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Patterning Nanoparticles into Rings by "2-D Pickering Emulsions"

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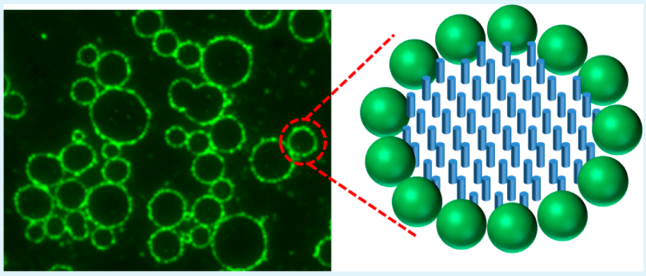
Supporting Information

ABSTRACT: We present a simple method for the two-dimensional self-assembly of CdSe/ZnS quantum dots (QDs) into well-defined rings at the air/water interface, through the formation of "2-D Pickering emulsions". Surfactant molecules assemble at the air/water interface into islands that are subsequently surrounded by adsorption of QDs from the aqueous subphase. The QD rings emanating from this process range from ~100 nm to several micrometers in diameter, as characterized by atomic force microscopy, scanning eectron microscopy, and fluorescence microscopy. The deposition and alignment of QD rings onto large areas (cm^2) were demonstrated by dip-coating onto a substrate. This simple method produces rings of QDs without the need for any templating or fabrication steps.



KEYWORDS: *QD rings, PEGylated quantum dots, air/water interface, phase transition, coverslip (microcover glass)*

INTRODUCTION

Semiconductor and metal nanoparticles (NPs) are attractive building blocks for fabricating nano- and microscale structures, which are important components of photonic, electronic, and magnetic devices for sensing, optical, and other applications.[1−7] In many cases, the ability to assemble NPs into ordered structures on substrates is critically important. For example, Keng et al. assembled polymer-coated ferromagnetic cobalt NPs into one-dimensional (1-D) and two-dimensional (2-D) structures, enabled by the inherent dipole moment of the NPs.[8] Kim et al. employed flow coating to produce well-aligned stripe and grid patterns of quantum dots (QDs),[2] where a QD solution is loaded and trapped in a confined geometry by capillary forces, and translation of an underlying substrate affords QD deposition along the contact line during solvent evaporation. Numerous approaches have been reported to fabricate patterns of nano- or microscale particles by template-based assembly.[4,5,9−12] However, self- or directed-assembly methods that eliminate the need for template fabrication remain of interest for assembling NPs over large areas in a simple fashion.

The formation of NP rings has attracted particular attention because of their suitability as optical and electronic resonators.[13−17] Chen et al. demonstrated the controlled formation of 2-D periodic arrays of nanorings from CdSe QDs by introducing an aqueous solution of microspheres and QDs onto a glass substrate.[1] QDs became confined to the meniscus of the microspheres during evaporation, leading to QD rings by capillary forces. Boker et al. produced well-ordered hexagonal patterns of QDs assembled at an oil/water interface.[18] Evaporative cooling of a volatile polymer solution containing QDs produced micrometer-sized water droplets on the polymer surface, giving "breath figures" in which the QDs segregate to the polymer solution/water droplet interface. Khanal and Zubarev demonstrated the formation of rings of polystyrene-functionalized gold nanorods using a similar breath figure technique.[19]

Here, we present a simple solution-based self-assembly method that affords 2-D QD ring structures. This began with the unanticipated formation of QD rings on the surface of water droplets containing PEGylated CdSe/ZnS core/shell QDs on borosilicate coverslips. Further investigation revealed that this behavior arose because of the presence of surface-active impurities present on the glass surface and led to experiments showing that such assemblies can be achieved by introducing a suitable concentration of insoluble surfactant. We speculate that the surfactant molecules form islands at the air/water interface [where gas (G) and liquid-expanded (LE) phases coexist] followed by QD adsorption to the three-phase interfacial line of the islands, in a process driven by a reduction in the interfacial energy. The area density of the surfactant molecules proved critical to the successful formation of QD rings, and the rings could be transferred to other substrates by dip coating.

