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Spotlight on Applications

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Colloidal Polymers via Dipolar Assembly of Magnetic Nanoparticle Monomers

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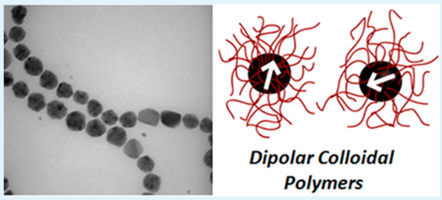

ABSTRACT: In this Spotlight on Applications, we describe our recent progress in the preparation of hierarchical one-dimensional (1-D) materials constructed from polymer-coated ferromagnetic cobalt nanoparticles. We begin with a general discussion of nanoparticles capable of 1-D self-organization to form 1-D assemblies, which we term *colloidal polymers*. The need for efficient, highly directional interactions prompted our investigation with polymer-coated ferromagnetic nanoparticles, which spontaneously form linear assemblies through coupling of north and south magnetic poles present in these single-domain ferromagnetic nanoparticles. These highly directional N−S interactions and the resulting formation of 1-D assemblies can be understood in the context of traditional polymer-forming reactions. The dipolar assembly of these ferromagnetic nanoparticles into chains and binary assemblies while dispersed in organic media has been investigated as a key foundation to form novel magnetic materials and heterostructured nanocomposites. These studies enabled the fabrication of magnetic nanoactuating systems resembling "artificial cilia and flagella". We then discuss our recent efforts to prepare cobalt oxide nanowires using various nanoparticle conversion reactions through a process termed *colloidal polymerization*. A series of novel functional "colloidal monomers" based on dipolar cobalt nanoparticles were also prepared, incorporating noble metal or semiconductor nanoinclusions to form heterostructured cobalt oxide nanocomposites.

KEYWORDS: *colloidal polymerization, colloidal polymers, cobalt nanoparticles, magnetic nanoparticles, dipolar assembly, cobalt oxide nanowires*

INTRODUCTION

In this Spotlight on Applications, we discuss the concept of using inorganic magnetic nanoparticles (MPs) to construct mesoscopic chains, termed *colloidal polymers*. One of the fundamental tenets of polymer science is the development of new monomers and polymerization methods to prepare novel polymeric materials possessing useful properties. While it is well-established that the controlled connectivity of small-molecule monomers into macromolecules enables the emergence of unique properties, the expansion of this paradigm to the polymerization of nanoparticles is still in its infancy.

The utilization of nanoparticles as "colloidal molecules" has gained significant recent attention as a route to prepare well-defined colloidal nanocrystals and polymer-like one-dimensional (1-D) mesostructures.[1−7] The 1-D assembly of particulate materials has been long been known in the area of colloid science, notably in systems such as magneto- and electrorheological fluids.[8−12] More recently, a wide range of magnetic polymeric beads or droplets have been utilized to form 1-D colloidal chains.[13−23] Asymmetric polymer colloids prepared via lithographic methods have also been observed to self-assemble into phase-separated copolymer-like domains.[24] In principle, 1-D assembly of colloids is phenomenologically identical to polymerization of nanoparticles, or *colloidal polymerization*. However, classical polymer science provides an established conceptual framework to direct the synthesis of 1-D nanoparticle assemblies with respect to structural features such as degree of polymerization, architecture (linear vs branched), and composition (homopolymers vs copolymers). *Hence, the application of the "principles of polymerization"*[25] *to nanoparticles as "colloidal monomers" offers a new approach to prepare new 1-D mesoscopic inorganic materials from the polymerization of nanoparticles as monomers.*

One of the major challenges in achieving polymerization of colloidal monomers is the need to embed strongly associative, highly directional interactions to form NP chains that overcome thermal fluctuations. Dipolar nanoparticles, based on cadmium telluride (CdTe) semiconductor nanoparticles reported by Kotov and co-workers,[26−28] demonstrated dipolar assembly and nanowire formation as a consequence of inherent electrostatic dipole−dipole associations between colloidal monomers. However, most nanoparticle compositions do not have an inherent electrostatic dipole and therefore do not undergo

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spontaneous 1-D assembly because of their isotropic reactivity. To overcome this challenge, selective functionalization of nanoparticle surfaces has been leveraged to induce anisotropic associations in colloidal monomer units. In an elegant example, Stellacci and co-workers utilized point defects in the ligand coverage on NPs (Au, Fe_3O_4) to form 1-D colloidal polymer chains.[7,29−31] Recent work by Kumacheva and co-workers has reported on differential ligand functionalization of Au nanorods with cetylammonium bromides occupying lateral nanorod facets and polystyrene-terminated thiol ligands (PS-SH) passivating the terminal ends of Au nanorods to promote polymerization upon exposure to selective solvent mixtures (Figure 1a,b).[32−40] The polymerization kinetics of these patchy PS−Au nanorods has been extensively studied and modeled after classical step-growth polymerization processes to form plasmonic colloidal polymers, also termed "nanopolymers".[34,41] Block-copolymer-encapsulated gold nanoparticles (AuNPs) have also been polymerized into colloidal polymer chains upon treatment with charged carboimide coupling agents by Taton and co-workers to induce sphere-to-string transitions to form plasmonic NP chains.[42,43] Chen and co-workers reported on "unconventional chain growth" colloidal polymerization of block-copolymer-encapsulated AuNPs to give a variety of different motifs by controlled destabilization of copolymer ligands (Figure 1c).[44−48] While these seminal systems demonstrate the viability of this overall synthetic approach, the development of robust and versatile synthetic methods to prepare colloidal monomers that undergo efficient 1-D polymerization remains an important challenge.

