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Communication

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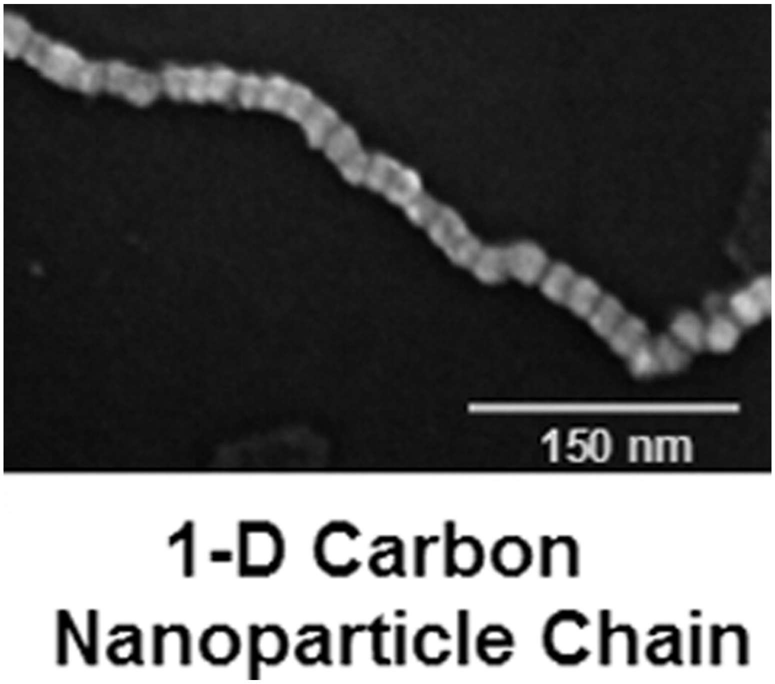

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COMMUNICATIONS

Magnetic Assembly and Pyrolysis of Functional Ferromagnetic Colloids into One-Dimensional Carbon Nanostructures

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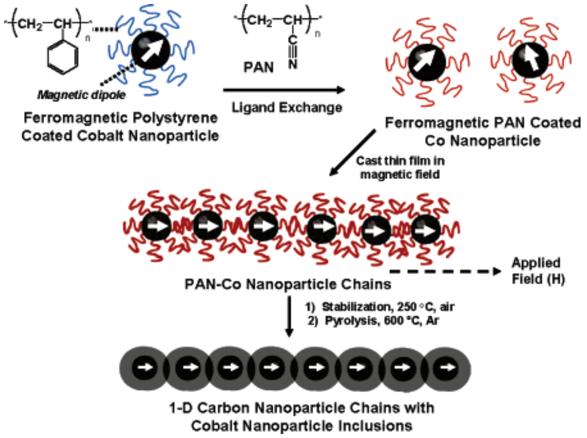
The synthesis and organization of nanoparticles have generated considerable interest as an approach to prepare novel materials.[1] Magnetic assembly of dipolar colloids is an intriguing strategy for "bottom-up" materials synthesis, as the directionality of magnetic dipoles enables selective one-dimensional (1-D) organization of ferromagnetic nanoparticles. While this phenomenon has been harnessed in the preparation of 1-D materials from iron-oxide-loaded latex particles, or emulsion droplets, similar approaches using nanoscale building blocks remain a difficult challenge.[2] The organization of ferromagnetic nanoparticles into chains and flux-closure rings has been observed both on surfaces and in solution.[3] However, the use of functional dipolar nanoparticles has not been extensively investigated.

In this communication, we report a novel methodology to functionalize and assemble ferromagnetic colloids into micron-sized chains that template the formation of 1-D carbon nanostructures after pyrolysis (Scheme 1). This strategy enables a modular assembly route to 1-D carbonaceous materials using soluble colloidal precursors that previously required block copolymer phase-separated thin films[4a,b] or hard templates.[4c,d] Similar core−shell colloids, or carbonized thin films composed of metal nanoparticle cores and carbon shells, have been reported using arc-discharge methods,[5a] ion-beam sputtering,[5b] or carbonizing polymer precursors.[5c,d] The salient feature of the reported method is the 1-D preorganization of functional ferromagnetic colloids containing soluble carbon precursor shells of polyacrylonitrile (PAN) that are preserved after pyrolysis to form continuous 1-D carbon nanoparticle chains with metal nanoparticle inclusions. The orientation of carbonized assemblies was controlled by the direction of applied external fields in the solution deposition process.

