

Nanoparticle-Induced Self-Assembly of Block Copolymers into Nanoporous Films at the Air-Water Interface

Seulki Kang¹, Du Yeol Ryu², Emilie Ringe³, Robert J. Hickey⁴, and So-Jung Park^{1,}*

¹ Department of Chemistry and Nanoscience, Ewha Womans University, 52 Ewhayeodae-gil,
Seodaemun-gu, Seoul 03760, Korea

² Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro,
Seodaemun-gu, Seoul 03722, Korea

³ Department of Materials Science and Metallurgy, Department of Earth Science, University of
Cambridge, Cambridge CB2 3EQ, United Kingdom

⁴ Department of Material Science and Engineering and Materials Research Institute, The
Pennsylvania State University, University Park, Pennsylvania 16802, United States

*Correspondence to: sojungpark@ewha.ac.kr (S.-J.P.)

Materials and Methods

Materials for polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP). Styrene ($\geq 99\%$), 2-vinylpyridine, calcium hydride (reagent grade, 90%), *sec*-butyllithium [1.4 M in cyclohexane], 2-propanol ($\geq 99.5\%$) dibutyl magnesium [1.0 M in heptane], and trioctyl aluminum [25 wt% in hexane] were purchased from Sigma-Aldrich. Tetrahydrofuran (THF) was purchased from Daejung.

Materials for iron oxide nanoparticles, quantum dots (QDs) and quantum rods. Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 97%), 1-octadecene (90% technical grade), oleic acid (90% technical grade), oleylamine (70% technical grade), cadmium oxide (CdO, 99.99%), selenium powder (99.5%), 1-octadecene (90% technical grade), stearic acid (95%), oleylamine (90%), tri-*n*-octylphosphine (TOP, 97%), trioctylphosphine oxide (TOPO, 99%), 1-octanethiol ($>98.5\%$), and octadecylamine (90% technical grade) were purchased from Sigma-Aldrich. Sodium oleate (95%) was purchased from TCI. Octadecylphosphonic acid (99%) and hexylphosphonic acid (99%) were purchased from Polycarbon Industries. Chloroform (99.5%), ethanol (95.0%) and acetone (99.5%) were purchased from Samchun. Toluene and methanol (extra pure grade) were purchased from Ducksan. All reagents were used without further purification.

Instrumentation. Transmission electron microscope (TEM) images were obtained on JEOL JEM-2100F or JEM-2100Plus TEM with an accelerating voltage of 200 kV. Scanning TEM high angle annular dark field (STEM-HAADF) images were obtained on a Thermo-Fisher Titan Krios operated at 300 kV. Noncontact-mode atomic force microscopy images were collected using a Park XE7 (Park systems). UV-vis absorption and fluorescence spectra were acquired using an

Agilent 8453 UV-visible spectrophotometer and the Perkin Elmer 5S 55 fluorescence spectrometer, respectively. ^1H nuclear magnetic resonance (NMR) spectra were acquired on a Bruker AVANCE III HD 300MHz FT-NMR Spectrometer using tetramethylsilane as the internal standard and deuterated dichloromethane (CD_2Cl_2) as the solvent. Gel-permeation chromatography (GPC) was measured by a Shimadzu liquid chromatography system using tetrahydrofuran (THF) as an eluent at a rate of 1.0 mL/min. The column temperature was set to 40 °C and polystyrene was used as standards for analyses of molecular weight.

Synthesis and characterization of PS-*b*-P2VP. PS-*b*-P2VP was synthesized *via* sequential living anionic polymerization of styrene and 2-vinylpyridine monomers in THF solvent at -78 °C under a purified argon environment using *sec*-butyllithium as an initiator.¹ The number-average molecular weight (M_n) and dispersity ($D = M_w/M_n$), determined by GPC, are 27 kg/mol and 1.03, 33 kg/mol and 1.02, and 50 kg/mol and 1.02 for PS_{22k}-*b*-P2VP_{4.7k}, PS_{27k}-*b*-P2VP_{5.8k}, and PS_{41k}-*b*-P2VP_{8.7k}, respectively. PS volume fraction (f_{PS}) of block copolymers was determined to be ~ 0.84 by ^1H NMR, based on the mass densities of two components (1.05 and 1.14 g/cm³ for PS and P2VP, respectively).

