

Pearls of Wisdom: Stringing Nanoparticles and Polymers into New Assemblies and Materials

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ABSTRACT From size considerations alone, polymers and nanoparticles should be natural partners for the preparation of composite materials. However, this prospect is more difficult than first glance would suggest, and clever synthetic, physical, and engineering considerations are required to optimize the merged value of polymers and nanoparticles. In this issue, Jeffrey Pyun and co-workers provide compelling evidence of the value of such composite materials, by stringing together magnetic nanoparticles into “pearl necklace” assemblies. In instructively interdisciplinary fashion, a full complement of polymer chemistry, nanoparticle synthesis, and nanostructural engineering (*via* solid-phase atomic diffusion) are combined to reveal artistically appealing products with novel properties that hold promise for the future of energy-storage devices and catalytic materials.

Preparative methods for nanoparticles have evolved rapidly, as solution nucleation and growth methods provide excellent size control relative to more primitive (but nonetheless useful) milling and grinding techniques. Such size control has provided new fundamental insights into the properties of nanoscale materials. Metal and semiconductor nanoparticles having identical composition to their bulk counterparts can display distinct properties (*i.e.*, fluorescence emission, magnetic, melting temperatures, *etc.*) relative to these bulk materials. Nanoparticles provide researchers with new tools for innovative exploration of many applications, including electronic materials, recording media, medical imaging devices, and solar cells, to name a few.

Polymers have likewise undergone a transformation by evolving from primarily an industrial enterprise of glues and plastics to a burgeoning field of academic intrigue and greater technological relevance. Patents and papers from General Electric, Inc. from the early 1900s described the potential importance of the “tarry residues” (polymeric byproduct) of organic reactions involving polyols and polyacids.^{1,2} Today, polymers are prepared with fine control over polydispersity and can contain any of a wide variety of functional chain ends and pendant groups, with architectural control approaching the level of proteins from Nature as seen in synthetic dendrimers. Such precise control over structure and functionality enables the generation of fine features and patterns in materials, exemplified by applying functional polymers and block copolymers to photolithography and self-assembly techniques that provide cutting-edge capabilities to the microelectronics industry.^{3,4}

Polymer—Nanoparticle Composites by Colloidal Polymerization. The parallel growth of the polymer and nanoparticle fields has naturally converged into a new field of polymer—nanoparticle composites, as expressed elegantly in Jeffrey Pyun’s article in this issue.⁵ Pyun combines state-of-the-art techniques in both nanoparticle growth and polymer synthesis to produce magnetic nanowires (more specifically, nanocomposite assemblies consisting of strings of magnetic nanoparticles that resemble pearl necklaces) that could not be realized by blending nanoparticles arbitrarily, with or without polymers, in any ratio and under any processing conditions. Using so-called “colloidal polymerization” techniques, Pyun exploits the ferromagnetic properties of Co nanoparticles in dipolar assembly, stringing them together into micrometer-length wires. Interestingly, these nanoparticle wires exhibit a characteristic length distribution that likens the nanoparticle stringing process to monomer/polymer coupling that is the kinetic basis of classic step-growth polymerization.

Pyun diversifies the properties of these Co nanowires by introducing porosity to the materials without disrupting the preorganized nanoparticle chains. Hollow inclu-

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sions are introduced to each individual nanoparticle embedded within the strings through a nanoscale version of the classic Kirkendall effect.⁶ Oxidation of the Co nanoparticle strings, performed by bubbling O₂ gas into a solution of dispersed strings, affords a surface cobalt oxide layer on each particle and a hollowing of the particle interior as Co atoms migrate from the center to the exterior, filling vacancies as they do so. Such strategic manipulation of Co nanoparticle structures was shown by Alivisatos and co-workers, who prepared hollow CoO and Co₃S₄ nanostructures using the Kirkendall principles.⁷ Such hollow nanoscale objects have great potential in applications where encapsulation and high surface areas are advantageous; along these lines, the gas permeability into the hollow nanoparticle interior (likely through grain boundaries on the shell) and activity of the hollow particles in heterogeneous catalysis have been demonstrated. Following magnetic-field-induced alignment of the Co particles into necklace-like strands, the assemblies could be converted to strands of hollow Au by galvanic exchange.⁸

