

Supplemental Information

Dumbbell-Like Au-Fe₃O₄ Nanoparticles: A New Nanostructure for Supercapacitors

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Experimental Details:

HAuCl₄·3H₂O (Strem Chemicals), borane tert-butylamine (BBA, 97%, Sigma-Aldrich), oleylamine (80-90%, Arcos Organics), oleic acid (80-90%, Arcos Organics), 1,2,3,4-tetrahydronaphthalene (tetralin, 99%, Sigma-Aldrich), 1-octadecene (ODE, 90%, Sigma-Aldrich), iron pentacarbonyl (98%, Sigma-Aldrich), potassium iodide (Sigma-Aldrich), iodine (Sigma-Aldrich), polyvinylidene fluoride (PVDF, MTI) and N-methylpyrrolidone (NMP, MTI) were used as received.

Synthesis of Au NPs:^{1, 2} In a typical synthesis of 5 nm Au NPs, HAuCl₄·3H₂O (0.2 g) was dissolved in a solution of tetralin (10 mL) and oleylamine (10 mL) in ice bath and stirred for 20 min. BBA (0.087g) was mixed with tetralin (1 mL) and oleylamine (1 mL)

by sonication and then injected into the above solution. The reaction mixture was further stirred at 0 °C for 2 h. Acetone was added into the solution to precipitate the Au NPs. After centrifugation, the Au NPs were redispersed in hexane and further washed with ethanol for two times.

7 nm Au NPs were obtained by seed-mediated growth using the 5 nm Au NPs as seeds in ODE and oleylamine solution at 80 °C. In a typical synthesis, HAuCl₄·3H₂O (0.08 g) was added to ODE (4 mL) and oleylamine (6 mL) and the mixture was slowly heated to 80 °C. The 5 nm Au NPs (30 mg) were injected into the solution and the reaction solution was kept at 80 °C for 2 h. Isopropanol and ethanol were used to precipitate and wash the NPs. The NPs were dispersed in hexane for next step use.

Synthesis of Au-Fe₃O₄ NPs: For a typical synthesis of 5-14 nm Au-Fe₃O₄ NPs, the 5 nm Au seeds (20 mg) dissolved in 0.5 mL hexane were added into the solution of ODE (20 mL), oleic acid (1 mL) and oleylamine (1 mL). The magnetically stirred mixture was heated up to 100 °C under N₂ flow to remove hexane. After 20 min, Fe(CO)₅ (0.1 mL) was injected into the solution under a N₂ blanket. The reaction system was then heated to 300 °C and kept at this temperature for 30 min. After the solution was cooled down to room temperature and exposed to air, Au-Fe₃O₄ NPs were precipitated by adding isopropanol and collected by centrifugation. The 5-14 nm were washed with ethanol twice and then redispersed in hexane. 5-21 nm Au-Fe₃O₄ NPs were obtained by varying the Fe(CO)₅ amount to 0.15 mL. Changing the Au seeds (5 nm, 20 mg) to Au seeds (7 nm, 25 mg), 7-14 nm and 7-21 nm Au-Fe₃O₄ NPs were collected.

Au etching from Au-Fe₃O₄ NPs:³ KI (800 mg) and I₂ (200 mg) were mixed in deionized water (10 mL) and Au-Fe₃O₄ NPs (30 mg) in hexane were added into this KI/I₂ solution. The mixture was shaken overnight. The dented Fe₃O₄ (called control Fe₃O₄) NPs were collected by adding ethanol to the hexane phase and centrifugation.

NP characterization: TEM images were acquired on a Philips CM 20 microscope at 150 kV. HRTEM experiments were carried out on a JEOL 2100 microscope at 200 kV. X-ray diffraction (XRD) patterns were obtained on a Bruker AXS D8-Advanced diffractometer with Cu K α radiation ($\lambda=1.5418 \text{ \AA}$).

Electrochemical measurements: The NPs were deposited on Ketjen carbon support (surface area 800 m² g⁻¹) (~33 wt% loading) by sonicating the mixture of NP hexane dispersion and carbon for 1 h.⁴ The supported NPs (NP/C) were then annealed in air at 150 °C for 8 h to remove surfactants. To obtain the supercapacitor electrode, PVDF was mixed with NP/C with the mass ratio of 5:95. The mixture was then dispersed in NMP and painted onto nickel foam. Thereafter, the electrode was dried under vacuum at 120 °C overnight to remove NMP. Normally, the total mass of electrode material paste is ~ 8 mg. The exact loading percentage of NPs on carbon support was obtained by measuring the Fe and Au concentration with ICP-AES. Cyclic voltammetry, galvanostatic charge discharge and electrochemical impedance spectroscopy measurements were carried out on Autolab 302 with Pt mesh as counter electrode and Hg/HgO as reference electrode in 6 M KOH.

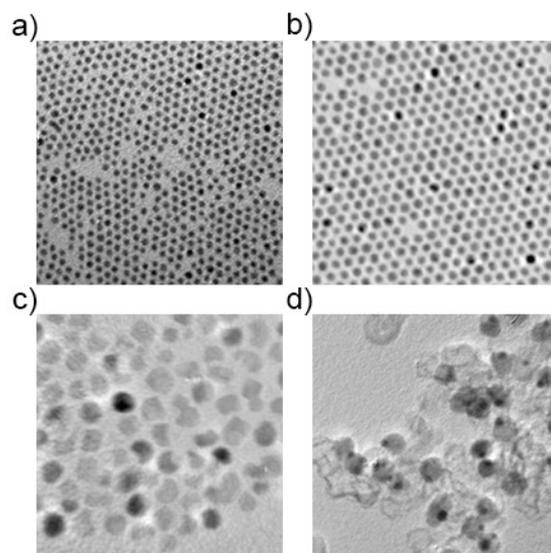


Figure S1. TEM images of a) 5 nm Au NPs, b) 7 nm Au NPs c) dented Fe₃O₄ NPs, and d) Au-Fe₃O₄ NPs on carbon. Scale bar: 20 nm.

