPs was investigated using transmission electron microscopy (TEM). The sample was prepared by placing a drop of the dispersion onto a carbon-coated copper grid and allowing it to dry in air. The TEM measurements were performed on a FEI (TECNAI G<sup>2</sup> F20) microscope at an accelerating voltage of 200 KV. From the TEM image analysis, the size of MAA-derivatized CdSe NPs (MAA-CdSe) was determined to  $6.0 \pm 0.4$  nm (Figure 1).

The electrophoretic mobility of the MAA-CdSe NPs was obtained from an average of five measurements in 0.1 M TRIS buffer solution (pH = 9), performed at the stationary level using an electrophoretic light scattering method (*Otsuka Electronics, Photal ELS-8000*). The mobilities ( $\mu$ ) were converted to the zeta ( $\zeta$ )-potential using the Smoluchowski relation  $\zeta = \mu\eta/\epsilon$ , where  $\eta$  and  $\epsilon$  are the viscosity and permittivity of the solution, respectively. The zeta potential of the negatively charged particles was determined to be  $-48.2$  mV when dispersed in 0.1 M TRIS buffer.

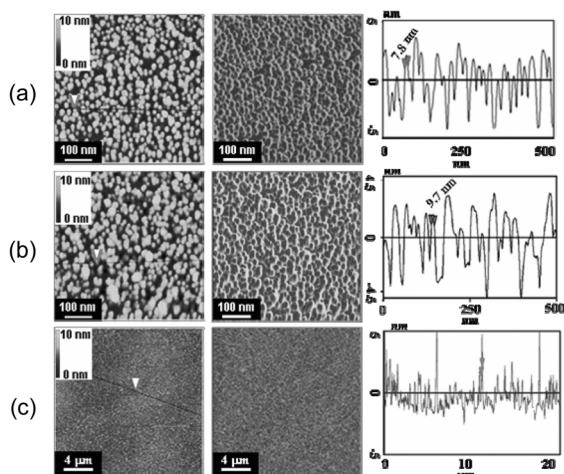
Among the several deposition methods available, we were particularly interested in SCESA, because it is expected to provide a unique condition for immobilizing NPs in a single layer on a solid substrate. Figure 2 is a simplified illustration for the immobilization of the MAA-CdSe NPs in a single layer on an amino-terminated monolayer, self-assembled during the aminopropylsilylation reaction on a silicon substrate, as described elsewhere.<sup>13</sup> The preparation of a MAA-CdSe monolayer based on the SCESA method was carried out in accordance with the well-established procedures described previously.<sup>9</sup> In this case, *ca.* 0.5 mL MAA-CdSe in TRIS buffer solution (~1 mg/mL, pH = 9) was deposited onto a silicon substrate, which was then spun at a speed of 5000 rpm for 20 seconds. Subsequently, 1 mL of



**Figure 1.** Diameter histogram (right) plotted based on TEM image (left) of MAA-capped CdSe nanoparticles ( $D = 6.0 \pm 0.4$  nm).



**Figure 2.** Schematic illustration for the immobilization of a single layer of MAA-CdSe nanoparticles on an amino-terminated self-assembled monolayer using the SCESA method.



**Figure 3.** Tapping mode AFM images of the MAA-CdSe nanoparticle monolayer deposited on an oppositely charged surface with either spin coating (a, c) or solution-dip ESA methods (b): (Left) Topographical image, (Middle) Phase image, (Right) Cross-section profile.

deionized water was placed on the substrate, which was then spun again at 5000 rpm for 20 seconds in order to remove the non-specifically adsorbed NPs sticking to the surface. The washing steps were repeated three times.