So where do polymers come into play in Pyun's colloidal polymerization? This Co nanoparticle necklace design hinges on a well-defined polymer functionalization of the Co nanoparticle surface. The polystyrene ligands are held on the Co surface by coordinating amines or phosphine oxides, placed intentionally at the polystyrene chain end. The uniform and well-defined polymer coating on each nanoparticle is enabled by the use of low-polydispersity polymer ligands, prepared by state-of-the-art living free-radical polymerization. The polystyrene coating serves multiple purposes, perhaps most importantly giving the nanoparticles (and the resultant nanowires) the critically important dispersibility and processability that prevents their irreversible aggregation, even allowing their ready-storage in the

solid state as powders. Such aggregation, a classic problem in nanoparticle synthesis and processing, is exacerbated by the strong dipolar interactions of Co nanoparticles. In addition to enabling particle dispersion, the polymer chains tune the "strength" of the dipolar assembly: longer chains weaken interparticle interactions, while shorter chains permit strong particle-particle coupling. Pyun exploits this subtle feature of the polymer coating by tuning the polymer ligand length to optimize the colloidal polymerization process, while simultaneously tailoring the oxidation chemistry such that growth of the cobalt oxide corona on one particle surface fuses it to the cobalt oxide coronas of its neighbors. In a final step, calcination of the now-fused nanowires at 400 °C removes the polystyrene shell but maintains the one-dimensional (1-D) morphology of the structures, as well as the porous inclusions. As shown in Figure 1, transmission electron microscopy (TEM) images of these 1-D nanostructures at all stages of the assembly process are striking and revealing of the sophisticated types of structures that can be generated through combining the properties, functionality, and size scale of polymers and nanoparticles. Notably, this work represents far more than aesthetic nanoassembly, as an extensive array of spectroscopic and electrochemical characterization techniques showed these CoO nanowires to be electroactive semiconductors, of interest for applications as energy-storage devices.

Template Directors. Template-free nanoparticle assembly methods, such as Pyun demonstrates, are convenient and powerful, and the concept can be generalized to many types of nanoparticle assembly, such as colloidal crystallization, nanoparticle superlattices, and various types of interfacial mediation using nanoparticles. However, template-driven or template-directed assembly provides access to a rich array of nanostructured

materials, in which the template can function solely as the director or, alternatively, as an active functional contributor to the assembled nanomaterial. Consider the ex-

Diblock copolymers are uniquely suited for directing nanoparticle assembly, as the inherent length scale of the polymer domains in microphase-separated diblock copolymers is ideal for nanoparticle localization and patterning.

amples of self-assembled lamellar and cylindrical diblock copolymer structures, containing polymer stripes and cylinders of controllable dimensions (ranging from a few nanometers to tens-of-nanometers).⁹ Removal of one of the components creates voids, in the form of "cups" and "trenches", that can be used for nanoparticle and nanorod deposition in what can be envisioned as a "nanogolf" event.^{10,11} While the relative sizes and shapes of the nanoparticles and voids are essential parameters (the objects have to fit in the holes), interfacial forces largely determine the success of the deposition, and as such, the nature of the nanoparticle ligands is critically important.

Surface-binding ligands can be embedded within diblock copolymer templates using functional diblock copolymers for the assembly process; more simply, nanoparti-

