Supplementary Information

Sub-20 nm-Fe₃O₄ squared and circular nanoplates: Synthesis and facet-dependent magnetic and electrochemical properties

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Part S1. Detailed experimental section

Chemicals

Fe(acac)₃, oleic acid and dibenzyl ether were purchased from Alfa-Aesar Corporation. Oleylamine and 1,2-hexadecanediol were purchased from Sigma-Aldrich Corporation. All chemicals in this study were used without pretreatment.

Preparation of squared and circular nanoplates

Fe(acac)₃ (0.05 mmol) and 1,2-hexadecanediol (0.25 mmol) were mixed in 5 mL dibenzyl ether. A certain amount of oleic acid and oleylamine (for Fe₃O₄ squared nanoplates: 0.5 mmol oleic acid and 0.5 mmol oleylamine; for Fe₃O₄ circular nanoplates: 1 mmol oleic acid and 1 mmol oleylamine) were added to the mixture at the temperature of 60 °C in hot water bath to form a homogeneous solution. The solution was transferred to a Teflon-lined stainless steel autoclave with a total volume of 23 mL and heated at 200 °C for 24 hours. After cooling to room temperature, the resulting particles were precipitated in ethanol and washed by ethanol for several times.

Fabrication of Fe₃O₄ Modified Electrode

A certain amount of the as-synthesized Fe₃O₄ squared and circular nanoplates, respectively, were added into absolute ethanol and ultrasonicated for 10 min to give a suspension (3.0 mg ml⁻¹). For fabricating the modified electrode, an aliquot of 10 μ L of the suspension was pipetted onto the surface of the carbon working electrode in screen printed carbon electrode (SPCE). The solvent was evaporated under a room

temperature to obtain the Fe₃O₄film modified SPCEs.

Electrochemical apparatus

Electrochemical measurements were performed with SPCEs (ref. 110, DropSens, EdificioSevero Ochoa, Spain). The electrochemical cell consists of a three-electrode arrangement with a carbon (4-mm diameter) serving as the working electrode, with a carbon used as the counter electrode. A silver pseudo reference electrode completed the circuit. All measurements were performed with a CHI 660D computer-controlled potentiostat (ChenHua Instruments Co., Shanghai, China).

Electrochemical behavior toward As(III)

Square wave anodic stripping voltammetry (SWASV) was used for discussing the electrochemical behavior of As(III).As(0) were deposited at the potential of -0.5 V for 120 s by the reduction of As(III) in 0.1 M NaAc-HAc (pH 5.0). The anodic stripping (reoxidation of As(0) to As(III)) of electrodeposited As(0) was performed in the potential range of -0.3 to 0.4 V at the following parameters: frequency, 15 Hz; amplitude, 25 mV; increment potential, 4 mV; vs. Ag. After each measurement, the modified electrode was regenerated in fresh stirred supporting electrolyte by electrolysis at +0.5 V for 140 s to remove the previous residual As(0) from the electrode surface.

General characterization

X-Ray diffraction (XRD) was performed on a X'Pert Pro MPD X-ray diffractometer, using CuK α ($\lambda_{K\alpha 1}$ =1.5418 Å) as the radiation source. The transmission electron microscopy (TEM) investigations were carried out in

JEOLJEM-2000EX operating at100keV. The atomic force microscopy (AFM) images were taken by using a scanning probe microscope (Veeco Multimode V). Magnetic studies were carried out on a Quantum DesignMPMS XL5 magnetometer.

Methodology

Our density functional theory (DFT) calculations were performed by using the Vienna abinitio simulation package (VASP)^{1,2} with the Perdew-Burke-Ernzerh parameterization³ of the generalized gradient approximation (GGA) for the exchange correlation potential. An energy cut of 400 eV were consistently used in our calculations. The lattice constants adopted in our calculations are taken from experimental values of bulk Fe₃O₄ (a = b = c = 8.396Å).^{4,5} A 2×2×1 Monkhorst-Pack k-point was used to sample the surface Brillouin zone. To simulate Fe₃O₄ (001) and (111) surfaces, we adopted the slab models including 9 and 11 atomic layers, respectively, in which a 12 Å of vacuum is included. During the structural optimizations, we fully relaxed atomic positions in the top four layers and fixed all other atoms in the bulk configuration. The atomic positions were fully relaxed with the conjugate gradient procedure until the residual forces vanished within 0.02 eV/Å. The side and top views of the optimized Fe_3O_4 (001)and (111) surfaces are shown in Figure S10. Here, tetrahedral Fe atom (Fe_{tet}) appear in the terminated layer.⁶ Toexplore adsorption behavior of H₃AsO₃ on two different surfaces, we define adsorption energy (E_{ads}) as $E_{ads} = E_{ads/surface} - (E_{surface} + E_{ads})$. Here, $E_{surface}$ and $E_{ads/surface}$ are the total energies of surface and adsorbate (i.e. H₃AsO₃)on surface, respectively, and E_{ads} is the total energy of adsorbate. Under this definition, the more negative

value stands for the more energetically stable adsorption.