The spin-assembled NP monolayer was visualized using atomic force microscope, as shown in Figure 3(a, c). The AFM was operated in the tapping mode at a scan rate of 1.0 Hz using carbon nanotube tips. Images were taken using a Digital Instruments (DI 3100) and data was manipulated using Nanoscope III software. Figure 3 (a, Left) shows an area ( $500 \times 500 \text{ nm}^2$ ) of the sample, which is compactly covered with NPs. The line scan profile in Figure 3 (a, Right) indicates that the surface is very smooth with an rms roughness of 0.390 nm. Also, the horizontal size (diameter) of an individual nanoparticle at the red-marked position was measured as 9.7 nm. This measurement is fairly consistent with the results of the TEM image analysis ( $D = 6.0 \pm 0.4 \text{ nm}$ ), since AFM images are generally slightly larger due to their dependence on the curvature of the AFM tip. Again, the phase image of the sample in Figure 3 (a, Middle) highlights the excellent quality of the NP monolayer.

Comparative AFM images are also obtained from the solution-dipped self-assembled NP monolayers, as revealed in the AFM topographical and phase images in Figure 3 (b, Left and Middle). The deposition of the MAA-CdSe NPs on the amino-derivatized surface was achieved by immersing the substrate into an aqueous TRIS buffer solution of MAA-CdSe (1 mg/mL, pH = 9) for 1 hr, and washing it thoroughly with ultrapure water in order to remove any additional particles sticking to the surface. Also, the line scan profile in Figure 3 (b, Right) confirms a particle size of  $D = 7.8 \text{ nm}$ , and indicates an almost identical surface smoothness (rms roughness = 0.418 nm). Further, it is demonstrated that the surface is very smooth in the  $20 \times 20 \text{ nm}^2$  area scan with rms roughness of 2.7 nm, as revealed in Figure 3(c). We should note that no other difference was detected in the random scan of the  $2 \times 2 \text{ cm}^2$  sample area.

In this paper, the SCESA method is successfully utilized for the fabrication of carboxylic acid-coated CdSe nanoparticles in a single layer on an oppositely charged surface. Amazingly, it was found that the quality (domain feature, surface roughness, packing density, etc) of the NP monolayer formed on a solid substrate rotating at 5000 rpm was comparable to that of a monolayer formed by solution-dipping, as revealed by AFM. Monolayer, it is emphasized that no other difference could be detected in the random scan of a large area ( $20 \times 20 \mu\text{m}^2$ ), reconfirming the domain feature in the AFM image of Figure 3(a). We could also reinforce our stand that the two-stage adsorption accelerated on the rotating substrate during the processing of the layer<sup>12</sup> is the main deriving force behind the dense packing of the nanoparticles via rapid formation of a “sharp interface”.

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## References

- Coe, S.; Woo, W.-K.; Bawendi, M.; Bulovic, V. *Nature* **2002**, *420*, 800.
- Freeman, R. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthrie, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. *Science* **1995**, *267*, 1629.
- Mulvaney, P.; Giersig, M. *Langmuir* **1993**, *9*, 3408.
- Heath, J. R.; Knobler, C. M.; Leff, D. V. *J. Phys. Chem.* **1997**, *101*, 189.
- Peschel, S.; Schmidt, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1442.
- Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. *Nature* **1996**, *382*, 607.
- Mayya, K. S.; Schoeler, B.; Caruso, F. *Adv. Funct. Mater.* **2003**, *13*, 183.
- Tiwari, S.; Rana, F.; Chan, K.; Hanafi, H.; Chan, W.; Buchanan, W. D. *IEDM Tech. Dig.* **1995**, 521.
- Lee, S.-S.; Lee, K.-B.; Hong, J.-D. *Langmuir* **2003**, *19*, 7592. Cho, J.; Char, K.; Hong, J.-D.; Lee, K.-B. *Adv. Mater.* **2001**, *13*, 1076.
- Decher, G.; Hong, J.-D. *Ber. Bunsenges. Phys. Chem.* **1991**, *95*, 1430.
- Qu, L.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 2049. Penf, A.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 3343.
- Peng, X.; Wickham, J.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1998**, *120*, 5343.
- Haller, I. *J. Am. Chem. Soc.* **1978**, *100*, 8050.