

Supporting Information

Superparamagnetic Sub-5 nm Fe@C Nanoparticles: Isolation, Structure, Magnetic Properties, and Directed Assembly

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Separation of Fe@C NPs.

The raw HiPco® materials were used as received or first functionalized with dodecyl groups via a reductive alkylation chemistry¹ to improve their dispersibility. In a typical experiment, 7.0 mg of dodecyl-functionalized material was dispersed in 12 ml

¹ Liang, F.; Sadana, A. K.; Peera, A.; Chattopadhyay, J.; Gu, Z.; Hauge, R. H.; Billups, W. E. *Nano Lett.* **2004**, *4*, 1257-1260.

1,2-dichlorobenzene (ODCB, 99%, Aldrich) by mild sonication using a bath sonicator (Branson model 2510) for 5 min. The resulting dispersion was then centrifuged at 30,000 g for 20 min, and the upper layer containing SWNTs and large fullerenes was decanted. The pellet was re-dispersed in clean ODCB by sonication for 5 min. This centrifugation-decant-redispersion process was repeated 7–10 times, or until the color of the supernatant became light grey. To remove remaining non-magnetic components, the solution was subjected to a conventional magnetic separator (Polysciences, Inc. BioMag® MultiSep). Approximately 60% of the material was attracted to the magnet, forming gray-to-black aggregates against the sidewall of the container. After the solvent was carefully removed, the magnetic materials were separated and redispersed in chloroform (99%, Aldrich). This magnetic purification step was repeated three times. All of the final product was responsive to a magnetic field at room temperature. The yield of the magnetic NPs was about 15 wt% of the starting HiPco material, which contains 35 wt% iron according to thermogravimetric analysis (TGA).²

Characterization.

TEM. For TEM experiments, the Fe@C NPs were dispersed in chloroform by sonication, and a drop of the dispersion was then added to a 3 nm thick carbon film on a TEM grid (Ted Pella, Inc.) and allowed to dry in air. High resolution TEM images were taken with a 2048×2048 CCD camera (Galtan) using a JEOL 2100F TEM operated at an accelerating voltage of 200 kV.

XPS: X-ray photoelectron spectral analysis was carried out with an Omicron spectrometer using an Al K α (1486.5 eV) anode at a power of 200 W (20 kV). XPS

² Wang, Y.; Shan, H.; Hauge, R. H.; Pasquali, M.; Smalley, R. E. *J. Phys. Chem. B* **2007**, *111*, 1249-1252.

spectra were gathered using a hemispherical energy analyzer operated at a pass energy of 70.0 eV for the survey scan and 20.0 eV for elemental analysis. Binding energies were referenced to the Au(4f) peak at 84.0 eV. The Ar⁺ sputtering was performed in a scanning mode with a sputtering rate of ~0.9 Å/min (sputtering conditions: 1.5 kV and 5.0 × 10⁻⁷ torr).

SQUID: A superconducting-quantum-interference-device (SQUID) magnetometer (Quantum Design, MPMS-5) was used to study the magnetic properties of the nanoparticles in the temperature range of 5-300 K and in fields up to 50 kOe. For the zero-field-cooled (ZFC) magnetization measurement, the sample was first cooled to 5 K in zero field. After applying a 500 Oe field, the magnetization was measured as the temperature increased to 300 K. The magnetization was then measured for decreasing temperature in the 500 Oe field, giving the field-cooled (FC) magnetization curves. The magnetization versus temperature behavior for the Fe@C NPs has the following characteristics: (1) a peak in the ZFC magnetization as the temperature is increased, (2) reversible behavior for the FC magnetization above the peak temperature, and (3) irreversible behavior for the FC magnetization below the peak temperature. The above features are characteristics of superparamagnetism.

Directed Assembly of Fe@C NPs.

Materials. 16-mercaptohexadecanoic acid (MHA, 90%), 1-octadecanethiol (ODT, 98%), and ethanol (200 proof, HPLC grade) were purchased from Sigma-Aldrich. Ti (99.7%) and Au (99.99%) wires were purchased from Alfa Aesar, Ward Hill.