EXPERIMENTAL SECTION

Water-Soluble CdSe/ZnS Core/Shell QDs. CdSe/ZnS core/shell QDs were synthesized according to literature methods.[20−22] Two QD samples were used, having 4 and 9 nm diameter as determined by UV−vis absorption[23] and TEM. Ligand exchange was conducted on the QDs, converting the surface functionality to poly(ethylene glycol) (PEG; M_n = 600) with a dihydrolipoic acid (DHLA) binding group (PEG-DHLA).[24] Briefly, 1−2 mg of TOPO or oleic acid-capped QDs, 50−100 mg of excess DHLA-PEG600 ligand, and 0.3−0.4 mL of

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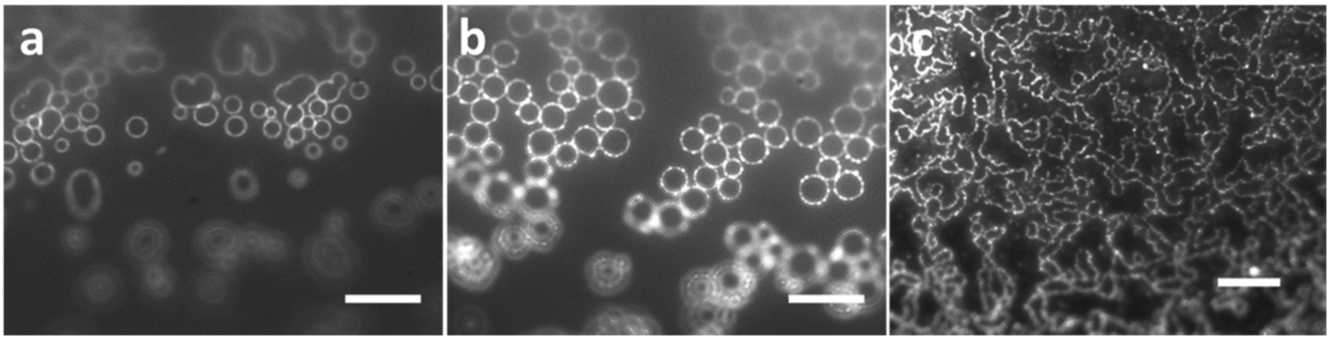

Figure 1. (a and b) Fluorescence microscopy images of QD rings formed at the edge of the droplet (scale bar = 10 μm). (c) QD network formed on top of the droplet surface (scale bar = 20 μm).