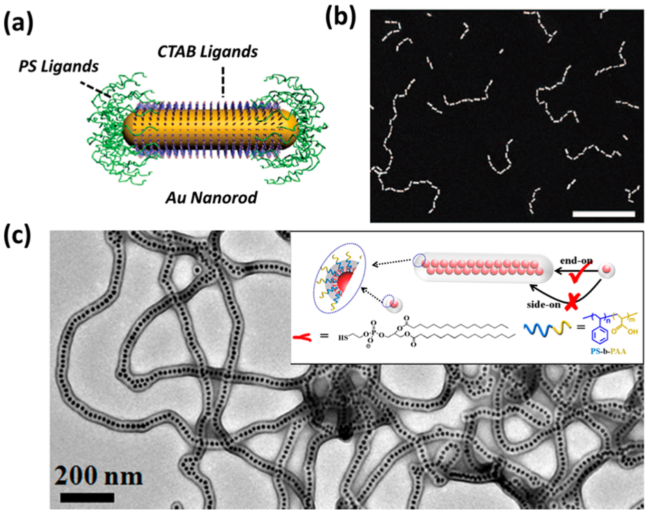

Figure 1. Examples of colloidal monomers and polymers: (a) patchy Au nanorods[33] and (b) colloidal polymers formed in selective solvent mixtures;[34] (c) polystyrene-*block*-poly(acrylic acid)-capped AuNPs that polymerize via a chain-growth-type process to form micrometer size colloidal polymer chains.[48] (a) Adapted with permission from ref 33. Copyright 2008 American Chemical Society. (b) Reproduced from ref 34. Copyright 2010 and reprinted with permission from AAAS. (c) Adapted with permission from ref 48. Copyright 2012 Wiley.

Magnetic dipolar nanoparticles based on ferromagnetic (e.g., Fe, Co, Ni) or ferrimagnetic (e.g., Fe_3O_4) materials have been long been known to polymerize and form colloidal polymer chains as a result of the magnetic spin dipoles on the discrete nanoparticle units.[49−53] The formation of nanoparticle chains of Fe_3O_4 colloids in magnetotactic bacteria is a naturally occurring example of the type of colloidal assemblies that form as a consequence of strong and directional magnetic north pole−south pole (N−S) dipolar associations.[54] Over the past decade, our group has elaborated upon these magnetic dipolar NPs with a focus on polymer-coated ferromagnetic cobalt nanoparticles to prepare a wide range of colloidal polymers (Figure 2).[55−70] In particular, we have focused on the development of facile and robust synthetic methods to prepare well-defined dipolar cobalt nanoparticles (CoNPs) in appreciable quantities, which further enabled the study of colloidal assemblies in solution and on surfaces. The use of ferromagnetic CoNPs proved to be advantageous, as the chemistry of these colloids was readily modified to introduce either noble-metal (i.e., Au, Pt), or semiconductor (CdSe@CdS) nanoinclusions to form dipolar heterostructured colloids. Furthermore, all of these dipolar CoNPs could be chemically converted to form permanently linked cobalt oxide (Co_3O_4) nanowires via a process termed *colloidal polymerization*.

In this report, we review the synthesis, assembly, polymerization, and characterization of dipolar colloidal monomers based on ferromagnetic CoNPs and other dipolar heterostructured cobalt colloids, with an emphasis on our recent efforts in this area. For reviews of the fundamental aspects of nanoparticle synthesis and assembly, the reader is directed elsewhere.[71−83]

■ SYNTHESIS OF FERROMAGNETIC NANOPARTICLE COLLOIDAL MONOMERS

The preparation of ferromagnetic metallic magnetic nanoparticles has historically been achieved by thermolysis of metal carbonyl complexes [e.g., $Fe(CO)_5$, $Co_2(CO)_8$] in the presence of stabilizing ligands. In the early reports by Thomas[84] and Hess and Parker[85] in the 1960s, thermolysis reactions of $Co_2(CO)_8$ were conducted using functional copolymer ligands to form ferromagnetic CoNPs that spontaneously formed colloidal polymer chains when cast onto substrates, as imaged by transmission electron microscopy (TEM). A number of other polymeric ligands have since been developed using a variety of homo- and copolymer ligands to prepare polymer-coated ferromagnetic nanoparticles.[86−91]

A significant breakthrough in the synthesis of uniformly sized ferromagnetic nanoparticles was the use of well-defined small-molecule ligands in thermolysis reactions of metal carbonyls to stabilize the growth of these dipolar colloids. Notable examples include the use of ligand mixtures based on oleic acid, oleylamine, and trioctylphosphine oxide (TOPO), as had been previously utilized as ligands in related systems based on semiconductor nanoparticles.[92−94] Modified resorcinarene ligands developed by Wei and co-workers also enabled the synthesis of dipolar CoNPs that formed nanoparticle bracelets or NP chains under zero-field conditions (i.e., in the absence of an applied external field).[95−100]