Dip-Pen Nanolithography. DPN experiments were performed with an NScriptor (NanoInk, Inc., Skokie, IL) or an AFM (ThermoMicroscopes CP-III, Veeco Instruments, Inc., Sunnyvale, CA) equipped with a 100- μm scanner and closed-loop scan control. All DPN patterning experiments were carried out under controlled environments ($\sim 35\text{-}50\%$ relative humidity, $20\text{-}24^\circ\text{C}$). Polycrystalline Au films were prepared by thermal evaporation of 5-10 nm of Ti on SiO_x followed by 25 nm of Au at a rate of 1 \AA/s and a base pressure of $\leq 5 \times 10^{-6}$ Torr.

Ultra-flat, Template-Stripped Gold Substrates. The substrates were prepared using a simplified and improved experimental procedure that combines several previous findings.^{3,4,5} Typically, a 25 mm \times 75 mm Grade I mica sheet (Structure Probe, Inc.) was fixed on a glass slide using double-sided carbon tape and then mounted onto the sample holder of the Edwards Auto 306 evaporator. The mica sheet was repeatedly cleaved using Scotch® Magic™ tape until the surface became uniformly transparent, indicating a complete mica layer. Thermal deposition of gold was carried out at a base pressure of $< 1 \times 10^{-6}$ torr. A fast initial rate, $\sim 0.5 \text{ nm/s}$ for the first 5 – 10 nm, is important to insure a high rate of nucleation and avoid formation of vacancies. The rate was then adjusted to $\sim 0.10 \text{ nm/s}$ for the remaining thickness to avoid stress buildup. A total thickness of 80 nm, compared to the literature reported 200 – 300 nm, was robust enough to survive the stripping process.

A small drop of epoxy resin (epo-tek® 377, Epoxy Technology Inc.) was added to the gold-on-mica surface, and a glass slide (c.a. 1 cm \times 1.5 cm \times 1.5 mm) was then brought into contact with the epoxy droplet. The glass slide protruded ~ 0.5 cm from the

³ Hegner, M.; Wagner, P.; Semenza, G. *Surface Science* **1993**, *291*, 39-46.

⁴ Mosley, D. W.; Chow, B. Y.; Jacobson, J. M. *Langmuir* **2006**, *22*, 2437-2440.

⁵ Priest, C. I.; Jacobs, K.; Ralston, J. *Langmuir* **2002**, *18*, 2438-2440

edge of the mica, providing a handle for the later stripping step. Upon contact, the epoxy spread uniformly to the overlapping area, owing to its low viscosity and capillary phenomena. The transparency of the glass slide makes it possible to observe the spreading process. The epoxy was then cured at 140°C for 2 hours in an oven under ambient conditions. After cooling down, the gold film was directly peeled off from the whole mica sheet using the glass slide as a handle.

The root-mean square (RMS) roughness of a typical surface was ~0.25 nm, smaller than gold-on-silicon substrates (typically 0.7 – 1.0 nm). These ultra-flat substrates allow for routine patterning of round MHA dot features down to a 40 nm dot diameter, significantly improving the resolution of DPN and subsequent imaging of the assembled Fe@C NPs.