Synthesis of iron oxide nanoparticles. Iron oxide nanoparticles were synthesized using oleic acid as the ligand following a modified literature method.² The iron oleate was prepared in a 100 mL round bottom flask by refluxing the hexane solution of 1.5 g of iron chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and 5.2 g of sodium oleate (17 mmol), 11.5 mL of ethanol, and 8.8 mL of distilled water at ~70 °C. The solution was kept at that temperature for 4 hours. After the ligand exchange, the upper organic layer was washed with 30 mL of water and centrifuged at 8,000 rpm for 10 min. After that, hexane

was evaporated and iron-oleate was stored under vacuum for about 12 hours. 7.5 nm iron oxide particles were synthesized by reacting 5.5 g of iron-oleate and 1.5 g of oleic acid (5.3 mmol) in 31 g of 1-octadecene in a 100 mL round bottom flask. The mixture was heated to 320 °C at a rate of 200°C/hour, and kept at that temperature for 30 min. After the reaction, the solution was cooled to room temperature and washed with ethanol (35 mL). Particles were purified by repeated washing, collected with centrifugation (8,000 rpm, 10 min), and finally re-dispersed in toluene (2.4 mg/mL).

Synthesis of CdSe QDs. CdSe QDs were synthesized by following a previously reported method.³ For the synthesis of 3.5 nm CdSe QDs, a mixture of CdO (0.0257 g, 0.2 mmol), stearic acid (0.2276, 0.8 mmol) and 2 mL of 1-octadecene was heated to 250 °C in 25 mL three-neck round bottom flask under nitrogen. When the solution became colorless, it was cooled down to 130 °C and degassed for an hour. 1 g of octadecylamine and 8 mL of 1-octadecene were then added into the flask and reheated to 270 °C under nitrogen flows. At this temperature, 2 mL of trioctylphosphine selenide (TOPSe) solution made by dissolving 2 mmol of selenium powder in 2 mL TOP was quickly injected. After 5 min at 250 °C, the resulting solution was cooled to room temperature. The solution was washed with ethanol (15 mL) and collected by centrifugation (10,000 rpm, 10 min). After washing three times, the precipitates were re-dispersed in chloroform (1 mg/mL).

Synthesis of CdSe/CdS core/shell QDs. CdSe/CdS core/shell QDs were synthesized by successive ionic layer adsorption and reaction.⁴ To prepare the precursor solution, Cd-oleate and 1-octanethiol, CdO (0.036 g, 0.28 mmol), oleic acid (0.36 ml, 1.1 mmol), and 6 mL 1-octadecene was heated to 240 °C under nitrogen. The solution was cooled down to 100 °C and degassed for

an hour. After that, 1-octanethiol (60 μL , 0.35 mmol) was added into the flask, and the solution was reheated to 140 $^{\circ}\text{C}$ under nitrogen gas flow. After 30 min cooling, the precursor solution was taken with syringe under the nitrogen flow. In another flask, dried 100 nmol of CdSe QDs was mixed with 1-octadecene (3 mL) and oleylamine (3 mL). The solution was degassed at room temperature for an hour and then further degassed at 120 $^{\circ}\text{C}$ for 30 min. Then, the solution was heated to 310 $^{\circ}\text{C}$ at a heating rate of 18 $^{\circ}\text{C}/\text{min}$ under the nitrogen flow. When the temperature reached 240 $^{\circ}\text{C}$, the precursor solution was added into the reaction solution at a rate of 1.5 mL/hr using a syringe pump. Then, 1 mL of oleic acid was quickly injected into the solution, which was then kept at 310 $^{\circ}\text{C}$ for an hour. The synthesized core/shell QDs were precipitated with acetone (15 mL) and centrifuged at 10,000 rpm for 15 min. The supernatant was discarded, and the precipitates were re-dispersed in toluene (2.4 mg/mL).