We expanded upon these established concepts by the preparation of end-functional polymeric surfactants bearing either amine ($-NH_2$), phosphine oxide ($-POR_2$), or carboxylic ($-COOH$) ligands to mediate the growth of ferromagnetic cobalt nanoparticles (Figure 3).[55,58,63] The use of end-functional polymers combined the advantageous characteristics of polymeric and small-molecule surfactant systems, enabling the synthesis of highly uniform ferromagnetic colloids possessing a hairy corona of stabilizing polymer chains. End-functional polystyrene (PS) ligands were readily synthesized using controlled radical polymerizations such as nitroxide-

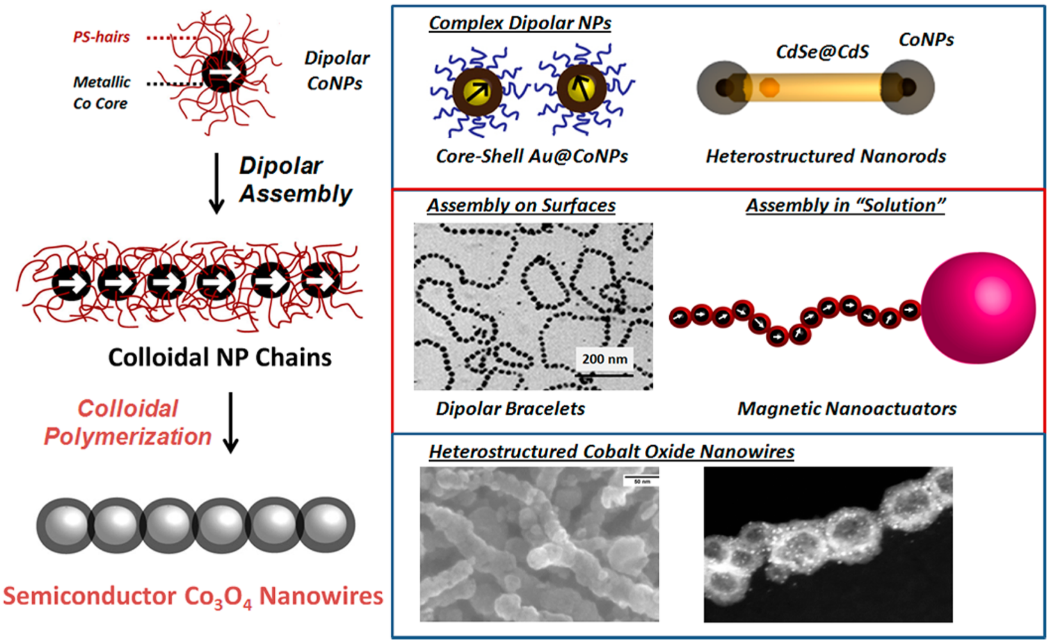

Figure 2. Overview of recent work by the Pyun group on the synthesis and dipolar assembly of polystyrene-coated cobalt nanoparticles (CoNPs). These magnetic nanoparticle assemblies have been used for the hierarchical construction of "artificial cilia and flagella." Colloidal polymerization of dipolar CoNPs via oxidation conversion reactions affords cobalt oxide nanowires. Complex dipolar nanoparticles with noble-metal or semiconductor inclusions have also been used to prepare functional cobalt oxide heterostructures.

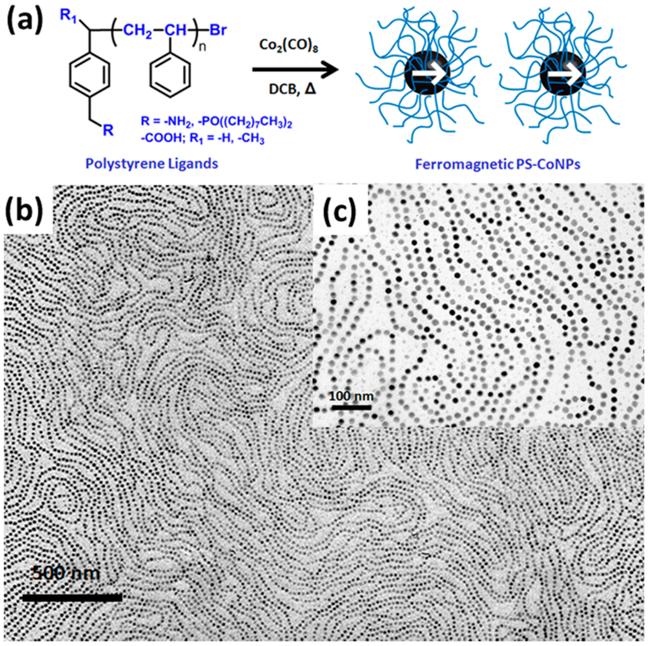

Figure 3. (a) Scheme for the synthesis of dipolar ferromagnetic cobalt nanoparticles using end-functional polystyrene ligands in the thermolysis of $Co_2(CO)_8$. (b) Low- and (c) high-magnification TEM images of dipolar PS-CoNPs cast onto a carbon-coated copper grid.[56] Reprinted with permission from ref 56. Copyright 2007 American Chemical Society.

mediated polymerization[101] and atom-transfer radical polymerization.[102] One-pot reactions using COOH-terminated PS ligands (of molar mass in the range of 5000−20000 g/mol) were then found to enable the growth of CoNPs by thermolysis of $Co_2(CO_8)$ in 1,2-dichlorobenzene (DCB). By simple control of the temperature (T = 120−170 °C), one-pot reactions between PS−COOH and $Co_2(CO)_8$ yielded well-defined ferromagnetic PS-CoNPs with controllable size in the range of 15−50 nm. This one-pot method also afforded access to larger batch sizes (2−25 g scale), which enabled more rigorous investigation of the dipolar assembly of these materials.