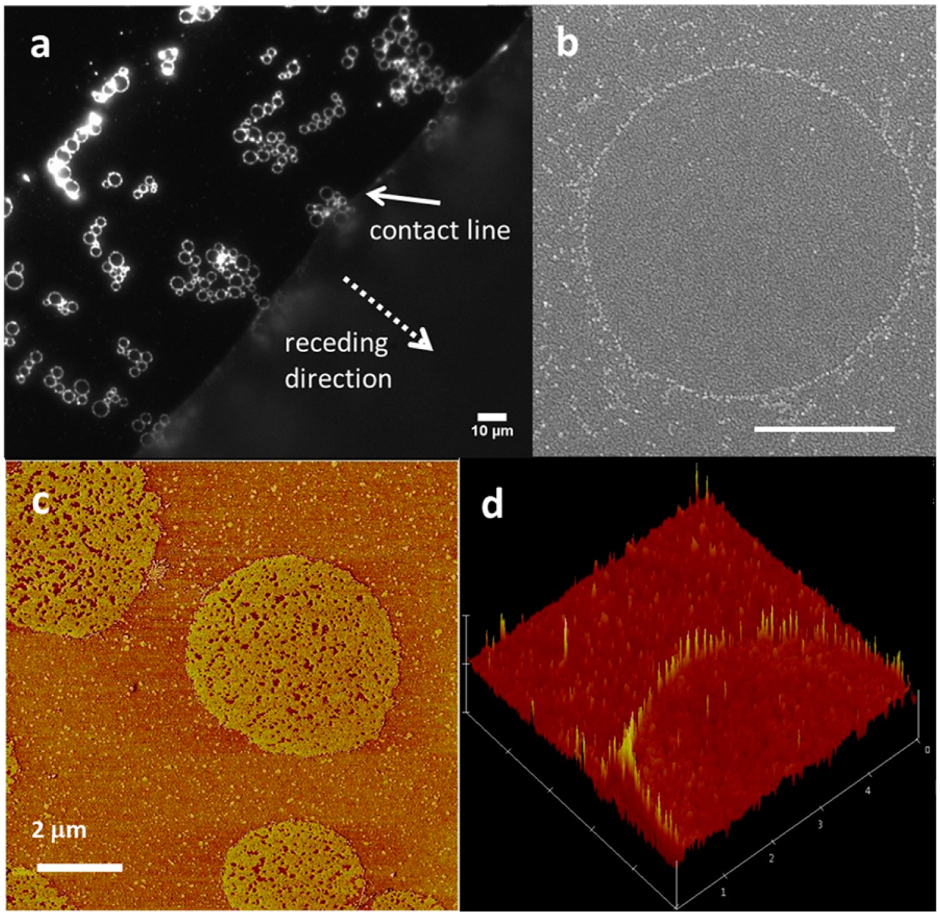

Figure 2. (a) Fluorescence microscopy image of QD rings deposited on borosilicate glass as the contact line recedes. The solid arrow indicates the contact line and the dotted arrow the receding direction. (b) SEM image of a QD ring (scale bar = 1 μm). (c) AFM phase image. (d) 3-D AFM height image. The lateral dimension is 5 μm × 5 μm, and the vertical dimension is ±5 nm.

methanol were placed in a 4 mL vial and degassed. This mixture was stirred overnight at 70 °C until the solution became clear, then cooled to room temperature, and precipitated by adding hexane and chloroform. The supernatant was removed, and water was added to dissolve the QDs. The aqueous QD solution was purified by passing through a centrifugal filter membrane (MWCO = 100 kDa) in RO water.

Synthesis of DHLA-PEG600. DHLA-PEG600 ligand was synthesized by following literature methods.[24,25] Thioctic acid (5.0 g, 24 mmol), PEG (MW = 600, 145 g, 242 mmol), a catalytic amount of 4-(dimethylamino)pyridine (890 mg, 7.3 mmol), and CH_2Cl_2 (240 mL) were combined in a flask and degassed with N_2. The mixture was cooled to 0 °C in an ice bath, and a solution of dicyclohexylcarbodiimide (6.5 g, 31 mmol) in CH_2Cl_2 (20 mL) was added dropwise. The mixture was stirred overnight at room temperature. The precipitate was filtered over a plug of Celite, and the residue was mixed with an aqueous sodium bicarbonate solution and extracted with ethyl acetate (three times). The combined organic phase was dried over $MgSO_4$, filtered, and evaporated to give a yellow oil. This oil was purified by column chromatography on silica gel (95:5 chloroform/methanol), and the product was recovered as a yellow oil (~60%). Sodium borohydride (13.8 mmol) in 1:4 ethanol/water (55 mL) was used to reduce the disulfide, giving PEG-DHLA.

Octadecyltrichlorosilane (OTS) Coating on Coverslips (Borosilicate Microcover Glasses). A coverslip (VWR microcover glasses, No. 1.5, catalog number 48393-194) was sonicated in toluene for 20 min and subjected to a UV/ozone treatment for 30 min. The cleaned coverslip was immersed in 0.1 vol % OTS in toluene, and the