Synthesis of CdSe seeds. CdSe/CdS core/shell quantum rods were prepared from CdSe seeds by a well-established seeded-growth method.⁵ For the synthesis of CdSe seeds, CdO (0.060 g), octadecylphosphonic acid (0.280 g), and TOPO (3 g) were mixed in a 50 mL round bottom flask. The mixture was degassed at 150 $^{\circ}\text{C}$ for an hour. Then, the solution was reheated to 380 $^{\circ}\text{C}$ under nitrogen atmosphere. When the solution turns colorless, 1 mL of TOP was added into the flask. When the temperature was recovered to 380 $^{\circ}\text{C}$, 0.38 mL of 2 M TOPSe was injected swiftly into the flask and the heating mantle was removed immediately. The cooled seed solution was precipitated with methanol and acetone and centrifuged at 10,000 rpm for 10 min. After several washing, the precipitates were dispersed in hexane.

Synthesis of CdSe/CdS core/shell quantum rods. The mixture of 0.086 g of CdO, 0.080 g of hexylphosphonic acid, 0.290 g of octadecylphosphonic acid, and 3 g of TOPO in a 50 mL round bottom flask was heated to 150 °C and degassed for an hour at that temperature. The solution was reheated to 350 °C under nitrogen flow. 1.5 mL of TOP was injected into the flask when the solution became colorless. At 350 °C, the mixture of sulfur precursor and CdSe seeds (80 nmol of CdSe seeds and 0.12 g of sulfur in 2 mL of TOP) was injected swiftly into the flask. After 8 min, the solution was cooled to room temperature. The resulting solution was washed with ethanol, and core/shell quantum rods were collected by centrifugation (10,000 rpm, 5 min). The supernatant solution was discarded and the precipitates were re-dispersed in toluene (2.4 mg/mL).

Table S1. Block copolymers used in this study. ^aThe average molecular weight and polydispersity index were acquired from GPC analyses. ^bThe volume fraction of PS was determined by NMR.

Polymer	Total M_n^a	$D (M_w/M_n)^a$	f_{PS}^b
PS _{22k} - <i>b</i> -P2VP _{4.7k}	27 kg/mol	1.03	0.84
PS _{27k} - <i>b</i> -P2VP _{5.8k}	33 kg/mol	1.02	0.84
PS _{41k} - <i>b</i> -P2VP _{8.7k}	50 kg/mol	1.02	0.84
PS _{82k} - <i>b</i> -P2VP _{42k}	125 kg/mol	1.03	0.68
PS _{39k} - <i>b</i> -P2VP _{67k}	106 kg/mol	1.03	0.39

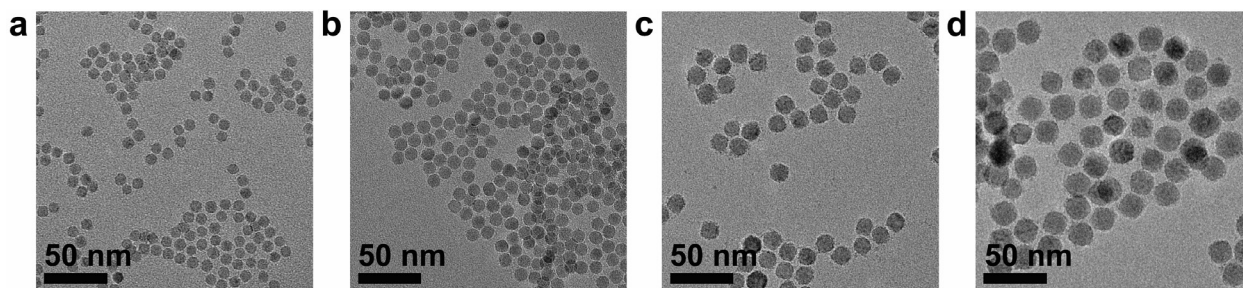


Figure S1. TEM images of iron oxide nanoparticles with varying diameters: (a) 7.5 ± 0.2 nm, (b) 10.4 ± 0.3 nm, (c) 16.0 ± 0.7 nm, and (d) 20.8 ± 1.0 nm.