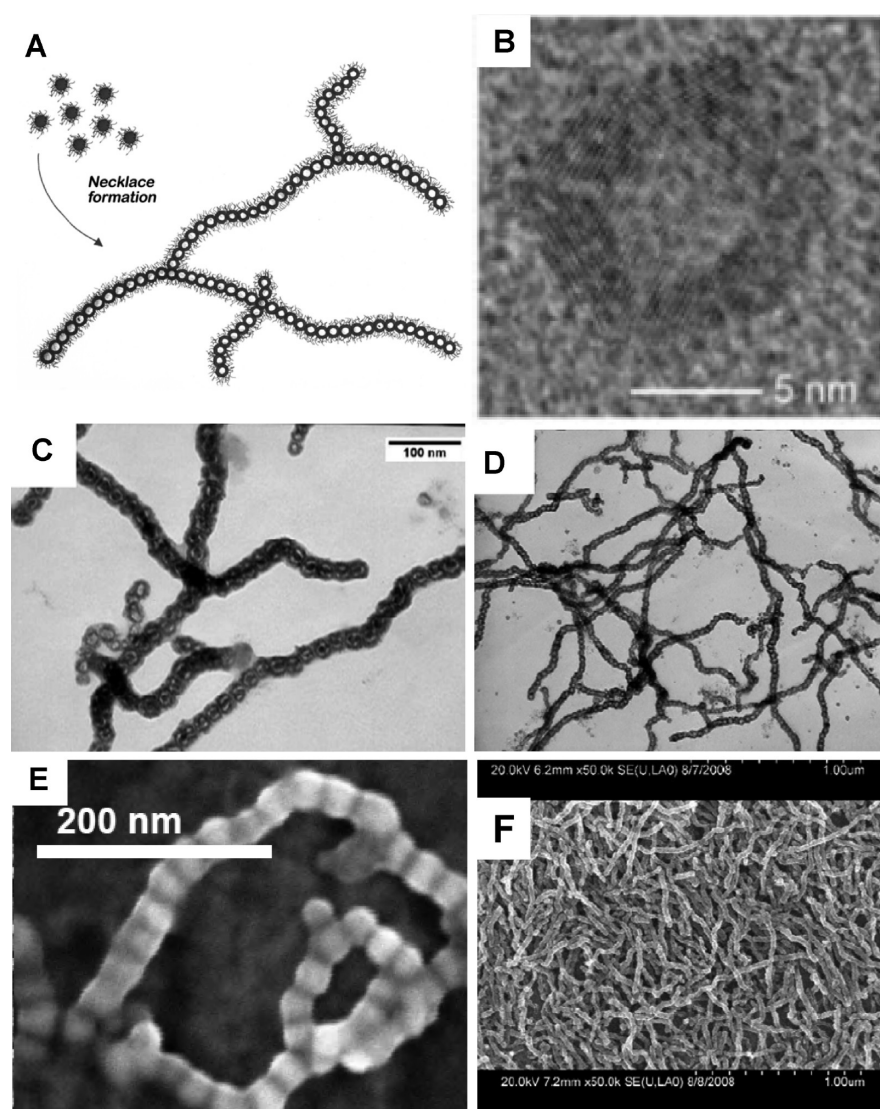


Figure 1. (A) Free-hand sketch depicting a branched nanoparticle necklace formed by colloidal polymerization. (B) High-resolution TEM image of a hollow cobalt oxide nanocrystal. (C) TEM image of polystyrene-coated cobalt oxide nanoparticle necklace, prepared from 20 nm diameter particles, after 3 h of oxidation. (D) Necklaces after storage for 1 week. (E) High-magnification field-effect scanning electron microscopy (SEM) image of discrete chains on indium tin oxide. (F) Low-resolution SEM image of calcined necklaces. Panel B reproduced with permission from ref 7. Copyright 2004 AAAS (www.sciencemag.org). Panels C–F reproduced from ref 5. Copyright 2009 American Chemical Society.

cles can be functionalized with ligands designed to interact less favorably with one region of the template, thus driving their localization into the other region. Diblock copolymer nanoparticle assemblies can also be fabricated without removing one of the blocks. Functionalization of nanoparticles to promote their segregation into one of the copolymer domains is straightforward, in principle, and has been demonstrated many times in practice, despite the complexities that arise when “nanofillers” are present

during the course of block copolymer self-assembly. Nanoparticles can also be localized selectively to the center of domains or to the interface of microphase-separated diblock copolymers. Guided by theoretical treatments that consider enthalpic and entropic contributions to such localization, such as those of Balazs,¹² experimentalists have designed clever methods for doing just that. Hawker and co-workers show that Au nanoparticles, when covered with mixed monolayers of polystyrene (PS)

