

Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Controlled Synthesis of Iron Oxide Nanoplates and Nanoflowers

Soubantika Palchoudhury,^a Yaolin Xu,^a Amanda Rushdi,^a Robert A. Holler,^b and Yuping Bao^{*a}

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

Experimental details

Chemicals

All reagents were used as purchased without further purification. These included: ferric chloride (98%, anhydrous, Acros Organics), potassium oleate (40 wt% paste in water, Fisher), oleic acid (OA, Fischer), tri-n-octylphosphine oxide (TOPO, 90%, Sigma-Aldrich), hexane (99%, Sigma-Aldrich), ethanol (VWR, 99%), 1-octadecene (90%, technical grade, Sigma-Aldrich), sodium hydroxide (99%, VWR).

Synthesis of the precursor, iron oleate complex

Iron oleate complex was prepared by reacting ferric chloride (6.5 g) and potassium oleate (96.2 g) in a solvent mixture (hexane/water/ethanol) following a similar procedure reported elsewhere.¹⁸ After phase separation, the hexane phase containing iron oleate complex was washed with de-ionized water to remove the by-products, and stored as precursor, where the hexane accounted for 6.5 wt%. The reason of using iron oleate hexane solution rather than the well-dried iron oleate waxy paste as precursor is two-fold: easy operation and control of the reaction temperature. The present of hexane, a low-boiling temperature solvent, allows for controlling the reaction temperature at 290 °C, instead of 315 °C, the boiling temperature of 1-octadecene, for nanosphere synthesis.

Synthesis of the iron oxide nanoplates and nanoflowers

The iron oxide nanoplates and nanoflowers were synthesized following a similar procedure to our previous reports of the spherical nanoparticle synthesis.¹⁸⁻²⁰ The key differences here were the amount of trioctylphosphine oxide (TOPO), a weakly-bounded ligand to iron and the reaction temperature. Specifically, iron oleate hexane solution (1.82 g) in 1-octadecene (13 mL) was heated to 290 °C for an hour in the presence of oleic acid (0.1 mL) and TOPO (0.2 g-nanoplates or 1 g-nanoflowers). After synthesis, the nanoparticles were centrifuged out of solution for further characterization.

Mechanistic study of the nanoplate and nanoflower formation

The time-dependent growth studies for both nanoplates and nanoflowers were conducted by taking samples out of reaction solution at various time intervals (10 min, 30 min, and 1 h). To further elucidate the growth mechanism of the nanoplates, sodium ethoxide, hexane, or sodium oleate was injected into the

reaction to understand the role of $\text{CH}_3\text{CH}_2\text{O}^-$. In contrast, for nanoflower formation, hexane, extra precursor, or additional TOPO injection was conducted to understand the multiple nucleation events. For all the injection reactions, well-dried iron oxide paste was used as precursor and the reaction temperature was set at 315 °C, a condition known for nanoparticle synthesis.

Characterization

The size and morphology of the iron oxide nanoplates and nanoflowers were examined on a FEI Tecnai F-20 transmission electron microscopy (TEM). The nanoplate thickness was determined by the TEM tilting experiment. The x-ray diffraction (XRD) pattern of the nanoplates and nanoflowers were collected on a Bruker AXSD-8-Advanced x-ray diffractometer using a Cu source ($K\alpha$, $\lambda = 1.54 \text{ \AA}$). The Fe and O valance states of the iron oxide nanoparticles were studied using x-ray photoelectron spectroscopy (XPS) on a Kratos AXIS 165 Multitechnique Electron Spectrometer, equipped with a monochromatic x-ray source (Al, $h\nu = 1486.6 \text{ eV}$). The magnetic moment versus applied magnetic field (M-H) curves of these nanoplates and nanoflowers were measured using a Princeton alternating gradient field magnetometer (AGM) at room temperature. Samples for both the XRD and AGM measurement were prepared by placing well-dried nanoparticle powders on double-sided tape.

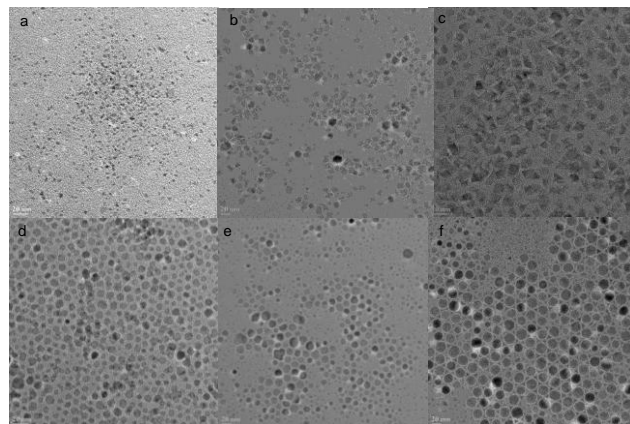


Fig.S1 Mechanistic studies of nanoplates: (a) 10 min, (b) 30 min, (c) 1 h, (d) ethanol injection, (e) hexane injection, and (f) sodium oleate injection.