The critical step in the synthesis of 1-D carbonaceous materials was the preparation of ferromagnetic PAN-coated cobalt nanoparticles (PAN-CoNPs). This was achieved via ligand exchange of PAN polymeric surfactants onto preformed ferromagnetic polystyrene-coated cobalt nanoparticles (PS-CoNPs).[6a] PAN surfactants (M_n = 28,000; $M_w/M_n = 1.13$) were synthesized using atom transfer radical polymerization (ATRP) and likely bound to Co surfaces through multiple binding interactions from nitrile side chain groups.[6a] Ferromagnetic PS-CoNPs (diameter = 20 nm ± 2 nm, M_s = 38 emu/g, H_c = 200 Oe at 25 °C) were prepared using our previously reported method.[6b] The organization and alignment of ferromagnetic PS-CoNPs spanning microns in length were observed under both zero field and field-induced assembly to form nanoparticle chains. Smaller, superparamagnetic nanoparticles were undesirable for this synthetic approach, as these materials were not easily associated into long-range 1-D assemblies.

***Scheme 1*. Synthesis of 1-D Carbon Nanostructures via Functionalization of Ferromagnetic Colloids with PAN, Magnetic Assembly, and Pyrolysis**



Field-induced assembly of PAN-CoNPs into single nanoparticle chains, or thin films, was conducted by drop casting DMF colloidal dispersions (0.5−10 mg/mL) onto silicon (Si) wafers in the presence of an applied field (100 mT). Field emission scanning electron microscopy (FE-SEM) confirmed the formation of both discrete and bundles of micron-sized chains composed of individual PAN-CoNP repeating units rigidly aligned in the direction of the applied field (Figure 1a,b).

Carbonization of aligned PAN-CoNP chains into 1-D carbon materials was achieved by a two-stage thermal conversion process (250 °C stabilization in air, 600 °C in argon for pyrolysis) of materials deposited onto Si wafers. FE-SEM imaging confirmed that the 1-D morphology of assembled nanoparticle chains remained intact after pyrolysis to form continuous carbon phases along the organized nanostructure (Figure 1c,d).

The morphology and height distributions of PAN-CoNP chains and carbonized materials were characterized using tapping-mode atomic force microscopy (AFM). AFM imaging of preorganized PAN-CoNP chains confirmed that robust 1-D assemblies were formed from both interdigitation of PAN shells and dipolar associations. Samples cast from dilute solutions enabled direct dimensional analysis of isolated 1-D assemblies at each stage of the thermal conversion process (Figure 2a−c). Height distributions were obtained using custom developed software to track dimensional changes between PAN precursors and carbonized assemblies. A progressive decrease in the average heights (H_{av}) of PAN-CoNP assemblies (H_{av} = 30 nm) was observed after stabilization (H_{av} = 25 nm) and pyrolysis (H_{av} = 21 nm) steps due to the volatization

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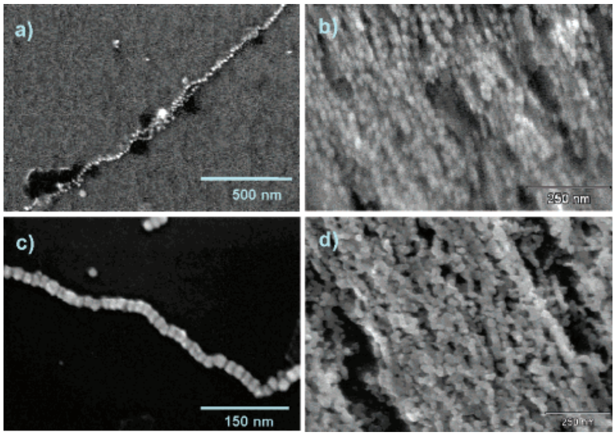

Figure 1. FE-SEM images of materials deposited from DMF onto Si wafers under a weak magnetic field (100 mT) of (a) an individual PAN-CoNP chain, (b) thin film of PAN-CoNP chains, (c) 1-D carbon nanoparticle chain after pyrolysis, and (d) carbonized thin film of magnetically aligned PAN-CoNP chains.