thiol and poly(2-vinyl pyridine) (P2VP) segregate to the PS–P2VP diblock interface, decoratively tagging the interface with “strings” of nanoparticles.¹³ The mobility of the thiol head groups on the Au particle surface, and thus the ability of the ligands to phase separate and to minimize the free energy of the composite assembly, contributes to the effectiveness of this system. However, polymer ligands are not always needed to generate such nanocomposite structures; mixed monolayers of small-molecule ligands on Au nanoparticles, where the ligands can interact with the polymer matrix by hydrogen bonding, provide similar assemblies. Having a small-molecule ligand coating permits a thermal responsiveness to these nanocomposites, in which particle ripening drives a rearrangement in nanoparticle localization within the diblock copolymer structure.¹⁴ Examples of such nanoparticle deposition, segregation, and interface tagging in polymer nanoparticle composites are shown in Figure 2. Notably, the free energy picture of nanoparticle interfacial mediation in these melt and solid-state systems mirrors qualitatively the case of nanoparticle segregation to an oil–water interface, in which monolayers of nanoparticles encase water droplets in oil or oil droplets in water.¹⁶ Polymerization of the ligands on such droplet assemblies provides robust structures with potential utility in encapsulation and release technologies.

Choosing Pearls; Diversifying Strings.

Focusing efforts on nanoparticle ligands has led to a number of necklace-like structures of the type Pyun described. For example, mixed monolayers on Au nanoparticles, designed to expose carboxylic acids on either pole, act as “A₂” monomers in what can be viewed as an A₂ + B₂ polycondensation, by amidation chemistry at an oil–water interface.¹⁷ This nanoparticle version of the “nylon rope trick”, well-known from popular grade-school demon-

strations, creates necklaces of Au nanoparticles. Kotov has shown that careful depletion of the surface density of conventional carboxylate ligands on CdTe quantum dots drives the formation of highly fluorescent necklaces, the morphology of which is remarkably robust, even without introducing ligand cross-linking to the assemblies.¹⁸ Gold nanoparticles can be aligned similarly, where the strongly coupled surface plasmons drive the chain formation;¹⁹ similar chain-alignment effects could be realized in hollow versions of Au nanospheres, as well.⁸

Polymer and Inorganic “Nano-Objects”. Nanoporous structures have been exploited to prepare objects that are used further in self-assembly techniques. Russell and co-workers fabricated high-density arrays of Co nanowires by electrodeposition methods using diblock copolymer templates,²⁰ while McCarthy showed that polymer objects, with dissimilarly shaped ends, are conveniently prepared by polymer uptake (by capillary forces) into porous alumina membranes.²¹

What happens when the nano-object contains well-defined inorganic and polymer components within the individual structure? Mirkin reported elegant two-dimensional (2-D) and three-dimensional (3-D) assemblies from mesoscopic (*i.e.*, *Small*, but not strictly nano) polymer–inorganic rods, generated by electrodeposition of Au into a porous Al template, followed by electrochemical polymerization of pyrrole.²² Bundle assemblies formed from these Au–polypyrrole rods are driven by the strongly interacting polymer ends. By varying the Au-to-polymer ratio, 3-D tubular structures are achieved. Using

