FePt concave nanocubes with high-index facets and enhanced

methanol oxidation activity

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Part 1. Chemicals, Nanocube Syntheses and Characterization Methods

1.1 Chemicals

1-Octadecene (ODE, 90%), Pt(II) acetylacetonate (Pt(acac)₂, 99%) and Hexacarbonyltungsten(W(CO)₆, 97%) were purchased from Alfa Aesar. Iron pentacarbonyl (Fe(CO)₅, 98%) was from Xin Ding Peng Fei Chemical Co. in China. Oleylamine (OAm, > 70%) and Oleic acid (OA, 90%) was purchased from Aldrich. Anhydrous ethanol, hexane, and toluene (99%) were used as received. All syntheses were carried out under air-free conditions, using a standard Schlenk-line setup.

1.2 Synthesis of FePt nanocubes

The FePt nanocubes were prepared by modifying a previously reported procedure. In a typical procedure, $Pt(acac)_2(0.10 \text{ g } 0.25 \text{ mmol})$, $W(CO)_6(0.13 \text{ g } 0.37 \text{ mmol})$, OAm(5 mL), OA(5 mL) and 1-octadecene (ODE 10 mL) were put into a four-neck flask. The mixture was heated to 60 °C and degased under vacuum for 30 min to remove oxygen and to make the reactants dissolve into uniform solution. Subsequently, the mixture was heated up to 120 °C under an argon atmosphere, and was kept at this temperature for 2 min before $Fe(CO)_5(0.15 \text{ ml } 1.2 \text{ mmol})$ was injected into the mixture solution. Then the temperature was quickly raised to 240 °C and maintained for 30 min before cooled down to room temperature. The FePt nanocubes were precipitated by adding 15 ml of ethanol and were rinsed twice with hexane and ethanol. The as-synthesized FePt nanocubes were finally dispersed in hexane for further characterization.

1.3 Characterization Methods

TEM, HRTEM, XRD, and ICP–AES techniques were employed to characterize the size, morphology, structure, and chemical composition of the samples, respectively. Samples for TEM characterization were prepared by placing 1–2 μ L of diluted (1 mg/mL) hexane solution of the sample on a carbon-coated copper grid. TEM images were obtained using a Tecnai T20 transmission electron microscope operated at an acceleration voltage of 200 kV. The HRTEM, selected- area electronic diffraction (SAED), and STEM/EDS line scanning analysis were performed using a FEI Tecnai F30 emission analytical transmission electron micros- cope operated at an acceleration voltage of 300 kV. XRD data were collected at room temperature on a Rigaku D/Max-2000 diffractometer (Cu K α , λ = 1.5406 Å, 40 kV and 100 mA, graphite monochromator, scintillator detector, step scanning 1 °/min). The elemental composition of the HNCs was estimated by ICP–AES of the solution obtained after digesting the samples in a HCl/HNO₃ mixture. Magnetic properties were studied using SQUID magnetometry (MPMS XL, Quantum Design). Zero-field-cooled (ZFC) and field cooled (FC) curves were recorded in the range of 5–300 K after cooling the sample in the absence or presence of a 50 Oe dc field, respectively. Field-dependent magnetization measurements were performed between -5 and 5 T both at 5 K and at room temperature. UV-vis absorbance spectra were obtained at 23°C± 2°C using quartz cells and a Shimadzu UV-2550 UV-vis spectrometer system. Cyclic voltammetry measurements were performed on an electrochemical workstation (CHI760C). Ag/AgCl and a piece of Pt foil of area 1 cm² were used as reference and counter electrodes, respectively. The as-synthesized FePt NRs or FePt-Au HNCs were dissolved in hexane in a 30 mL vial and 10 mL ethanol containing a Vulcan XC 72 carbon support was carefully added to it. This colloidal mixture was sonicated for 2 h (to ensure complete adherence of FePt-Au HNCs onto the carbon support). A measured amount of ethanol was added, resulting in a 2 mg/mL solution. This mixture was sonicated for 1 h to ensure uniform distribution. A 20 µL aliquot of FePt-Au/C suspension was placed on a glassy carbon working electrode and dried. The sample was fixed on the electrode by deposition a layer of 0.1% Nafion. The samples were cleaned to remove the surfactant residue by scanning in 0.5 mol/L HClO4 solution for at least 50 scans.

Part 2. Experimental Results



Figure S1. TEM (a) and HRTEM (b) images of FePt nanocubes.



Figure S2. TEM images of (a)FePt concave nanocubes and (b) nanocubes deposited onto the Vulcan carbon.



Figure S3. TEM images of FePt concave nanocubes deposited on Vulcan carbon (a)before and (b)after electrochemical cleaning process(200 cycles).



Figure S4. Cyclic voltammograms of (a)FePt concave nanocubes (b) FePt nanocubes and (c) the three samples in 0.5M HClO₄ solution. Scan rate: 50 mV/s.