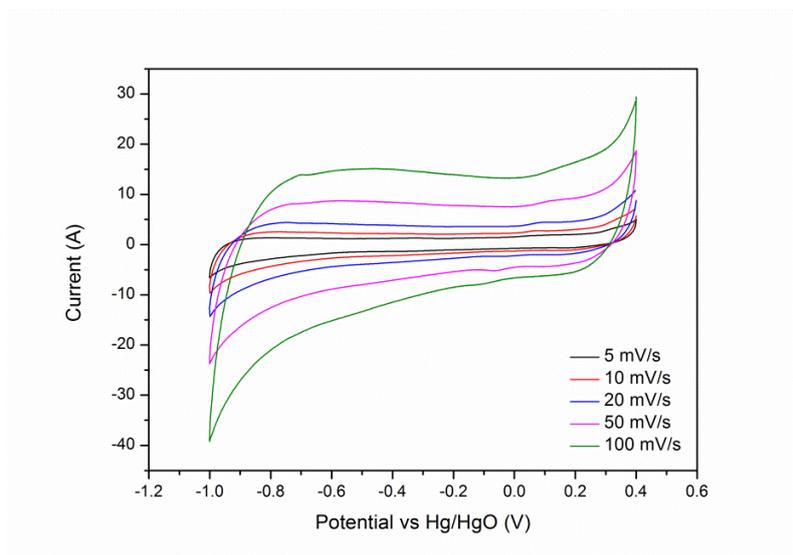


Figure S2. Cyclic Voltammetry of 7-14 nm Au-Fe₃O₄ NPs under scan rates 5 mV s⁻¹ to 100 mV s⁻¹.

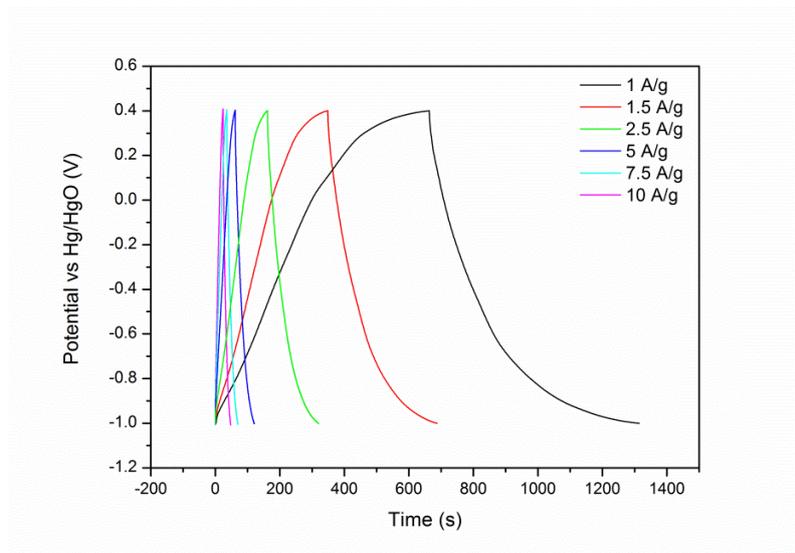


Figure S3. Galvanostatic charge-discharge test of 7-14 nm Au-Fe₃O₄ NPs under current density 1 A g⁻¹ to 10 A g⁻¹.

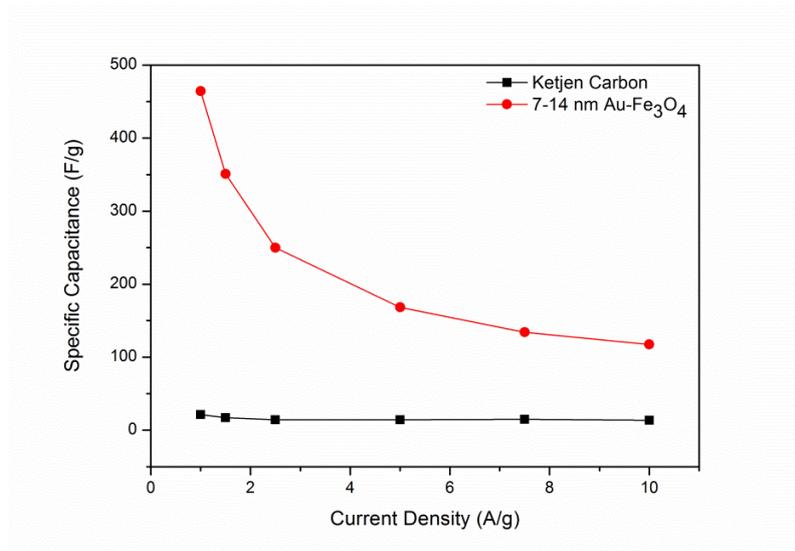


Figure S4. Specific Capacitance of Ketjen Carbon and 7-14 nm Au-Fe₃O₄ NPs under different current densities.

Figure S4 shows the specific capacitance comparison between 7-14 nm Au-Fe₃O₄ and Ketjen Carbon under different current densities. Since the NPs were loaded on Ketjen

Carbon support, the specific capacitance were calculated using the equation below to eliminate the contribution of the carbon support:

$$C = \frac{I(\Delta t_{total} - \Delta t_{KC})}{m\Delta V}$$

where C is the specific capacitance, I is the charge/discharge current, Δt_{total} is the total discharge time, Δt_{KC} is the discharge time of Ketjen Carbon under its true current density, m is the mass of active materials on the electrode and ΔV is the potential window.

References:

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