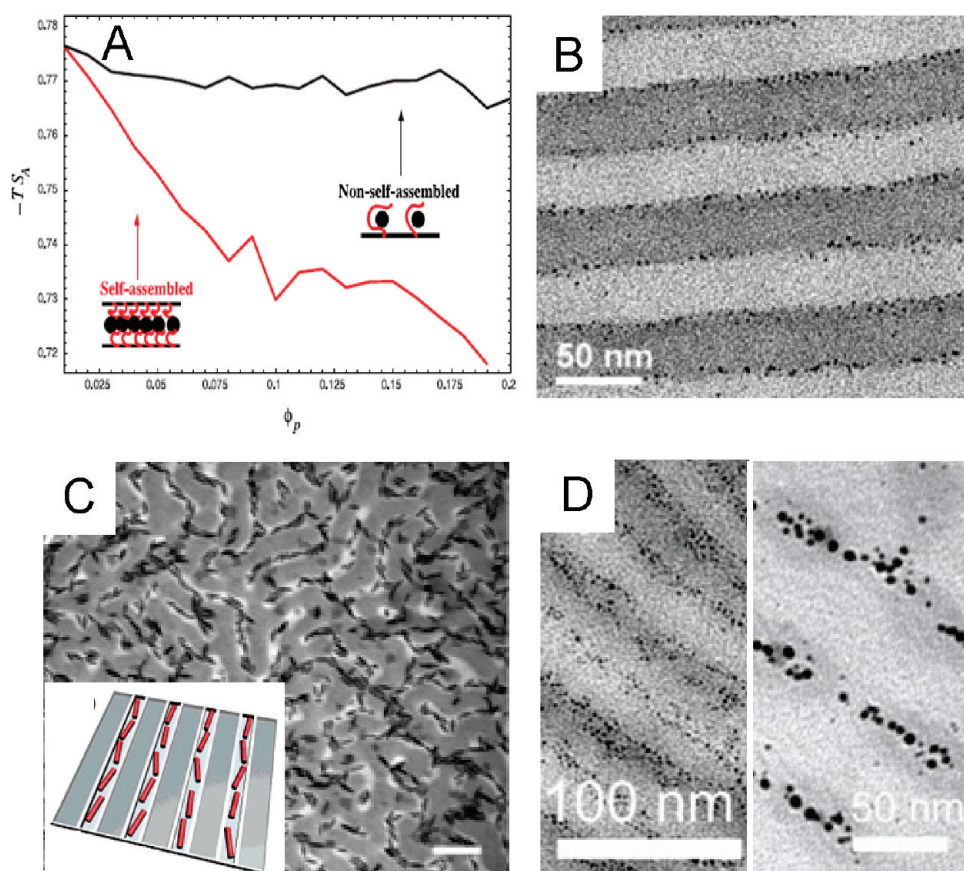


Figure 2. (A) Chain-stretching “entropic penalty” expressed as a plot of the conformational entropic free energy contribution ($-TS_A$) per polymer chain for large particles ($R = 0.3R_0$, red curve) and small particles ($R = 0.15R_0$, black curve), as a function of the particle volume fraction in the nanocomposite. (B) Cross-sectional TEM image of polymer-functionalized Au nanoparticles localized to the PS–P2VP diblock copolymer interface. (C) TEM micrograph of poly(ethylene oxide)-covered CdSe nanorods embedded in the trenches of diblock copolymer template (inset, idealized lamellar structure of this assembly product; scale bar 100 nm). (D) Thermally responsive Au nanoparticle–polymer composite: (left) initial interfacial assembly; (right) localization after thermal annealing and particle ripening. Panel A reproduced with permission from ref 15. Copyright 2001 AAAS (www.sciencemag.org). Panel B reproduced from ref 13. Copyright 2007 American Physical Society. Panel C reproduced from ref 11. Copyright 2006 American Chemical Society. Panel D reproduced with permission from ref 14. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

Au nanorods functionalized with PS at each chain end, Kumacheva demonstrated exquisite control over their 1-D assembly.²³ These nanostructures, analogous to ABA triblock copolymers, introduce hydrophobic polymers on either side of the hydrophilic Au rod, which allows their assembly into a range of geometries (including end-to-end chains akin to bugle-bead bracelets) by simply tuning solvent strength and using solvent mixtures. The assembly of Au nanorods leads to the coupling of longitudinal surface plasmons, resulting in substantial shifts in the absorption spectra relative to the rods dispersed in solution. By employing small-molecule

linkers, such as amino acids, the distance between the assembled rods could be reduced, resulting in stronger surface plasmon coupling.²⁴

Polymer micelles also form useful objects and add considerable breadth to the range of feasible assembly options, as exploited recently by Hayward for the assembly of magnetic nanoparticles.²⁵ Polystyrene-*block*-poly(ethylene oxide) (PS–PEO) structures, obtained at the interface of a dried droplet, give either spherical or wormlike micelles which take up polystyrene-covered iron oxide nanoparticles, embedding them as lines of particles within the micellar nanostructure. A range of assemblies possible