DIPOLAR ASSEMBLY OF FERROMAGNETIC PS-CONP COLLOIDAL MONOMERS

As a result of the presence of strong spin dipole−dipole associations between ferromagnetic CoNPs, the formation of colloidal polymer chains was observed when the NPs were cast onto surfaces or dispersed in organic or aqueous media. We found that our ferromagnetic PS-CoNPs exhibit interparticle association energies ranging from $-8kT$ to $-30kT$ depending on the size, magnetization, and interparticle spacing governed by the polymer ligand (polymer corona typically ∼2−3 nm in the solid state). The formation of randomly entangled colloidal polymer chains was the most readily observed morphology when dispersed dipolar NPs were cast onto supporting substrates. Interestingly, the formation of dipolar NP bracelets, or flux closure rings, has also been observed by several groups using a variety of different processing conditions.[99,103−108] In our studies of colloidal polymer chains cast from dipolar PS-CoNPs (see Figure 2 for an example), we observed the formation of bracelet-type assemblies when longer, higher-molecular-weight PS ligands were placed on the exterior of ferromagnetic CoNPs ($D \approx 20$ nm).[58] An unusual nematic-type liquid-crystalline (LC) assembly was observed in the dipolar assembly of PS-CoNPs, where both strong N−S dipolar and weak antiferromagnetic coupling between NP dipoles was found, resulting in intermittent folding of the chains to afford a "pearl necklace"-type of morphology.[56,58] While this LC-type dipolar NP morphology had been predicted via mesoscale modeling,[109] our report was the first experimental observation of this morphology (see Figure 3b for an example).

In addition to imaging of dipolar assemblies on surfaces, characterization of dispersed colloidal polymer chains in organic or aqueous media was also conducted using dilute-solution small-angle X-ray or neutron scattering or microscopy.[110−113] Dilute-solution scattering has been used to study dipolar fluids, but these techniques cannot readily differentiate between branched and linear polymeric structures. Philipse et al. used cryogenic TEM to image the dipolar self-assembly of ferrimagnetic magnetite (Fe_3O_4) nanoparticles (D = 21 nm) into flux-closure bracelets and short 1-D chains in decalin-coated[114] and polyisobutylene-coated[115] iron colloids. To enable rapid screening of different processing conditions (e.g., concentration, temperature, magnetic field strength, etc.), an analytical method termed *fossilized liquid assembly* (FLA) was developed by Benkoski and Karim to examine nanoparticle assemblies at interfaces of immiscible liquids.[116−121] We recently demonstrated that a wide range of nanoparticles can be organized at oil−water interfaces, where the oil phase can be flash-cured when exposed to UV light (FLA).[122] Nanoparticle assemblies formed at the interface are immobilized by curing of the oil phase, which can then be imaged using atomic force microscopy (AFM). With this methodology, PS-CoNPs (D = 24 nm; M_s = 38 emu/g; H_c = 254 Oe) were assembled and photo-cross-linked to afford a rigidified colloidal polymer chain with a length of 9 μm, corresponding to a degree of polymerization (DP) of over 350 PS-CoNP repeat units (Figure 4).[56] This long-range dipolar assembly encouraged us to investigate the use of these colloidal assemblies as components of still larger nano-objects.

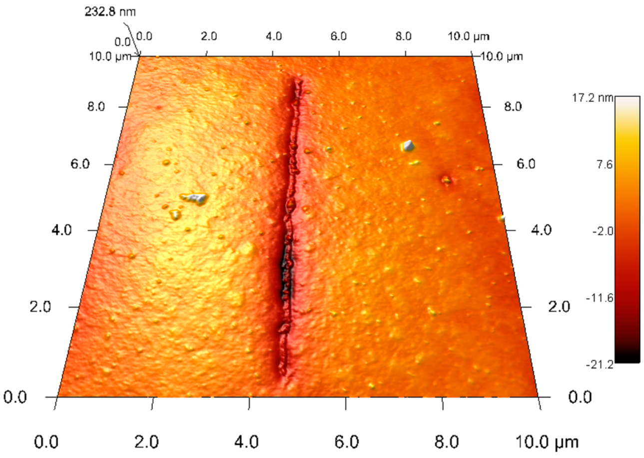

Figure 4. AFM height image of an aligned colloidal polymer chain assembled under the influence of an 8 mT magnetic field from 24 nm PS-CoNPs, corresponding to a DP of >350 NP units.[56] Reprinted with permission from ref 56. Copyright 2007 American Chemical Society.