Reference List for Supporting Information

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Part S2. Additional experimental data



Figure S1. (a) XRD patterns of the as-prepared squared and circular nanoplates; (b)

Mössbauer spectroscopy of the as-prepared samples.

Effect of the ratio of Fe(acac)₃ to surfactants



Figure S2. Effect of the ratio of Fe(acac)₃ to mixed surfactants (the mixed surfactants were oleic acid and oleylamine with the ratio of 1:1): (a) Fe:surfactants=1:1; (b) Fe:surfactants=1:5; (c) Fe:surfactants=1:10; (d) Fe:surfactants=1:20. (The scale bars represent 10 nm.)

The mole ratio of Fe(acac)₃ to surfactants were varied in 1:1, 1:5, 1:10, and 1:20, in which the surfactants were oleic acid and oleylamine with the mole ratio of 1:1. Figure S2 (shown in the Supporting Information) shows the TEM images of the as-obtained products with different ratios of Fe(acac)₃ to surfactants. From the TEM images, it can be found that the mole ratio of Fe to surfactants plays an important role in the control of the morphology of the Fe₃O₄ nanoparticles. When the mole ratios of Fe to surfactant were 1:1 and 1:5, it can not obtain the homogeneous Fe₃O₄ nanoparticles. While the mole ratios were 1:10 and 1:20, uniform squared and circular nanoplates were obtain, respectively.

Effect of the ratio of mixed surfactants



Figure S3. Effect of the ratio of mixed surfactants (oleic acid:oleylamine): (a)10:0; (b) 10:5; (c) 5:10; (d) 0:10. (The scale bars represent 30 nm.) and (e) FTIR spectra of four samples: Solution A and Solution B stand for the supernatant liquids after synthesis of squared and circular nanoplates, respectively; oleylamine; and oleic acid.

Fixed the mole ratio of Fe to surfactants at 1:10, the mixed surfactants mole ratio of oleic acid to oleylamine was varied in 10:0, 10:5, 5:10, and 0:10. TEM images of the products with the different mole ratio mixed surfactants were shown in Figure S3 (Supporting Information). With the absence of oleylamine, the products with the size range in 70~130 nanometes were obtained (shown in Figure S3a). With the presence

of oleylamine, the sizes of the products were limited in several to less than 20 nanometer (shown in Figure S3b~3d). To further study on the function of the mixed surfactants, the supernatant liquids after synthesis of Fe_3O_4 squared and circular nanoplates were characterized by FTIR and compared with oleic acid and oleylamine. The IR spectra (in Figure S3e) showed that the peak at 1710 cm⁻¹ corresponding to the stretching C=O bond in oleic acid was shifted to 1702 cm⁻¹, which can be attributed to the formation of dioleamide from oleic acid and oleylamine during the solvothermal process according to the literature.^{7,8} The peak at 1723 cm⁻¹ can assigned to the stretching C=O bond in the acetylacetone from the decomposition of Fe(acac)₃. The TEM observation revealed that the sample with the regular morphology can be obtained only under the mixed surfactants mole ratio of oleic acid to oleylamine at 1:1. Therefore, the new surfactant formed from oleic acid and oleylamine played the important role in the control of the morphology and growth direction of magnetite nanocrystals.

Effect of the different alcohols



Figure S4. Effect of the reductants on the morphology of the products: (a) ethylene glycol; (b) propanediol; (c) diethanol amine; (d) polyethylene glycol (400). (The scale bars represent 50 nm.)

In this case, several diols have been tested for their reactions with $Fe(acac)_3$. It was found that short-chain diols, including ethylene glycol, propanediol, and diethanol amine, reacted with $Fe(acac)_3$ to yield relative large Fe_3O_4 nanoparticles without regular morphology (shown in Figure S4a~c in the Supporting Information). Long-chain diols, such as 1,2-hexadecanediol and polyethylene glycol (PEG400), can be used to form relative small Fe_3O_4 nanoparticles (shown in Figure S3d). Compared to 1,2-hexadecanediol, PEG400 reacted with $Fe(acac)_3$ to yield smaller nanoparticles with the size of 5~6 nm, but the morphology of the products was not regular. Effect of the reaction temperature



Figure S5. Effect of the reaction temperature with the same reaction time of 6 hours on the morphology of the products: (a) 160 $^{\circ}$ C; (b) 180 $^{\circ}$ C. (The scale bars represent 50 nm.)