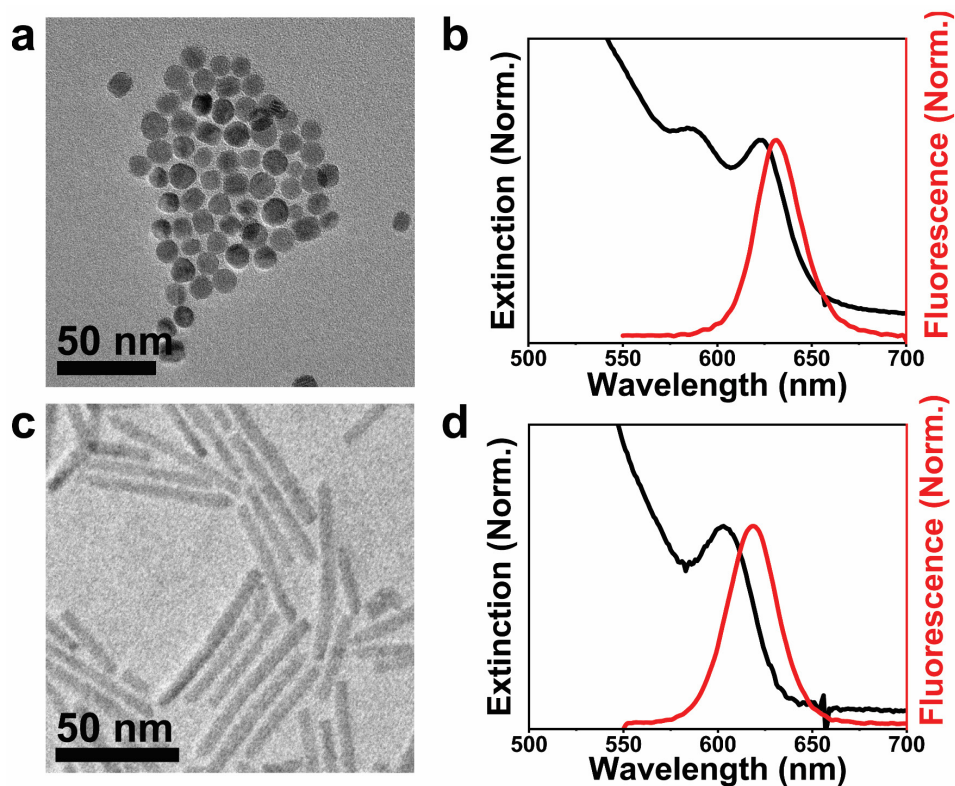


Figure S2. (a, b) TEM images (a) and UV-Vis absorption and fluorescence spectra (b) of CdSe/CdS core/shell QDs. The average size of spherical QDs is 11.7 ± 1.1 nm. (c, d) TEM images (c) and UV-Vis absorption and fluorescence spectra (d) of CdSe/CdS core/shell quantum rods. The average length and width of quantum rods are 61 ± 7.1 nm and 5.3 ± 0.5 nm, respectively.

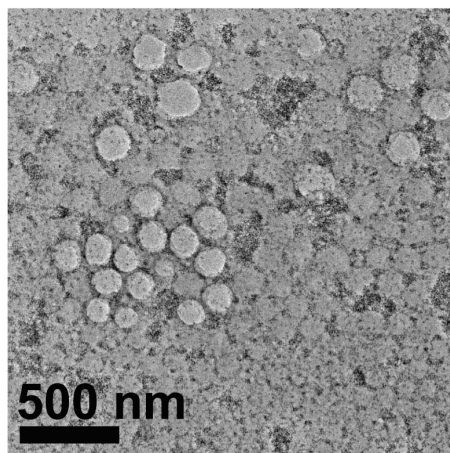


Figure S3. Self-assembly of 7.5 nm iron oxide particles and PS_{27k}-*b*-P2VP_{5.8k} formed under the fast evaporation of toluene in an open container.