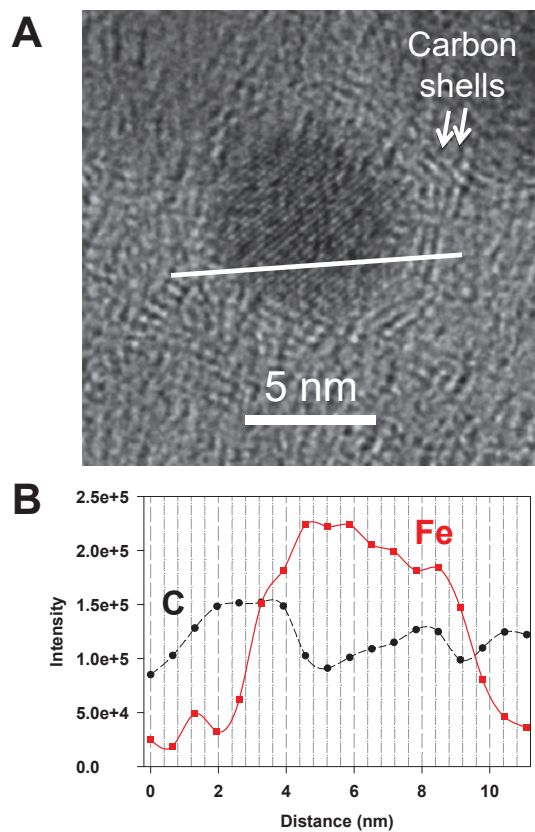


Figure S1. High resolution TEM and electron energy loss spectroscopy (EELS) line profiles of a 10 nm Fe@C NP.

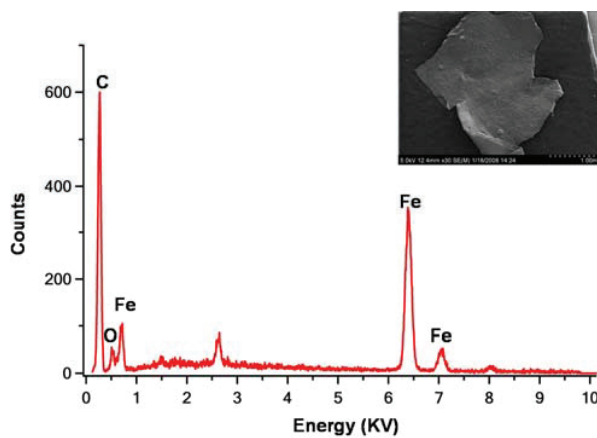


Figure S2. SEM and EDX analysis of a Fe@C NP film formed a gold-on-silicon substrate.

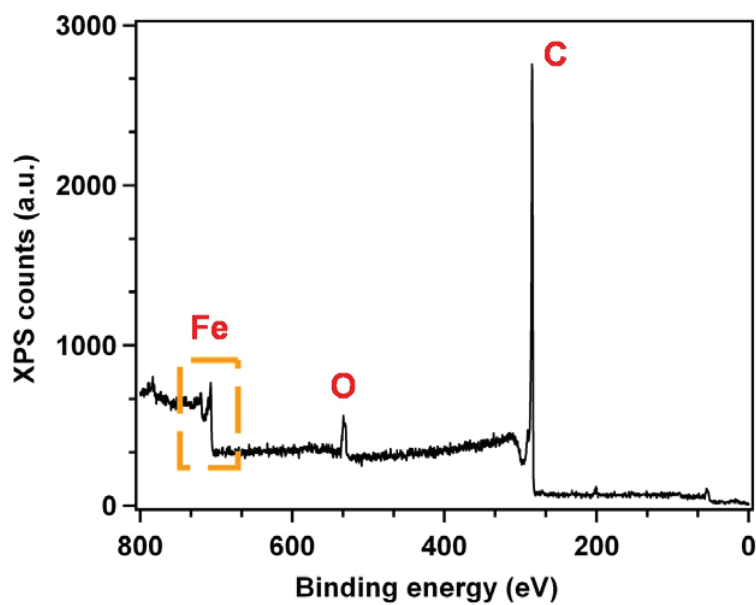


Figure S3. XPS survey of Fe@C NPs.