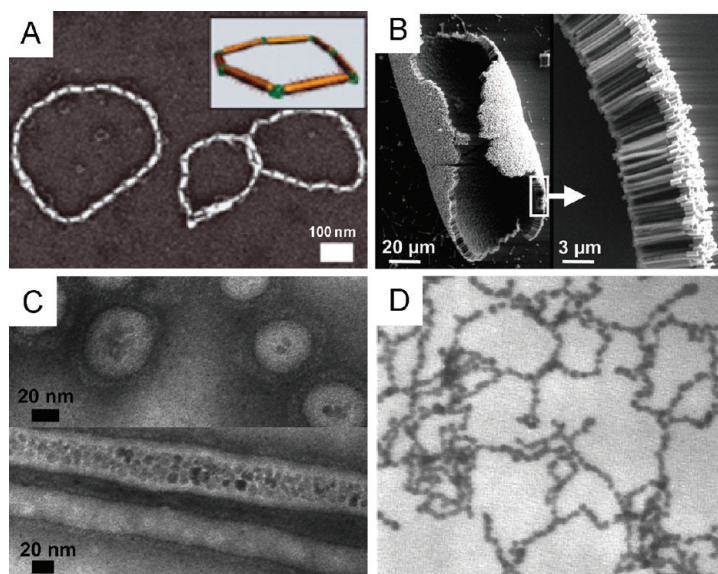


Figure 3. (A) Self-assembled, PS-tethered, Au nanorod necklaces. (B) SEM image of Au-polypyrrole rod objects. (C) TEM images of FeO nanoparticle-filled micelles formed by interfacial instabilities of emulsion droplets containing amphiphilic block copolymers. (D) TEM image of intermediate state of fluorescent strings of CdTe quantum dots. Panel A reproduced with permission from ref 30. Copyright 2008 Nature Publishing Group (<http://www.nature.com/nmat>). Panel B reproduced with permission from ref 22. Copyright 2004 AAAS (<http://www.sciencemag.org>). Panel C reproduced from ref 26. Copyright 2006 American Chemical Society. Panel D reproduced from ref 18. Copyright 2002 AAAS (<http://www.sciencemag.org>).

from such nano-objects is shown in Figure 3.

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OUTLOOK

While the scope of polymer-nanoparticle composite research is too broad to cover thoroughly in this Perspective, Pyun's article can guide researchers who seek innovative methods for assembling nano-objects that offer novel

and enabling optoelectronic properties. While dispersing nanoparticles in polymers can provide definitive improvements in mechanical properties over polymers alone, many in the field now look to photophysical and charge transfer aspects of such nanocomposite structures, for example, by tailoring the surface of quantum-confined nanoparticles with conjugated polymers. These efforts have already led to higher efficiency of solution-processable (nonsilicon) solar cells²⁷ and brighter displays²⁸ and, moreover, provide clues into the complex optoelectronic behavior of quantum dots as manifested in their blinking statistics (*i.e.*, the temporal stability of their photoluminescence emission)²⁶ and other emission characteristics in which the polymer ligand and quantum dot core interact.²⁹ New efforts to bring polymer chemistry, specifically polymer functionalization, to all-carbon "nanoparticles" (fullerenes, carbon nanotubes, and graphene sheets) are also fruitful. Some examples

include (1) comparative studies of solar cells prepared from polythiophene-fullerene blend morphologies³⁰ compared to those in which polythiophene is covalently bound to the fullerenes;^{31,32} (2) click chemistry to connect polymers with carbon nanotubes,³³ thus increasing processability and dispersion of the tubes in polymer matrices; and (3) bottom-up chemical approaches toward polymer-graphene composite structures.³⁴ The rapid increase in pace of such studies assures researchers that polymer-nanoparticle composite research is a long-term mission with impact that can only be realized through understanding the interface, or the connectivity, between the polymers and particulate components of any composite system. Pyun's article provides graphic visualization of this connectivity and inspiration to focus on the polymer-nanoparticle interface in the continuing quest for generating new materials with novel properties.