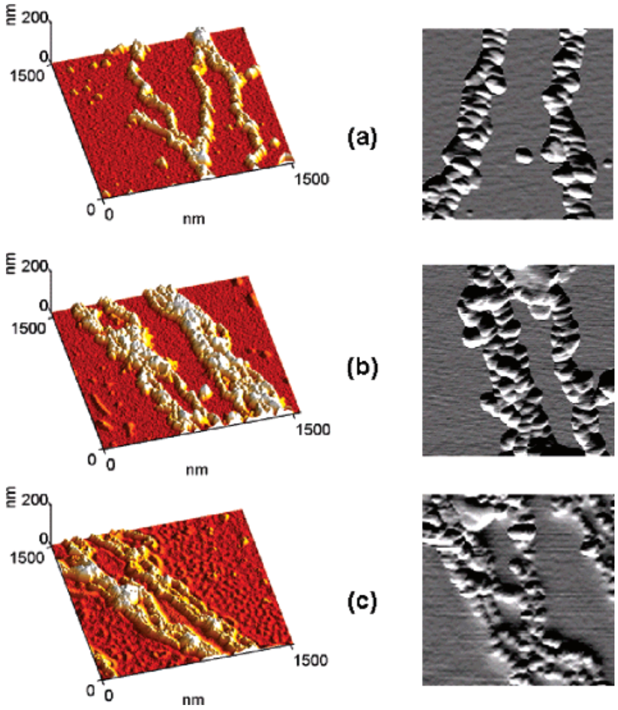

Figure 2. AFM images of materials deposited from DMF onto Si wafers under a weak magnetic field (100 mT): (a) PAN-CoNP chains, (b) after stabilization in air, $T = 250$ °C, and (c) 1-D carbon chains after pyrolysis in argon, $T = 600$ °C. Left column: 3-D height images. Right column: high-pass filtered zoomed-in 500 nm × 500 nm portions of height images.

of byproducts in the carbonization process. Furthermore, after pyrolysis, continuous carbon phases were formed along the PAN-CoNP chain template.

Vibrating sample magnetometry (VSM) and powder X-ray diffraction (XRD) confirmed that cobalt nanoparticle inclusions remained intact after carbonization of 1-D assemblies.[6a]

The thermal conversion of PAN-CoNP chains to carbonized nanostructures was monitored using Raman spectroscopy by following the onset of vibronic bands between 1200 and 1700 cm^{-1}. In particular, the formation of graphitic carbon phases was tracked by the presence of peaks at 1600 cm^{-1}, which is a spectroscopic signature of Raman allowed graphitic modes (G-bands). The formation of disordered carbon phases was also observed at 1350 cm^{-1}, which is characteristic of defect sites (D-bands) (Figure 3).

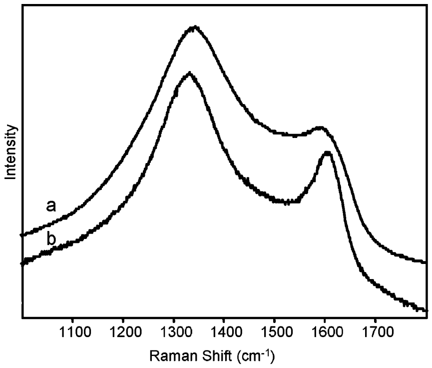

Figure 3. Raman spectrum of PAN (a) and PAN-CoNP (b) after stabilization in air at 250 °C and pyrolysis in argon at 600 °C.

On the basis of the ratio of G-band and D-band heights, the size of graphitic domains did not exceed 20 Å[7] and was comparable to the overall thickness of the carbon shell around Co cores inferred from AFM imaging. Electrical conductivity measurements are currently in progress.

In conclusion, a bottom-up assembly approach is reported to prepare 1-D carbon nanoparticle chains containing ferromagnetic nanoparticle inclusions. This general methodology using functional dipolar colloids harnesses the utility of magnetic assembly to prepare well-defined carbon materials.

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Supporting Information Available: Experimental procedures and additional SEC, TEM, AFM, XRD, and VSM data. This material is available free of charge via the Internet at http://pubs.acs.org

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