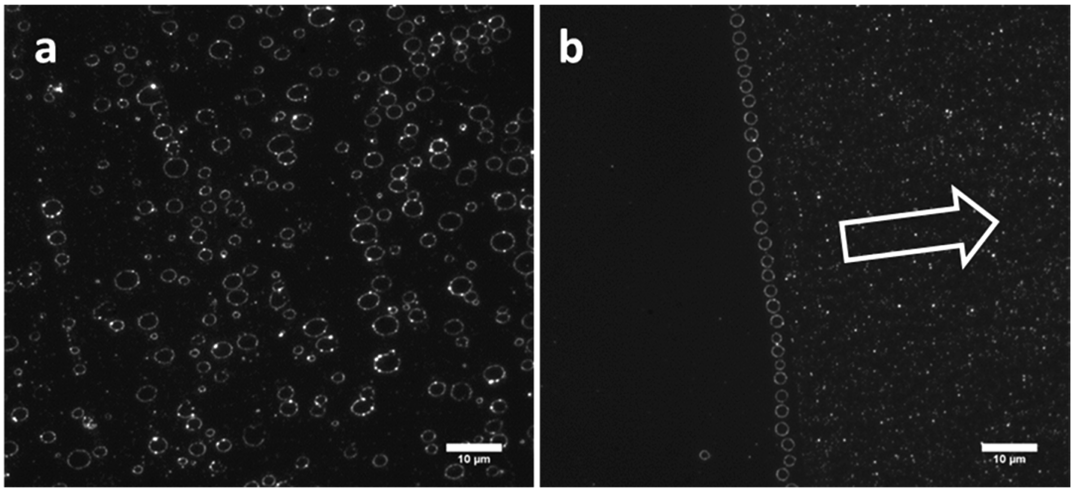

Figure 3. (a) QD rings deposited on a coverslip by dip coating at an angle of ~35°. (b) Aligned QD rings by a controlled dip-coating method at an angle of ~45°. The white arrow shows the pulling direction of the substrate in part b. Scale bars = 10 μm.

solution was stirred for 1 h. Then, the OTS-treated coverslip was washed with toluene and isopropyl alcohol several times. To reduce the water contact angle (CA) of OTS-treated substrates to ~35°, it was exposed to UV/ozone for ~6 min, resulting in the partial oxidization of the OTS layer.

QD Ring Formation on Substrates. A droplet of a 0.4 wt % aqueous solution of acrylamide, containing PEGylated QDs (~1 nM), was placed on various substrates, such as a coverslip, silicon wafer, TEM grid, OTS-treated glass, and soda-lime glass slide (1 mm thickness). Among all of these substrates, QD rings formed only on the glass coverslips. The coverslips were used as received with brief rinsing with water.

QD Ring Deposition and Alignment by Dip Coating. A 0.4 wt % aqueous solution of acrylamide, containing PEGylated QDs (~1 nM), was filled in a cylindrical chamber, and a coverslip (22 mm × 50 mm) was immersed in a solution. After ~15 min, QD rings formed at the interface were deposited on a coverslip by dip coating with a continuous withdrawal rate of 1 μm/s using a servo motor (Parker Daedal, Parker Hannifin Corp., Cleveland, OH). The alignment of the rings was achieved by dip coating in a controlled manner, with 1 min stopping time between 2 mm/s withdrawal steps. The movement of the substrates was controlled at a computer interface with *LabView* (National Instruments, Austin, TX) software.

RESULTS AND DISCUSSION

The unexpected observation of the 2-D QD assembly into rings at the air/water interface occurred when a droplet of an aqueous solution containing ~0.4 wt % acrylamide and ~1 nM QDs was placed onto a borosilicate coverslip substrate. The fluorescence micrographs of Figure 1a,b represent typical examples of QD rings formed at the air/water interface near the contact line of the droplet. In contrast, Figure 1c shows a network morphology of QDs on the top of a droplet. In Figure 1a,b, QD rings in the center of the images are in focus, while the rings in the upper and lower regions are out of focus; this is caused by the curvature of the droplet near the contact line. The QD rings were observed near the edge of the droplet of this solution during evaporation rather than on the whole of the droplet. The observed QD rings covered a range of sizes, from hundreds of nanometers to ~10 μm in diameter.

Figure 2a shows a fluorescence microscopy image of QD rings deposited on the coverslip substrate upon evaporation of water and recession of the contact line. The solid arrow denotes the contact line and the dashed arrow the receding direction. The upper left portion of the image shows QD rings after deposition; in the lower right of the image, no QD rings are visible because the rings are out of focus (the substrate is in focus). After deposition, the QD rings were characterized by electron microscopy and atomic force microscopy (AFM). Parts b–d of Figure 2 show scanning electron microscopy (SEM) and AFM images of the QD rings. The SEM image of Figure 2b shows an easily recognized ring with a continuous rim consisting of QDs. The AFM image of Figure 2d shows a discrete circular pattern, with a height corresponding to the QD diameter of ~5 nm, while the phase image in Figure 2c indicates the presence of material, likely the ring template-forming material, inside the rings.