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REFERENCES AND NOTES

- Callahan, M. J. U.S. Patent 1,091,627, 1914.
- Kienle, R. H.; Hovey, A. G. The Polyhydric Alcohol-Polybasic Acid Reaction. I. Glycerol-Phthalic Anhydride. *J. Am. Chem. Soc.* **1929**, *51*, 509-519.
- Hawker, C. J.; Russell, T. P. Block Copolymer Lithography: Merging "Bottom-Up" with "Top-Down" Processes. *MRS Bull.* **2005**, *30*, 952-966.
- Macdonald, S. A.; Willson, C. G.; Frechet, J. M. J. Chemical Amplification in High-Resolution Imaging Systems. *Acc. Chem. Res.* **1994**, *27*, 151-158.
- Keng, P. Y.; Kim, B. Y.; Shim, I.-B.; Sahoo, R.; Veneman, P. E.; Armstrong, N. R.; Yoo, H.; Pemberton, J. E.; Bull, M. M.; Griebel, J. J. *et al.* Colloidal Polymerization of Polymer Coated Ferromagnetic Nanoparticles into Cobalt Oxide Nanowires. *ACS Nano* **2009**, *3*, 3143-3157.

6. Smigelskas, A. D.; Kirkendall, E. O. Zinc Diffusion in Alpha-Brass. *Trans. AIME* **1947**, *171*, 130–142.
7. Yin, Y. D.; Rioux, R. M.; Erdonmez, C. K.; Hughes, S.; Somorjai, G. A.; Alivisatos, A. P. Formation of Hollow Nanocrystals through the Nanoscale Kirkendall Effect. *Science* **2004**, *304*, 711–714.
8. Zeng, J.; Huang, J.; Lu, W.; Wang, X.; Wang, B.; Zhang, S.; Hou, J. Necklace-like Noble-Metal Hollow Nanoparticle Chains: Synthesis and Tunable Optical Properties. *Adv. Mater.* **2007**, *19*, 2172–2176.
9. Tsui, O. K. C.; Russell, T. P. *Polymer Thin Films*; World Scientific Publishing: River Edge, NJ, 2008.
10. Misner, M. J.; Skaff, H.; Emrick, T.; Russell, T. P. Directed Deposition of Nanoparticles Using Diblock Copolymer Templates. *Adv. Mater.* **2003**, *15*, 221–224.
11. Zhang, Q.; Gupta, S.; Emrick, T.; Russell, T. P. Surface-Functionalized CdSe Nanorods for Assembly in Diblock Copolymer Templates. *J. Am. Chem. Soc.* **2006**, *128*, 3898–3899.
12. Lee, J. Y.; Thompson, R.; Jasnow, D.; Balazs, A. C. Entropically Driven Formation of Hierarchically Ordered Nanocomposites. *Phys. Rev. Lett.* **2002**, *89*, 155503-1–155503-4.
13. Kim, B. J.; Bang, J.; Hawker, C. J.; Chiu, J. J.; Pine, D. J.; Jang, S. J.; Yang, S. M.; Kramer, E. J. Creating Surfactant Nanoparticles for Block Copolymer Composites through Surface Chemistry. *Langmuir* **2007**, *23*, 12693–12703.
14. Li, Q. F.; He, J. B.; Glogowski, E.; Li, X. F.; Wang, J.; Emrick, T.; Russell, T. P. Responsive Assemblies: Gold Nanoparticles with Mixed Ligands in Microphase Separated Block Copolymers. *Adv. Mater.* **2008**, *20*, 1462–1466.
15. Thompson, R. B.; Ginzburg, B. B.; Matsen, M. W.; Balazs, A. C. Predicting the Mesophases of Copolymer–Nanoparticle Composites. *Science* **2001**, *292*, 2469–2472.
16. Lin, Y.; Skaff, H.; Emrick, T.; Dinsmore, A. D.; Russell, T. P. Nanoparticle Assembly and Transport at Liquid–Liquid Interfaces. *Science* **2003**, *299*, 226–229.
17. DeVries, G. A.; Brunnbauer, M.; Hu, Y.; Jackson, A. M.; Long, B.; Neltner, B. T.; Uzun, O.; Wunsch, B. H.; Stellacci, F. Divalent Metal Nanoparticles. *Science* **2007**, *315*, 358–361.
18. Tang, Z.; Kotov, N. A.; Giersig, M. Spontaneous Organization of Single CdTe Nanoparticles into Luminescent Nanowires. *Science* **2002**, *297*, 237–240.