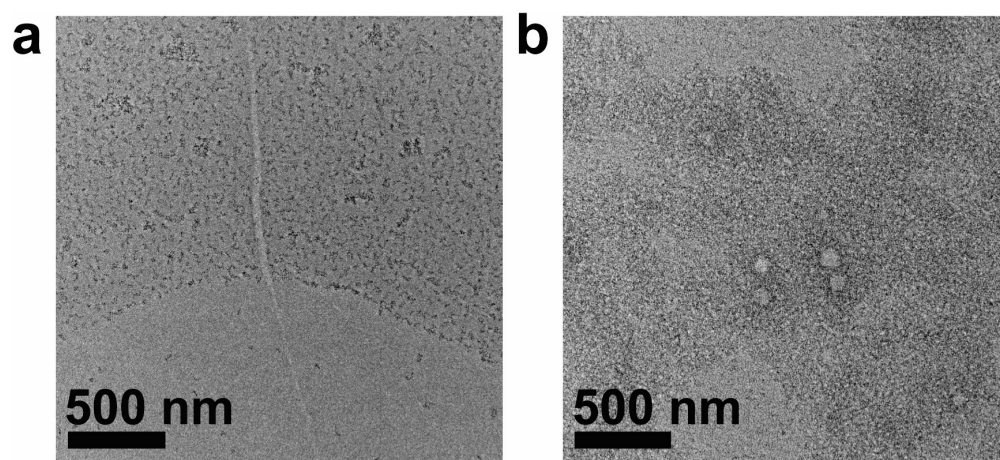


Figure S4. Interfacial self-assembly of 7.5 nm iron oxide particles and PS_{27k}-*b*-P2VP_{5.8k} with different weight fraction of nanoparticles: (a) 4.6 wt% and (b) 73 wt%.

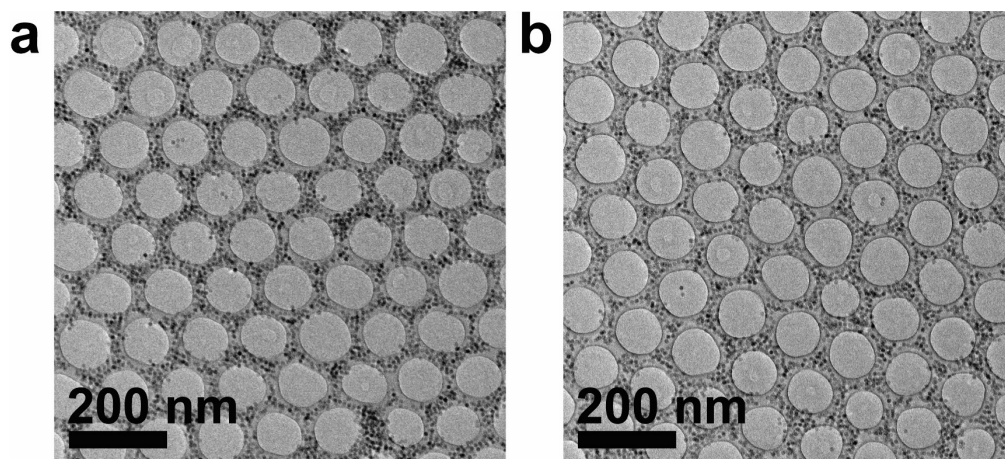


Figure S5. TEM images showing self-assembly of 7.5 nm iron oxide particles (35 wt%) and PS_{27k}-*b*-P2VP_{5.8k} (a) before and (b) after the selective staining of P2VP domains by iodine vapor.