Fig. S1a-c show the time-dependent growth studies of nanoplates (10 min, 30 min, and 1 h). Small, non-spherical iron oxide NPs (~ 4 nm) were formed after 10 min (Fig. S1a). After 30 min, plate-like nanostructures with a wide size distribution were observed, indicating nanoparticle growth (Fig. S1b). Iron oxide nanoplates of side length ~18 nm were formed after 1 h (Fig. S1c). Compared to the nanoparticle sizes at 30 min, a much narrower size distribution was observed due to the size focusing. Fig. S1d-f shows the nanostructures produced with the injection of ethanol, hexane, and sodium oleate.

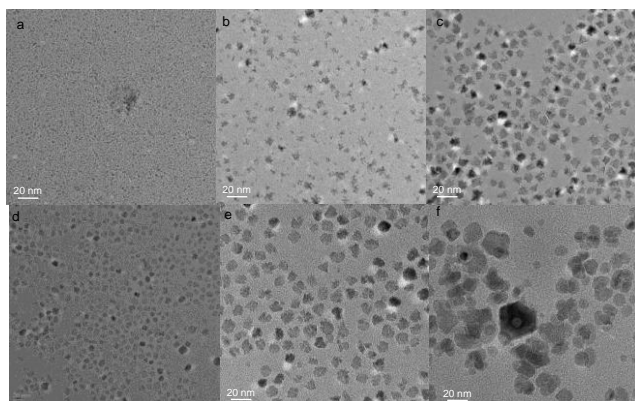


Fig. S2. Mechanistic studies of nanoplates: (a) 10 min, (b) 30 min, (c) 1 h, (d) TOPO injection, (e) hexane, and (f) iron oleate precursor injection

Figure S2a-c show the time-dependent studies of the nanoflowers. At 10 min, very small iron oxide nuclei (< 2 nm) were formed (Fig. S2a). As the reaction proceeded to 30 min, some nanoflowers (~ 20 nm) could be seen clearly (Fig. S2b). After an hour, uniform iron oxide nanoflowers became the main product (Fig. S2c). Fig. S2d-f show the nanostructures produced with the injection of TOPO, hexane, and excess precursors. Both TOPO and hexane injection produced aggregated NPs to some extent. The additional precursor injection caused aggregation of larger NPs and the size distribution was wide. The synthesis of both iron oxide nanoplates and nanoflowers, described above were highly reproducible in terms of nanoparticle size and shape, which were summarized in Table 1.

Table S1. A summary of all the reaction condition and their corresponding morphologies.

Precursor	Reaction condition	variables	Morphology
Iron oleate in hexane	TOPO-0.2g, 290 °C, 1 h	N/A	nanoplate
Iron oleate in hexane	TOPO-1g, 290 °C, 1 h	N/A	nanoflowers
Dried iron oleate	TOPO-0.2g, 315 °C, 1 h	Injection of ethanol, hexane, sodium oleate	Spheres with wide size distribution
Dried iron oleate	TOPO-0.2g, 315 °C, 1 h	Injection of C ₂ H ₅ O	nanoplate
Dried iron oleate	TOPO-1g, 290 °C, 1 h	Injection of TOPO, hexane	flower-like nanoparticles
Dried iron oleate	TOPO-1g, 290 °C, 1 h	Injection of excess precursor	Aggregated spheres

Optical properties of the nanoplates and nanoflowers

The UV-vis spectra of the nanoplates and nanoflowers were collected on a Shimadzu UV-visible spectrophotometer (UV-1700 series). Figure S3 shows the absorption of these nanoparticles in hexane in the range of 300-700 nm and magnetite nanosphere were used as a comparison. The optical transition of iron oxide nanoparticles were normally resulted from the Fe³⁺ ligand field transition, ligand-metal charge transfer, and the magnetically coupled Fe³⁺ pair excitation. The spectra indicate that nanoplates have similar magnetic coupling between the neighbouring ions, but the ligand-charge transfer significantly affected the optical properties of nanoflowers.

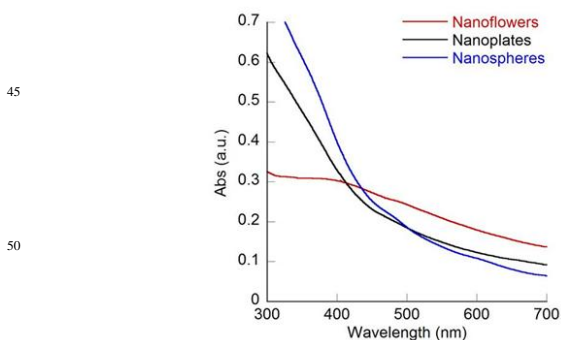


Fig. S3. UV-vis spectra of nanoflowers, nanoplates and nanospheres.