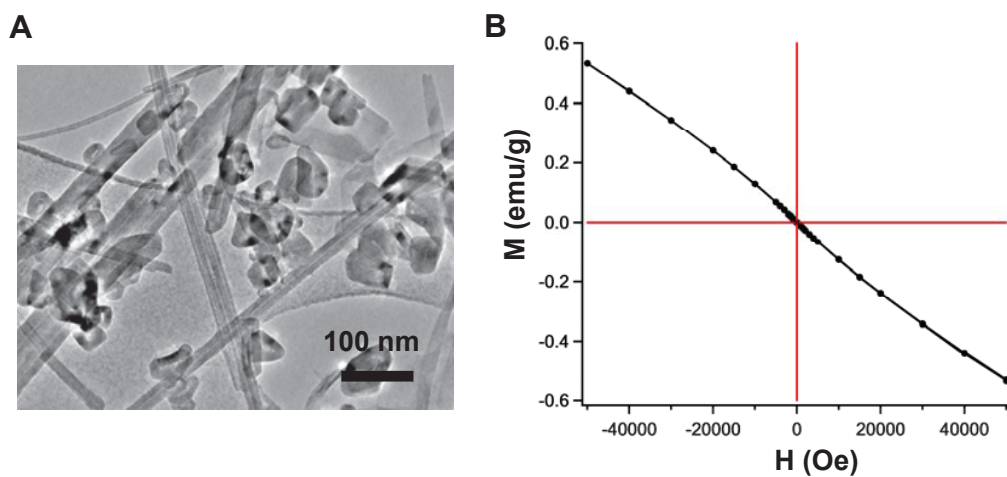


Figure S4. Metal-free carbon nanotubes and carbon nanoparticles produced by arc discharge of pure graphite. (A) Representative TEM image. (B) Field dependence of magnetization at 10 K. This behavior is indicative of diamagnetism.

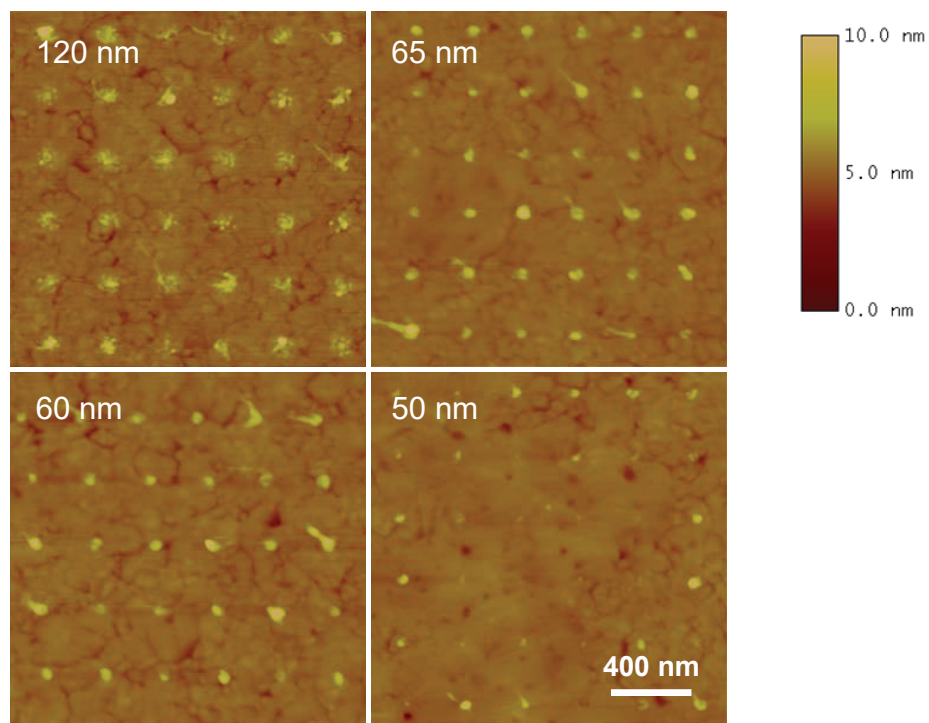


Figure S5. AFM topographic images showing Fe@C NPs assembled on MHA dot features of different diameters. The dot arrays were patterned by Dip-Pen Nanolithography on the same template-stripped gold substrate (RMS: 0.25 nm over a $2 \mu\text{m} \times 2 \mu\text{m}$ area). The assembly was carried out under an identical set of assembly conditions.