Reaction temperature is the key point to form the monodisperse nanoparticles. When the temperature was lower than 160 °C, Fe(acac)₃ could not decompose to form Fe(III) intermedia, resulting that no product was yield. At the temperature of 160 °C, Fe(acac)₃ began to decompose and then reacted with diols to form Fe₃O₄ nanoparticles in the size of 2~5 nm (shown in Figure S5a). With the temperature increasing to 180 °C, the size of the yield nanoparticles increased to about 10 nm, but the morphology was still not regular (shown in Figure S5b). Regular squared and spherical morphology of Fe₃O₄ nanoparticles could be obtained only at the reaction temperature of 200 °C.

Effect of reaction time



Figure S6. Effect of the reaction time at the temperature of 200 $^{\circ}$ C on the morphology of the products: (a) 1 hour; (b) 2 hours; (c) 4 hours; (d) 6 hours; (e) 12 hours; (f) 24 hours. (The scale bars represent 30 nm.)

The key to success of making uniform nanoparticles with regular morphology is the reaction time. In the synthesis procedure of squared nanoplates, when the reactants mixture was heated at 200 °C for 1 hour, amorphous Fe_3O_4 clusters were obtained (shown in Figure S6a). With the reaction time elongating to 2 hours, the crystalline nanoparticles without regular morphology could be obtained. Rough squared nanoplates could be found in the products with the reaction time of 4 hours. Through 6 hours heating, uniform squared nanoplates were obtained. Over 6 hours, there was a trend of the sizesplitting in the products. From Figure S6e, it can be found that there are two parts in the products: one part is smaller than 15 nm in size; the other is larger than 15 nm in size. When the reaction time was elongating to 24 hours, the trend was more obvious. It indicates that the Ostwald repining process existed in the syntheses.



Figure S7. Cyclic voltammograms a) and Nyquist diagram of electrochemical impedance spectra b) for bare and squared and circular Fe_3O_4 nanoplates modified SPCE in the solution of 5 mM $Fe(CN)_6^{3-/4-}$ containing 0.1 MKCl. Scan rate: 100 mV s ⁻¹.



Figure S8. Plots of current versus the square root of the scan rate with a linear trendline at a) squared and b) circular Fe_3O_4 nanoplates modified SPCE. Data were collected from scan rate study in the solution of 5 mM $Fe(CN)_6^{3-/4-}$ containing 0.1 M KCl.



Figure S9. Typical SWASV response of a) squared and b) circular Fe_3O_4 nanoplates modified SPCE for analysis of As(III) in different concentration range. Supporting electrolyte: 0.1 M acetate buffer (pH 5.0). Deposition potential, -0.5 V; deposition time, 120 s; amplitude, 25 mV; increment potential, 4 mV; frequency, 15 Hz. The dotted line refers to the baseline.



Figure S10. Side and top views of slab models for Fe_3O_4 two different surfaces. (a), (b) for $Fe_3O_4(001)$ surface, (c), (d) for $Fe_3O_4(111)$ surface. The red and gray spheres stand for is O and Fe atoms, respectively.



Figure S11. The projected densities of states for H_3AsO_3 and H_3AsO_3 on $Fe_3O_4(001)$ and $Fe_3O_4(111)$ planes, respectively.



Figure S12. Side view of optimized adsorption of H_2AsO_3 , $HAsO_3$ and AsO_2 on different Fe₃O₄ crystal planes: a-c) (001), d-f) (111) planes, and the related adsorption energies. Red, gray, purple and white spheres stand for O, Fe, As and H atoms, respectively.

Table S1 The adsorption energies (in eV) of H₃AsO₃, H₂AsO₃, HAsO₃ and AsO₂ on Fe₃O₄(001) and Fe₃O₄(111) planes, respectively.

	H ₃ AsO ₃	H ₂ AsO ₃	HAsO ₃	AsO ₂
Fe ₃ O ₄ (001)	-1.73	-3.82	-5.00	-5.14
Fe ₃ O ₄ (111)	-1.06	-2.44	-2.20	-2.87

We also examined the adsorption behavior of the other As(III) species with dehydrogenation including H₂AsO₃, HAsO₃ and AsO₂onFe₃O₄(001) and Fe₃O₄(111)surfaces. Their optimized adsorption configurations are plotted in FigureS12. The corresponding adsorption energies are summarized in Table S1. It is clear that all As(III) species with dehydrogenation also display the facet-dependent behavior, similar to H₃AsO₃ on Fe₃O₄ two different facets. Compared with Fe₃O₄(111) surface, the interactions between all other As(III) species with dehydrogenation on Fe₃O₄(001) surface are stronger.