MAGNETORESPONSIVE NANOACTUATORS FROM DIPOLAR CONPS

In collaboration with Benkoski and co-workers, we achieved the hierarchical construction of "artificial cilia and flagella" by dipolar assembly of dispersed PS-CoNPs.[62,65,69] While the assembly of micrometer-sized paramagnetic beads into colloidal polymer chains had been extensively investigated, the use of much smaller nanoscopic dipolar NPs had not been widely studied. These smaller nanoscopic dipolar NPs also presented technical challenges for imaging of dispersed assemblies: TEM and field-effect scanning electron microscopy (FE-SEM) of solution-cast materials were required to determine the particle size and morphology of the colloidal polymers, but only optical imaging methods could be employed to image the dispersed colloids. Hence, as a beginning model system, colloidal brushlike surfaces were fabricated by magnetic assembly of PS-CoNPs into vertically aligned colloidal polymer chains and laterally bundled filaments. Modulation of the lateral bundling of the colloidal chains using different applied field conditions enabled the fabrication of filament arrays both at the single-chain level and as aggregated fibers. Furthermore, in situ imaging of the magnetic actuation of these cilia-like arrays was performed.[62,69]

The binary assembly of larger magnetite (Fe_3O_3) colloids with dipolar PS-CoNPs was also investigated with the aim of fabricating colloidal flagella-like systems composed of a single Fe_3O_4 bead (D ≈ 500 nm) conjugated to a single PS-CoNP chain (~1 μm in length, single NP unit in width; see Figure 5).

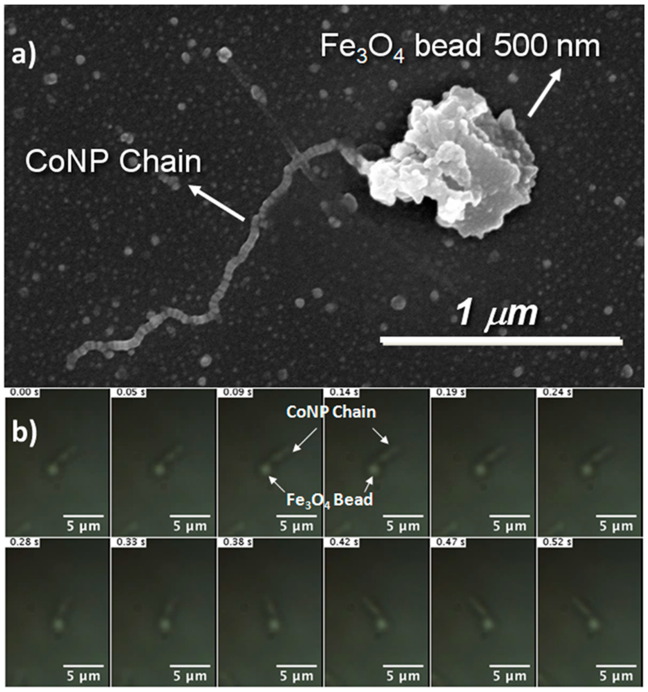

Figure 5. (a) FE-SEM image of "artificial flagella" coassembly of a binary mixture of Fe_3O_4 colloids (D ≈ 500 nm) with dipolar PS-CoNPs (D ≈ 20 nm). (b) Optical microscopy of CoNP-Fe_3O_4 assembly in DMF with time-lapse images of magnetic actuation of the CoNP microscopic filament.[65] Reproduced with permission from ref 65. Copyright 2011 The Royal Society of Chemistry.

Optimization of the applied magnetic fields enabled the self-assembly of the targeted artificial flagella morphology along with structural variations of colloidal PS-CoNP chains with two or more Fe_3O_4 beads and free PS-CoNP colloidal polymer chains. FE-SEM and optical imaging of these structural variations was conducted to enable visualization of the single-bead−single-chain flagella-like assembly dispersed in organic media [i.e., *N*,*N*-dimethylformamide (i.e., DMF)] and magnetic actuation upon exposure to an oscillating field.[65]

COLLOIDAL POLYMERIZATION OF DIPOLAR CONPS

Chemical methods were then established to irreversibly bind together the individual colloidal monomer units obtained by dipolar assembly. The preparation of either PS-coated or calcined Co_3O_4 nanowires was achieved via dipolar assembly and chemical oxidation of metallic PS-CoNPs in a process we described as *colloidal polymerization* (Figure 6).[61,64,66,70] This polymerization process utilized earlier chemical transformations of magnetic metal nanoparticles based on the Kirkendall effect,[123−126] galvanic exchange reactions,[127−130] or other related alloying reactions[131] to covert the metallic zero-valent phase to metal oxides, chalcogenides, or noble-metal products. Dipolar CoNPs are able to polymerize by a combination of magnetic assembly into polymer-like colloidal chains followed by a chemical transformation of these preorganized NP chains into fused nanowires via conversion of the metallic cobalt into fused nanowires. This process is reminiscent of the step-growth polymerization of A−B small-molecule monomers to form macromolecules, as dipolar metallic PS-CoNPs were employed as "colloidal monomers" to form interconnected 1-D mesostructures by the combination of dipolar assembly and a chemical reaction to fuse NPs. Prior to our work in this area, the elegant work of Xu[132] and Hou[133] demonstrated the polymerization of dipolar CoNPs to form either cobalt sulfide, cobalt selenide, or noble-metal nanowires. The colloidal polymerization of dipolar CoNPs to form $CoSb_3$ nanowires as potential electrode materials for lithium batteries was also investigated by Zhu et al.[131]