Beyond the formation of individual QD rings, we found that the rings could be aligned over a large area (approximately cm^2) by dip coating onto untreated coverslips (Figure 3). For example, an aqueous acrylamide solution (~0.4 wt %) containing QDs was poured into a chamber with a circular opening, and a coverslip was immersed at an angle of ~35–45°. Figure 3a shows a fluorescence microscopy image of deposited QD rings after dip coating, with a continuous withdrawal rate of 1 μm/s at an angle of ~35°. Alignment of the rings was accomplished by implementing a 1 min stopping time between 0.5 s withdrawal steps at 2 mm/s at an angle of ~45°. In Figure 3b, the pulling direction of the substrate is indicated by the arrow, and QD rings were aligned on the substrate at the initial contact line, with the quick slip motion of the substrate, to give lines of rings along the contact line (see Figure S1 in the Supporting Information for more images of successive QD ring alignment). Interestingly, the aligned rings in Figure 3b are rather uniform in size compared to those in Figure 3a. However, we note that in many cases the sizes of the aligned rings are more broadly distributed. This dip coating demonstrates a very simple and effective method of QD ring deposition over a large area (approximately cm^2).

Interestingly, attempts to form QD rings on numerous other substrates (TEM grids, silicon wafers, or other glass substrates) failed. Indeed, we were able to reproduce QD ring formation from the droplets only on the glass coverslips used in our initial experiments. The water CA of these coverslips was higher (~35°) than that of the other glass substrates tested (~10°). We suspect that this difference in the CA reflects the presence of organic impurities on the untreated borosilicate coverslip surfaces, as described by Sumner et al.[26] Extensive cleaning

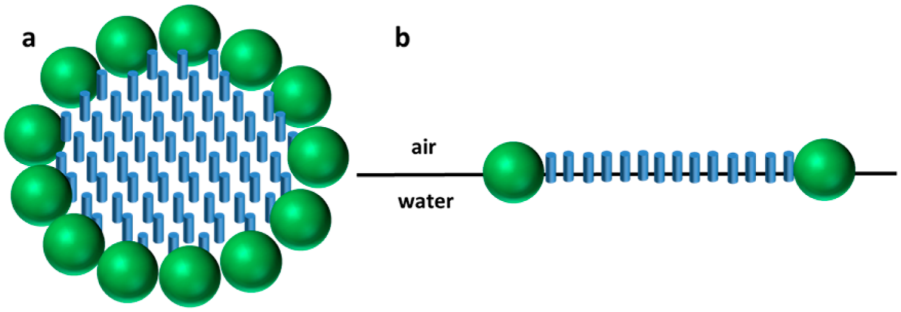

Figure 4. Schematic of "2-D Pickering emulsions" at the air/water interface. (a) Top and (b) side views of "2-D Pickering emulsions", where green dots refer to QDs and blue rods surface-active impurities.

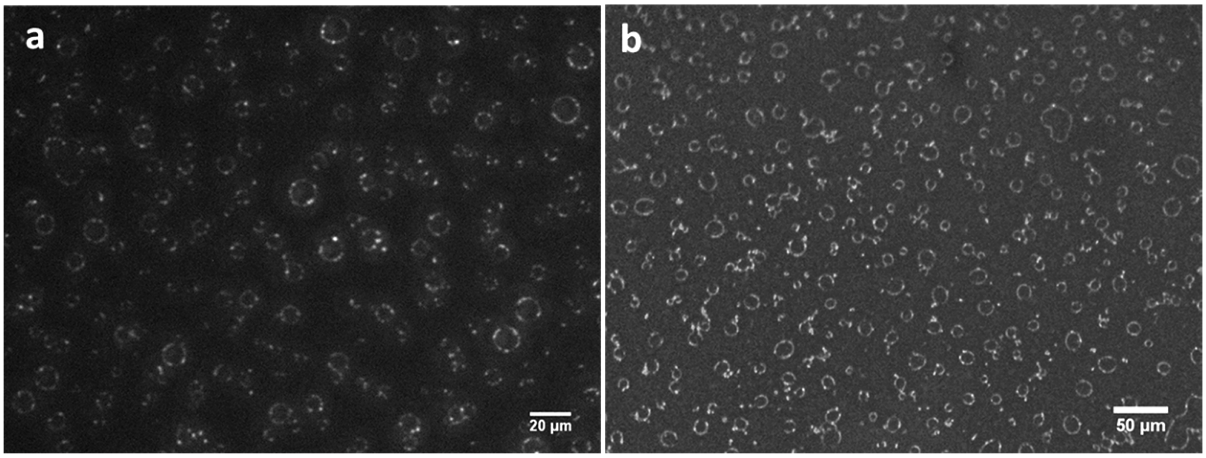

Figure 5. Fluorescence microscopy images of QD rings formed in the presence of MA at the air/water interface: (a) QD rings on the top of a droplet surface (scale bar = 20 μm); (b) QD rings formed on a flat air/water interface (scale bar = 50 μm).