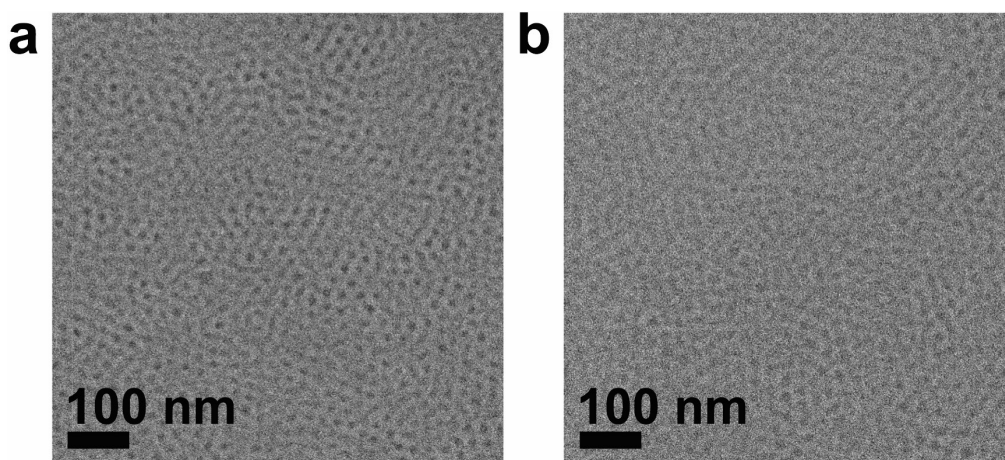


Figure S6. Interfacial self-assembly of (a) PS_{22k}-*b*-P2VP_{4.7k} and (b) PS_{41k}-*b*-P2VP_{8.7k} in the absence of nanoparticles. P2VP domains appear dark with iodine vapor staining.

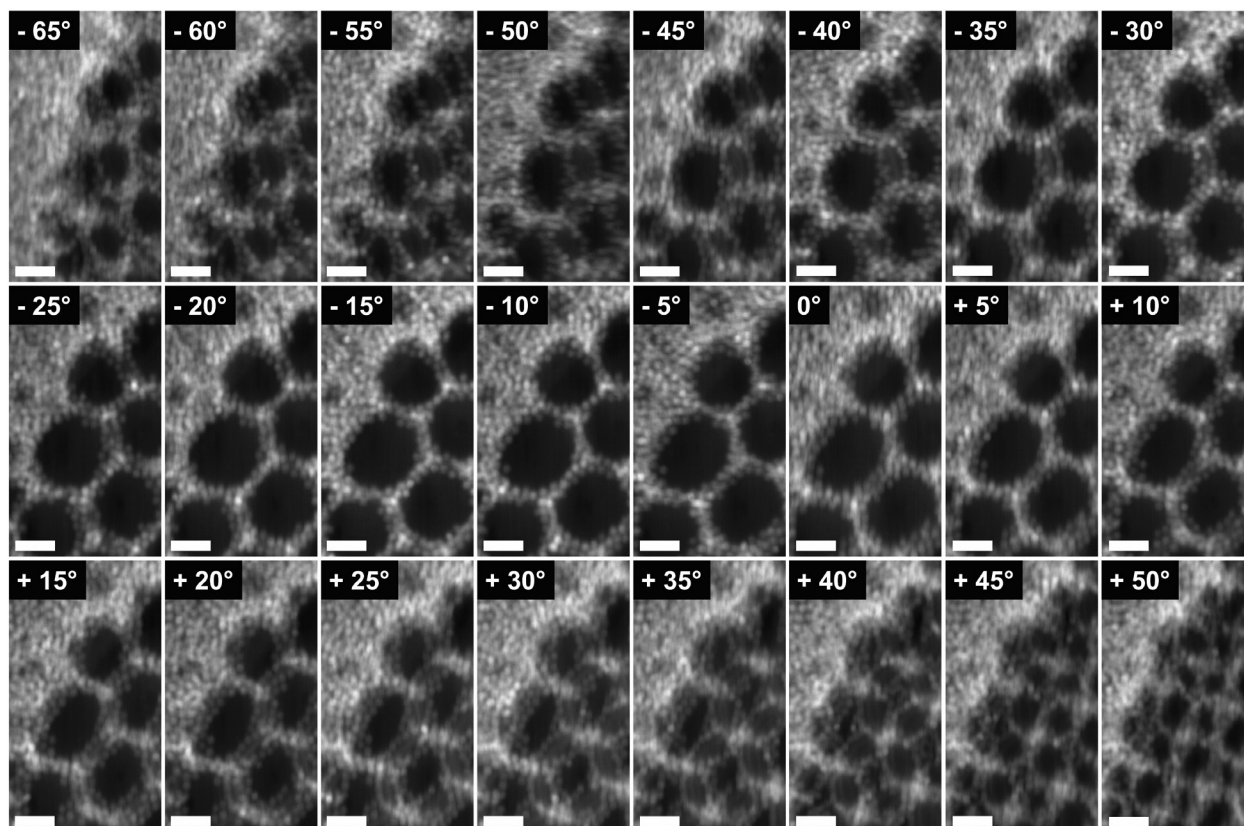


Figure S7. STEM-HAADF images taken at various tilting angles for a honeycomb-like film formed with 16.0 nm iron oxide particles and PS_{27k}-*b*-P2VP_{5.8k}. Scale bars, 100 nm.