The synthesis of PS-coated cobalt oxide nanowires was conducted by bubbling O_2 into DCB dispersions of ferromagnetic PS-CoNPs at 175 °C for varying reaction times in the absence of an external magnetic field (i.e., zero-field conditions) (Figure 6).[61] The use of ferromagnetic PS-CoNPs was essential to the formation of cobalt oxide nanowires under zero-field conditions, as superparamagnetic CoNPs were unable to polymerize because of the absence of a permanent dipole above cryogenic temperatures.[132] TEM and FE-SEM confirmed the formation of fused cobalt oxide nanowires that were micrometers in length and a single NP unit in width, accompanied by the formation of a hollow core in every repeating unit of the colloidal polymer chain. An attractive feature of this colloidal polymerization process was the ability to permanently lock-in the morphology of the dipolar CoNP chains preassembled in solution without the need to use the in situ imaging methods of dispersed colloids as previously described (see Figures 4 and 5). Cyclic voltammetry of indium tin oxide (ITO) modified with calcined Co_3O_4 confirmed that cobalt oxide nanowires were electrochemically active when cycled in a potential from −1 V to 1 V in alkaline media, forming a variety of phases [Co_xO_y, $Co_x(OH)_y$]. Conductive-probe AFM confirmed that these nanowires behaved as semiconducting materials. Both optical spectroscopy and UV photoelectron spectroscopy indicated that these materials possessed valence- and conduction-band energies of 5.2 and 3.04 eV with respect to vacuum, respectively, with a direct band gap of 2.26 eV. These results indicated striking changes in the properties of these colloidal polymers following oxidation, which led us to investigate the incorporation of additional functionality.

COMPLEX DIPOLAR COLLOIDS AND HETEROSTRUCTURED NANOMATERIALS

To further expand upon the functionality and properties of dipolar CoNPs and Co_3O_4 nanowires (after colloidal polymerization), the synthesis of core−shell dipolar NPs and the integration of multiple nanoparticle conversion reactions (e.g., Kirkendall oxidation, galvanic exchange) were investigated. In these systems, the incorporation of noble-metal inclusions (Au, Pt) was achieved in either the interior or exterior of the dipolar CoNPs, which after oxidative colloidal polymerization enabled the preparation of heterostructured cobalt oxide nanowires with controllable placement of noble-metal inclusions.[64,66] This approach enabled enhancement of the electrical and electrochemical properties of cobalt oxide nanowires, presumably via the creation of nano-Schottky-type junctions between the p-type metal oxide and the metallic nanoinclusions.

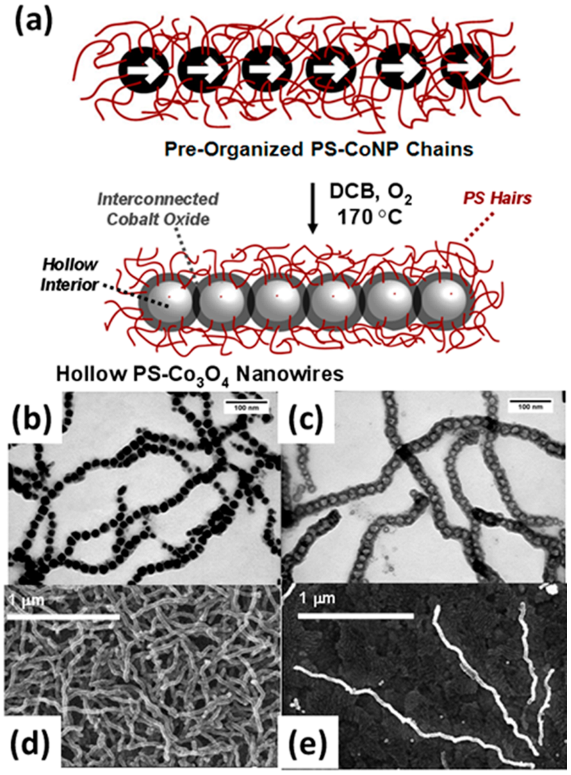

Figure 6. (a) Synthetic scheme for *colloidal polymerization* of dipolar CoNPs into cobalt oxide nanowires. (b) TEM image of dipolar PS-CoNPs colloidal monomers. (c) TEM image of cobalt oxide nanowires after colloidal polymerization of PS-CoNPs. (d) FE-SEM image of high-coverage films of cobalt oxide nanowires. (e) Image of single isolated cobalt oxide nanowires.[61] Reprinted with permission from ref 61. Copyright 2009 American Chemical Society.

Core−shell Au−Co_3O_4 nanowires were prepared via the synthesis and colloidal polymerization of PS-coated dipolar Au−CoNPs.[64] Dipolar core−shell colloids were prepared using oleylamine-capped AuNPs ($D = 13 \pm 3$ nm) as seeds to grow a dipolar PS-CoNP shell ($D = 22 \pm 4$ nm). Despite the presence of only a thin shell of the ferromagnetic Co phase, these core−shell NPs were capable of 1-D assembly, as observed by the formation of colloidal polymer chains with lengths of hundreds of nanometers to micrometers. The colloidal polymerization of PS-coated Au−CoNPs then afforded fused cobalt oxide nanowires with AuNP inclusions in every repeating unit of the colloidal polymer chain. In contrast, a control experiment conducted with PS-CoNPs of comparable diameter afforded PS-cobalt oxide nanowires with completely hollow cores (Figure 7). Electrochemical characterization of Au−Co_3O_4 versus Co_3O_4 nanowire films revealed a 2-fold enhancement of the (background-corrected) Faradaic electrochemical activity associated with redox transitions at the active sites (i.e., CoO_2 >