(solvent washing, plasma, or UV/ozone cleaning) of these coverslips reduced the water CA to <10°, but this treatment precluded the formation of QD rings. Thus, it seems that organic impurities are key to QD ring formation, rather than acrylamide, although we note the possibility for acrylamide to function as a surfactant as well.[27] Indeed, in some cases, the QD rings formed on the coverslips when acrylamide was excluded from the experiments. This variability of QD ring formation is also found in the presence of acrylamide, and this variability may reflect different amounts of impurities on the coverslips in each trial.

Thus, a further investigation was undertaken, with the objective of producing QD rings on substrates other than the more hydrophobic commercial coverslips. Attempts to form QD rings on OTS-treated coverslips (CA ~ 90°) and an oxidized OTS-treated coverslip (~35°), where impurities are excluded, both failed, suggesting that the CA is not the key determining factor in QD ring formation. We hypothesize that the impurities from the coverslip are surface-active and leach from the surface to the air/water interface, followed by the adsorption of QDs surrounding the impurity islands, which can be considered "2-D Pickering emulsions", as depicted in Figure 4.[28] Motivated by this hypothesis, we examined the effect of added surfactant, such as myristic acid (MA), which is known to form islands at the air/water interface because of the coexistence of G and LE phases.[29−31] Solutions of MA were first prepared in chloroform at concentrations from 0.1 to 50 μM, and then 10 μL of a QD solution (~1 nM in water) was placed on OTS-treated coverslips (exposed with UV/ozone for partial oxidation) followed by a 0.5 μL drop of a surfactant stock solution that spread at the air/water interface. Figure 5a shows fluorescence microscopy images of QD rings formed from experiments having a 0.5 μM surfactant stock solution. QD ring formation occurred quickly in these experiments (~1 min), suggesting fast adsorption kinetics of QDs to the interface. The MA concentration proved important because no ring formation was observed at values substantially above or below ~0.5 μM. Assuming that MA spread uniformly over the droplet surface, this corresponds to an area of ~10^4 Å^2/molecule, which is far greater than the value of ~200−400 Å^2/molecule reported for the G−LE transition in MA.[31,32] Thus, while the density is too low for G−LE coexistence in the absence of QDs, we speculate that adsorption of QDs to the air/water interface would have the effect of decreasing the area density per molecule. Once QD rings form on the surface of the droplets, they change shape as water evaporates because of the decrease in surface area, while QD rings formed at a flat air/water interface do not show shape deformation over time (Figure 5b). As seen in Figure 5, although QD rings formed with MA were found to appear less organized than those in Figure 3a, the formation of QD rings in the presence of MA strongly supports our hypothesis that surface-active impurities from the coverslip were responsible for the formation of QD rings. Whether other types of NPs (metallic, magnetic, etc.) could participate in such ring formation is an open question and a topic of future investigation.

In summary, we report the 2-D self-assembly of PEG-functionalized QDs into rings at the air/water interface. This study emanated from the unanticipated observation of QD rings formed on the surface of droplets placed on coverslips.

On clean (impurity-free) coverslips, surfactants were used to generate the QD rings. We manipulate the concentration of the surfactant at the air/water interface to produce self-assembled surfactant islands (G−LE coexistence phase) driving QDs to adsorb at the three-phase interface (air, water, and surfactant island) to reduce the interfacial energy, thereby resulting in the formation of QD rings. The deposition and alignment of QD rings onto a large area were demonstrated by dip coating. The method demonstrated here for the fabrication of QD rings is very simple and allows for a large-area deposition by dip coating without requiring complex template fabrication steps.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Series of fluorescence microscopy images of aligned QD rings shown with numbers indicating the *n*th pulling of the substrate by dip coating. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Chen, J.; Liao, W.-S.; Chen, X.; Yang, T.; Wark, S. E.; Son, D. H.; Batteas, J. D.; Cremer, P. S. Evaporation-Induced Assembly of Quantum Dots into Nanorings. *ACS Nano* **2008**, *3*, 173−180.