19. Lin, S.; Li, M.; Dujardin, E.; Girard, C.; Mann, S. One-Dimensional Plasmon Coupling by Facile Self-Assembly of Gold Nanoparticles into Branched Chain Networks. *Adv. Mater.* **2005**, *17*, 2553–2559.
20. Thurn-Albrecht, T.; Schotter, J.; Kastle, G. A.; Emley, N.; Shibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C. T.; Tuominen, M. T.; Russell, T. P. Ultrahigh-Density Nanowire Arrays Grown in Self-Assembled Diblock Copolymer Templates. *Science* **2000**, *290*, 2126–2129.
21. Moon, S. I.; McCarthy, T. J. Template Synthesis and Self-Assembly of Nanoscopic Polymer “Pencils”. *Macromolecules* **2003**, *36*, 4253–4255.
22. Park, S.; Lim, J.-H.; Chung, S.-W.; Mirkin, C. A. Self-Assembly of Mesoscopic Metal–Polymer Amphiphiles. *Science* **2004**, *303*, 348–351.
23. Nie, Z.; Fava, D.; Kumacheva, E.; Zou, S.; Walker, G. C.; Rubinstein, M. Self-Assembly of Metal–Polymer Analogues of Amphiphilic Triblock Copolymers. *Nat. Mater.* **2007**, *6*, 609–614.
24. Sudeep, P. K.; Shibu Joseph, S. T. S.; Thomas, K. G. Selective Detection of Cysteine and Glutathione Using Gold Nanorods. *J. Am. Chem. Soc.* **2005**, *127*, 6516–6517.
25. Zhu, J.; Hayward, R. C. Spontaneous Generation of Amphiphilic Block Copolymer Micelles with Multiple Morphologies through Interfacial Instabilities. *J. Am. Chem. Soc.* **2008**, *130*, 7496–7502.
26. Odoi, M. Y.; Hammer, N. I.; Sill, K.; Emrick, T.; Barnes, M. D. Observation of Enhanced Energy Transfer in Individual Quantum Dot–Oligophenylene Vinylene Nanostructures. *J. Am. Chem. Soc.* **2006**, *128*, 3506–3507.
27. Saunders, B. R.; Turner, T. L. Nanoparticle–Polymer Photovoltaic Cells. *Adv. Colloid Interface Sci.* **2008**, *138*, 1–23.
28. Wood, V.; Panzer, M. J.; Chen, J. L.; Bradley, M. S.; Halpert, J. E.; Bawendi, M. C.; Bulovic, V. Inkjet-Printed Quantum Dot–Polymer Composites for Full-Color AC-Driven Displays. *Adv. Mater.* **2009**, *21*, 2151–2155.
29. Sudeep, P. K.; Sill, K.; McCarthy, M. 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*, 384–2385.
30. Campoy-Quiles, M.; Ferenczi, T.; Agostinelli, T.; Etchegoin, P. G.; Kim, Y.; Anthopoulos, T. D.; Stavrinou, P. N.; Bradley, D. D. C.; Nelson, J. Morphology Evolution via Self-Organization and Lateral and Vertical Diffusion in Polymer:Fullerene Solar Cell Blends. *Nat. Mater.* **2008**, *7*, 158–164.
31. Zhou, Z. Y.; Chen, X. W.; Holdcroft, S. Stabilizing Bicontinuous Nanophase Segregation in π CP-C₆₀ Donor–Acceptor Blends. *J. Am. Chem. Soc.* **2008**, *130*, 11711–11718.
32. Yang, C.; Lee, J. K.; Heeger, A. J.; Wudl, F. Well-Defined Donor–Acceptor Rod–Coil Diblock Copolymers Based on P3HT Containing C₆₀: The Morphology and Role as a Surfactant in Bulk-Heterojunction Solar Cells. *J. Mater. Chem.* **2009**, *19*, 5416–5423.
33. Li, H. M.; Cheng, F. O.; Duft, A. M.; Adrnov, A. Functionalization of Single-Walled Carbon Nanotubes with Well-Defined Polystyrene by “Click” Coupling. *J. Am. Chem. Soc.* **2005**, *127*, 14518–14524.
34. Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. Graphene-Based Composite Materials. *Nature* **2006**, *442*, 282–286.