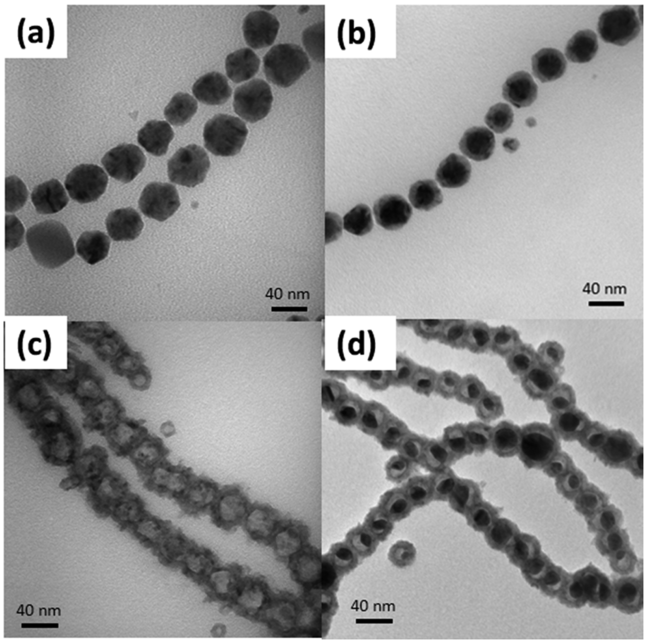

Figure 7. TEM images of ferromagnetic (a) PS-CoNPs ($D = 24 \pm 3$ nm), (b) PS Au−Co core−shell NPs ($D = 22 \pm 4$ nm, $D_{\text{core}} = 13 \pm 3$ nm), (c) PS-cobalt oxide nanowires ($D = 33 \pm 3$ nm), and (d) PS-cobalt oxide nanowires with Au cores ($D = 31 \pm 4$ nm).[64] Reprinted with permission from ref 64. Copyright 2010 American Chemical Society.

CoOOH > Co_3O_4; Figure 8). The capacitive current was also enhanced, giving a specific capacitance per NP ($C_{\text{Au}-\text{Co}_3\text{O}_4}$) of 1.21×10^{-13} F, compared with $C_{\text{Co}_3\text{O}_4} = 4.50 \times 10^{-14}$ F. The electrochemical activity of Au−Co_3O_4 nanocomposites was further confirmed by their formulation into negative electrodes for lithium batteries.

To prepare more complex polymeric architectures, we investigated the synthesis of dipolar CoNPs functionalized with heterostructured nanorods, where CoNP tips were deposited onto semiconductor nanorods composed of CdSe-seeded CdS (CdSe@CdS) nanorods.[70] Heterostructured nanorods tipped with magnetic[134−139] or noble-metal materials[139−151] in either "matchstick" or "dumbbell" topologies have received recent attention as a route to well-defined nanocomposites. Banin and co-workers demonstrated the synthesis of dumbbell-shaped heterostructured nanorods composed of CdSe nanorods with various terminal metal NPs.[149−152] These seminal systems demonstrated the ability to be used in the preparation of a number of different heterostructured nanorods; however, the incorporation of dipolar magnetic NP tips onto semiconductor nanorods had previously not been achieved. The preparation of these hybrid nanorods was also targeted as an approach to enhance the photoelectrochemical and photocatalytic properties of cobalt and cobalt oxide phases.

The key step to introduce our dipolar PS-CoNPs onto the ends of CdSe@CdS nanorods was the deposition of PtNP tips onto the nanorods as seeds, followed by thermolysis of $Co_2(CO)_8$ with PS-COOH ligands. By means of this approach, heterostructured nanorods with ferromagnetic dipolar CoNPs with PS ligands (sizes 10−20 nm) were deposited onto a series of alkylphosphonic acid-capped CdSe@CdS nanorods with fixed diameters of 5−7 nm and tunable lengths of 40−170 nm. The terminal cobalt domains were then selectively oxidized to afford Co_xO_y-tipped nanorods without degradation of the CdSe@CdS nanorods, as confirmed by high-resolution TEM, power spectrum analysis, and X-ray diffraction (Figure 9). We further discovered that kinetic control of the Pt deposition step could be achieved, enabling the deposition of either one or two PtNPs onto the CdSe@CdS nanorods. This further allowed for the selective synthesis of CoNP-tipped CdSe@CdS nanorods with either two CoNPs (with a dumbbell morphology) or one CoNP (with a matchstick morphology). These fused nanorod assemblies from cobalt oxide NP tip junctions formed as a consequence of the dipolar assembly of CoNP-tipped nanorods (Figure 9b), which were captured in solution during oxidation (Figure 9c) as previously observed for dipolar ferromagnetic CoNPs.[61] Interestingly, colloidal polymerization of these