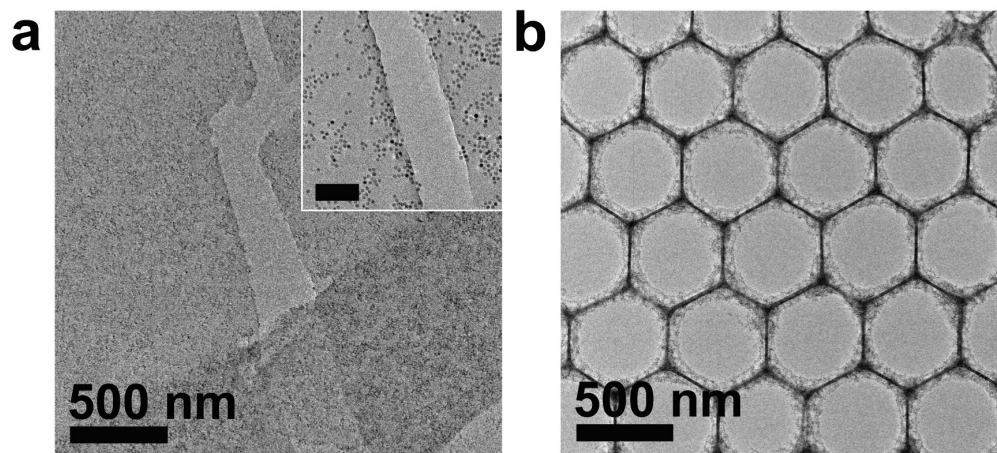


Figure S8. Self-assembly of (a) a non-amphiphilic block copolymer, polystyrene-*block*-poly(methyl acrylate) (PS_{21k}-*b*-PMA_{6.3k}) and (b) an amphiphilic block copolymer, polystyrene-*block*-poly(ethylene oxide) (PS_{7k}-*b*-PEO_{1.7k}) with 35 wt% of 7.5 nm iron oxide particles. A scale bar of the inset image, 100 nm.

References

1. Naidu, S.; Ahn, H.; Gong, J.; Kim, B.; Ryu, D. Y., Phase Behavior and Ionic Conductivity of Lithium Perchlorate-Doped Polystyrene-*b*-Poly(2-Vinylpyridine) Copolymer. *Macromolecules* **2011**, *44*, 6085-6093.
2. Park, J.; An, K.; Hwang, Y.; Park, J.-G.; Noh, H.-J.; Kim, J.-Y.; Park, J.-H.; Hwang, N.-M.; Hyeon, T., Ultra-Large-Scale Syntheses of Monodisperse Nanocrystals. *Nat. Mater.* **2004**, *3*, 891-895.
3. Hao, J.-j.; Zhou, J.; Zhang, C.-y., A Tri-*n*-Octylphosphine-Assisted Successive Ionic Layer Adsorption and Reaction Method to Synthesize Multilayered Core–Shell CdSe–ZnS Quantum Dots with Extremely High Quantum Yield. *Chem. Commun.* **2013**, *49*, 6346-6348.
4. Chen, O.; Zhao, J.; Chauhan, V. P.; Cui, J.; Wong, C.; Harris, D. K.; Wei, H.; Han, H.-S.; Fukumura, D.; Jain, R. K., Compact High-Quality CdSe–CdS Core–Shell Nanocrystals with Narrow Emission Linewidths and Suppressed Blinking. *Nat. Mater.* **2013**, *12*, 445-451.
5. Carbone, L.; Nobile, C.; De Giorgi, M.; Sala, F. D.; Morello, G.; Pompa, P.; Hytch, M.; Snoeck, E.; Fiore, A.; Franchini, I. R.; Nadasan, M.; Silvestre, A. F.; Chiodo, L.; Kudera, S.; Cingolani, R.; Krahn, R.; Manna, L., Synthesis and Micrometer-Scale Assembly of Colloidal CdSe/CdS Nanorods Prepared by a Seeded Growth Approach. *Nano Lett.* **2007**, *7*, 2942-2950.