(2) Kim, H. S.; Lee, C. H.; Sudeep, P. K.; Emrick, T.; Crosby, A. J. Nanoparticle Stripes, Grids, and Ribbons Produced by Flow Coating. *Adv. Mater.* **2010**, *22*, 4600−4604.

(3) Tang, Z.; Kotov, N. A.; Giersig, M. Spontaneous Organization of Single CdTe Nanoparticles into Luminescent Nanowires. *Science* **2002**, *297*, 237−240.

(4) Lu, N.; Chen, X.; Molenda, D.; Naber, A.; Fuchs, H.; Talapin, D. V.; Weller, H.; Müller, J.; Lupton, J. M.; Feldmann, J.; Rogach, A. L.; Chi, L. Lateral Patterning of Luminescent CdSe Nanocrystals by Selective Dewetting from Self-Assembled Organic Templates. *Nano Lett.* **2004**, *4*, 885−888.

(5) Henzie, J.; Barton, J. E.; Stender, C. L.; Odom, T. W. Large-Area Nanoscale Patterning: Chemistry Meets Fabrication. *Acc. Chem. Res.* **2006**, *39*, 249−257.

(6) Anker, J. N.; Hall, W. P.; Lyandres, O.; Shah, N. C.; Zhao, J.; Van Duyne, R. P. Biosensing with Plasmonic Nanosensors. *Nat. Mater.* **2008**, *7*, 442−453.

(7) Lee, D. Y.; Pham, J. T.; Lawrence, J.; Lee, C. H.; Parkos, C.; Emrick, T.; Crosby, A. J. Macroscopic Nanoparticle Ribbons and Fabrics. *Adv. Mater.* **2013**, *25*, 1248−1253.

(8) Keng, P. Y.; Shim, I.; Korth, B. D.; Douglas, J. F.; Pyun, J. Synthesis and Self-Assembly of Polymer-Coated Ferromagnetic Nanoparticles. *ACS Nano* **2007**, *1*, 279−292.

(9) Babayan, Y.; Barton, J. E.; Greyson, E. C.; Odom, T. W. Templated and Hierarchical Assembly of CdSe/ZnS Quantum Dots. *Adv. Mater.* **2004**, *16*, 1341−1345.

(10) Gleiche, M.; Chi, L. F.; Fuchs, H. Nanoscopic Channel Lattices with Controlled Anisotropic Wetting. *Nature* **2000**, *403*, 173−175.

(11) Werts, M. H. V.; Lambert, M.; Bourgoin, J.-P.; Brust, M. Nanometer Scale Patterning of Langmuir−Blodgett Films of Gold Nanoparticles by Electron Beam Lithography. *Nano Lett.* **2001**, *2*, 43−47.

(12) Ancona, M. G.; Kooi, S. E.; Kruppa, W.; Snow, A. W.; Foos, E. E.; Whitman, L. J.; Park, D.; Shirey, L. Patterning of Narrow Au Nanocluster Lines Using V_2O_5 Nanowire Masks and Ion-Beam Milling. *Nano Lett.* **2002**, *3*, 135−138.

(13) Pauzauskie, P. J.; Sirbuly, D. J.; Yang, P. Semiconductor Nanowire Ring Resonator Laser. *Phys. Rev. Lett.* **2006**, *96*, 143903.

(14) Lorke, A.; Johannes Luyken, R.; Govorov, A. O.; Kotthaus, J. P.; Garcia, J. M.; Petroff, P. M. Spectroscopy of Nanoscopic Semiconductor Rings. *Phys. Rev. Lett.* **2000**, *84*, 2223−2226.

(15) Bozhevolnyi, S. I.; Volkov, V. S.; Devaux, E.; Laluet, J.-Y.; Ebbesen, T. W. Channel Plasmon Subwavelength Waveguide Components Including Interferometers and Ring Resonators. *Nature* **2006**, *440*, 508−511.

(16) Ramakrishna, G.; Dai, Q.; Zou, J.; Huo, Q.; Goodson, T. Interparticle Electromagnetic Coupling in Assembled Gold-Necklace Nanoparticles. *J. Am. Chem. Soc.* **2007**, *129*, 1848−1849.

(17) Kyung-Young, J.; Teixeira, F. L.; Reano, R. M. Au/SiO_2 Nanoring Plasmon Waveguides at Optical Communication Band. *J. Lightwave Technol.* **2007**, *25*, 2757−2765.