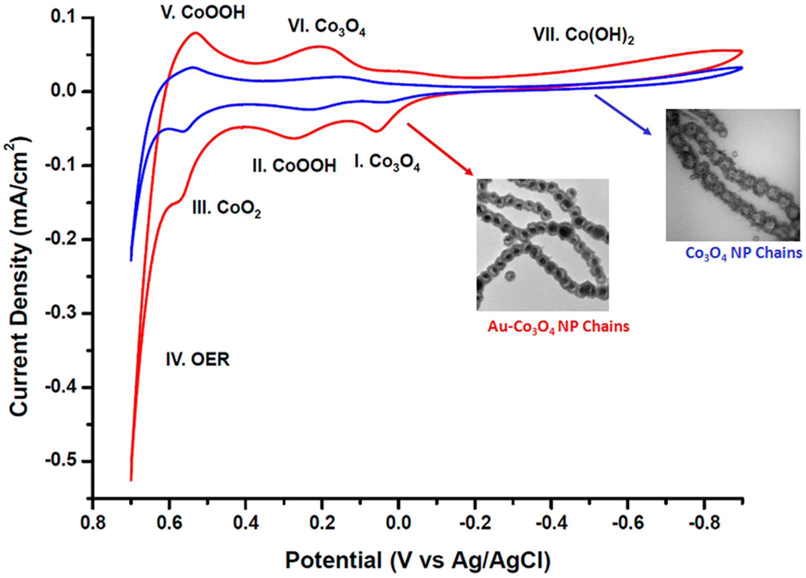

Figure 8. Overlay of cyclic voltammograms of calcined Au−Co_3O_4 (red) and Co_3O_4 (blue) films on ITO at a scan rate of 20 mV/s in 0.1 M NaOH electrolyte solution.[64] Reprinted with permission from ref 64. Copyright 2010 American Chemical Society.

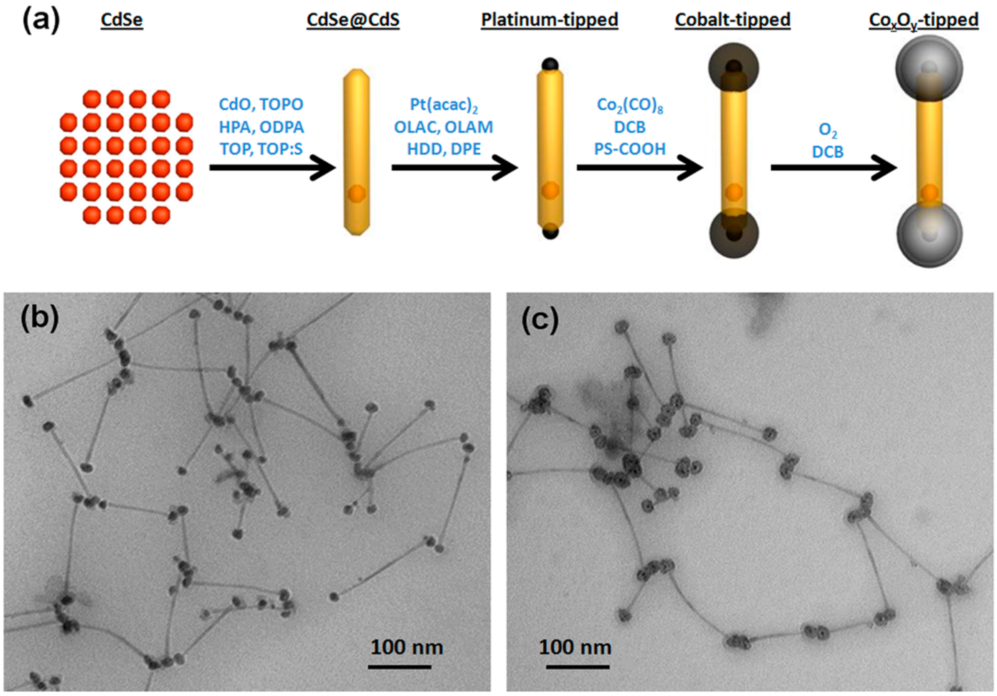

Figure 9. (a) Scheme showing the five-step synthesis of Co_xO_y-tipped nanorods with a dumbbell morphology. CdSe quantum dot seeds (D = 2.3−2.7 nm) were synthesized and used to form heterostructured CdSe@CdS nanorods of varying length (40−174 nm). PtNP deposition onto the CdSe@CdS nanorod termini was then conducted for the series of CdSe@CdS nanorods to enable cobalt deposition. Selective oxidation of cobalt-tipped nanorods afforded the final product. (b, c) TEM images of (b) Co-tipped CdSe@CdS nanorods and (c) fused Co_xO_y-tipped CdSe@CdS nanorods after colloidal polymerization.[70] Reprinted with permission from ref 70. Copyright 2012 American Chemical Society.

heterostructured CoNP-tipped nanorods revealed the formation of end-to-end nanorod assemblies that carried the semiconducting nanorod functionality into the polymerized cobalt oxide network. This phenomenon is one of the few examples of the creation well-defined p−n junctions, which arise from the precise structure of nanorod colloidal monomers. Current efforts on the photoelectrochemical and photocatalytic characterization of these materials are in progress.

■ CONCLUSION

In this Spotlight on Applications, a brief summary of the use of dipolar magnetic nanoparticles as a new class of colloidal monomers for the construction of colloidal polymer chains has been reviewed. Current challenges lie in the synthesis and characterization of complex colloidal monomer compositions and the resulting colloidal polymer architectures. Furthermore, orthogonal nanoparticle conversion chemistries still require investigation to identify reactions that can lock-in dispersed 1-D assemblies without undesirable modification of various nanoparticle components. With continuing advances in the synthesis and assembly of complex nanoparticles, the preparation of a wider range of novel nanocomposites and colloidal polymers is envisioned, which will further open new avenues of research in the area of materials chemistry.

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Notes

The authors declare no competing financial interest.

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