(18) Boker, A.; Lin, Y.; Chiapperini, K.; Horowitz, R.; Thompson, M.; Carreon, V.; Xu, T.; Abetz, C.; Skaff, H.; Dinsmore, A. D.; Emrick, T.; Russell, T. P. Hierarchical Nanoparticle Assemblies Formed by Decorating Breath Figures. *Nat. Mater.* **2004**, *3*, 302−306.

(19) Khanal, B. P.; Zubarev, E. R. Rings of Nanorods. *Angew. Chem.* **2007**, *119*, 2245−2248.

(20) Sudeep, P. K.; Early, K. T.; McCarthy, K. D.; Odoi, M. Y.; Barnes, M. D.; Emrick, T. Monodisperse Oligo(phenylene vinylene) Ligands on CdSe Quantum Dots: Synthesis and Polarization Anisotropy Measurements. *J. Am. Chem. Soc.* **2008**, *130*, 2384−2385.

(21) Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. (CdSe)ZnS Core-Shell Quantum Dots: Synthesis and Characterization of a Size Series of Highly Luminescent Nanocrystallites. *J. Phys. Chem. B* **1997**, *101*, 9463−9475.

(22) Bae, W. K.; Char, K.; Hur, H.; Lee, S. Single-Step Synthesis of Quantum Dots with Chemical Composition Gradients. *Chem. Mater.* **2008**, *20*, 531−539.

(23) Yu, W. W.; Qu, L.; Guo, W.; Peng, X. Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals. *Chem. Mater.* **2003**, *15*, 2854−2860.

(24) Uyeda, H. T.; Medintz, I. L.; Jaiswal, J. K.; Simon, S. M.; Mattoussi, H. Synthesis of Compact Multidentate Ligands to Prepare Stable Hydrophilic Quantum Dot Fluorophores. *J. Am. Chem. Soc.* **2005**, *127*, 3870−3878.

(25) Mei, B. C.; Susumu, K.; Medintz, I. L.; Mattoussi, H. Polyethylene Glycol-Based Bidentate Ligands to Enhance Quantum Dot and Gold Nanoparticle Stability in Biological Media. *Nat. Protoc.* **2009**, *4*, 412−423.

(26) Sumner, A. L.; Menke, E. J.; Dubowski, Y.; Newberg, J. T.; Penner, R. M.; Hemminger, J. C.; Wingen, L. M.; Brauers, T.; Finlayson-Pitts, B. J. The Nature of Water on Surfaces of Laboratory Systems and Implications for Heterogeneous Chemistry in the Troposphere. *Phys. Chem. Chem. Phys.* **2004**, *6*, 604−613.

(27) Zhu, J.-H.; Shao, F.; Zhan, Y.-H.; Yan, X.-L.; Zhang, B. Acrylamide as Cosurfactant and Hydrotrope in the Pseudoternary Span 80-Tween 85/Isopar M/Water Emulsion/Microemulsion Forming system. *Colloids Surf., A* **2006**, *290*, 19−24.

(28) Aveyard, R.; Binks, B. P.; Clint, J. H. Emulsions Stabilised Solely by Colloidal Particles. *Adv. Colloid Interface Sci.* **2003**, *100*−*102*, 503−546.

(29) Honig, D.; Overbeck, G. A.; Mobius, D. Morphology of Pentadecanoic Acid Monolayers at the Air/Water Interface Studied by BAM. *Adv. Mater.* **1992**, *4*, 419−424.

(30) Moore, B. G.; Knobler, C. M.; Akamatsu, S.; Rondelez, F. Phase Diagram of Langmuir Monolayers of Pentadecanoic Acid: Quantitative Comparison of Surface Pressure and Fluorescence Microscopy Results. *J. Phys. Chem.* **1990**, *94*, 4588−4595.

(31) Henon, S.; Meunier, J. Microscope at the Brewster Angle: Direct Observation of First-Order Phase Transitions in Monolayers. *Rev. Sci. Instrum.* **1991**, *62*, 936−939.

(32) Kaganer, V. M.; Möhwald, H.; Dutta, P. Structure and Phase Transitions in Langmuir Monolayers. *Rev. Mod. Phys.* **1999**, *71*, 779−819.