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Shape-dependent magnetic and microwave absorption properties of iron oxide nanocrystals

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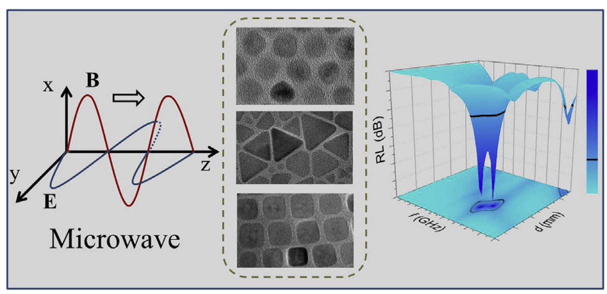
HIGHLIGHTS

- A facile solution route to monodisperse iron oxide nanocrystals with tunable shapes.
- The magnetic properties of iron oxide nanocrystals are greatly affected by their shapes.
- The microwave absorption performance of nanospheres, nanocubes and nanoplates is compared.
- Triangular Fe_3O_4 nanoplates exhibit superior microwave absorption properties.

GRAPHICAL ABSTRACT



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ABSTRACT

Synthesis of uniform magnetic nanocrystals with tunable shape is valuable to investigate the microwave absorption properties that depend closely on the shape and size. In this study, we utilize an efficient method to synthesize nano-sized iron oxide nanocrystals with different shapes through thermal decomposition of $Fe(acac)_3$ in oleylamine. While the spherical Fe_3O_4 nanocrystals display a typical superparamagnetic behavior at room temperature, the triangular nanoplates exhibit a blocking behavior at an unexpected high temperature. The antiferromagnetic-ferrimagnetic core-shell structure of FeO@-Fe_3O_4 nanocubes presents exchange bias behavior. We also investigate the high frequency properties of all samples by a network analyzer. Compared to spherical and cubic shapes, the triangular Fe_3O_4 nanoplates exhibit significantly enhanced microwave absorption performance in terms of strong reflection loss and wide bandwidth. Moreover, the triangular Fe_3O_4 nanoplates have obvious dielectric and magnetic resonance behaviors responding to the microwave at the frequency range of 2–18 GHz. The dielectric and magnetic resonance behaviors may be derived from the interface polarization and exchange resonance. The minimum reflection loss of triangular Fe_3O_4 nanoplates reaches −32.1 dB at 11.7 GHz and the bandwidth less than −10 dB is from 10.6 to 13.3 GHz at a thickness of 2.5 mm.

1. Introduction

Electromagnetic (EM) wave absorption materials have become a cutting-edge subject due to the EM problems such as the EM pollution and EM interference in rapid development of wireless

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Table 1
Reaction parameters for the synthesis of iron oxide nanocrystals. The quantity of $Fe(acac)_3$ was kept as 0.6 mmol and the reaction temperature was kept at 275 °C in all syntheses.

Number	OAm (mL)	BE (mL)	DH (mmol)	DTAC (mmol)	Time (h)	Shape
1	8	–	0.1	–	0.5	Sphere
2	8	–	0.4	–	0.5	Sphere, cube
3	8	–	0.6	–	0.5	Cube
4	8	–	0.6	–	3	Cube
5	8	1	–	–	0.5	Sphere
6	8	1	–	0.3	0.5	Sphere, nanoplate
7	8	1	–	0.6	0.5	nanoplate
8	8	1	–	1.2	0.5	nanoplate

communication or the military purpose for stealth materials to reducing the reflection area of radar [1–6]. As one of the promising microwave absorption materials, the iron oxides are paid more particularly attentions due to their strong magnetic moment, relative earth abundance, easy to prepare, nontoxicity and low cost [7–13]. The iron oxide nanocrystals with controllable size and shape have long attracted the interests of researchers because the microwave absorption properties are closely related to the shape and size. Firstly, the nanocrystals have the features of the nano-size properties [14–18]. The quantum size effect of nanocrystals leads to the electron energy level splitting and the energy level is located in the range of microwave energy (10^{-2}–10^{-5} eV). Moreover, large specific surface area of nanocrystals has lots of dangling bonds which increase the interface polarization and multiple scattering to improve the microwave absorption [19–21]. The electromagnetic parameters, such as the complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and the complex permeability ($\mu_r = \mu' - j\mu''$) are dependent on the shape and size of nanocrystals. So many efforts have been devoted to investigate the microwave absorption mechanism with different shapes and sizes. Ding et al. investigated the microwave absorption properties of different size Fe_3O_4 nanodiscs [22]. Liu et al. found that large specific surface area and shape anisotropy of elliptical polycrystalline Fe_3O_4 contributed to significantly enhanced microwave absorption performance [23]. Shang et al. utilized one-pot *in-situ* molten salt synthesis of octahedral Fe_3O_4 for efficient microwave absorption application [24]. Song et al. synthesized the monodisperse Fe_3O_4 nanoparticles which exceed natural resonance frequency limit *via* superparamagnetic relaxation [7]. In addition to the above studies, cube-like [14], flower-like [25], hollow hemisphere-like [26], hollow nanoring and nanotube [27] and dendrite-like Fe_3O_4 particles [9] have been fabricated and their microwave absorption properties have been investigated.

Despite extensive efforts have been made on the investigation of the magnetic and microwave absorption properties of Fe_3O_4 nanocrystals, reports are not common on Fe_3O_4 nanocrystals with an anisotropic shape such as triangular nanoplates. Meanwhile, the synthesis of the nanocrystals with strong microwave absorption in a relatively lower frequency still has challenges. Hence, it is valuable to fabricate a microwave absorber with tunable shape to satisfy the above mentioned demands. In this study, we have synthesized triangular nanoplates with the edge length about 15 nm. To investigate the mechanism of microwave absorption of Fe_3O_4 triangular nanoplates, we have also studied the electromagnetic properties of Fe_3O_4 nanocrystals with spherical and cubic shapes. As a result, the anisotropic architectures of triangular Fe_3O_4 nanoplates had unique electromagnetic properties. Compared to Fe_3O_4 nanospheres, the obvious resonance behaviors of complex permittivity and permeability were observed in dielectric and magnetic spectra of the triangular Fe_3O_4 nanoplates. The mechanism of microwave absorption was further discussed.

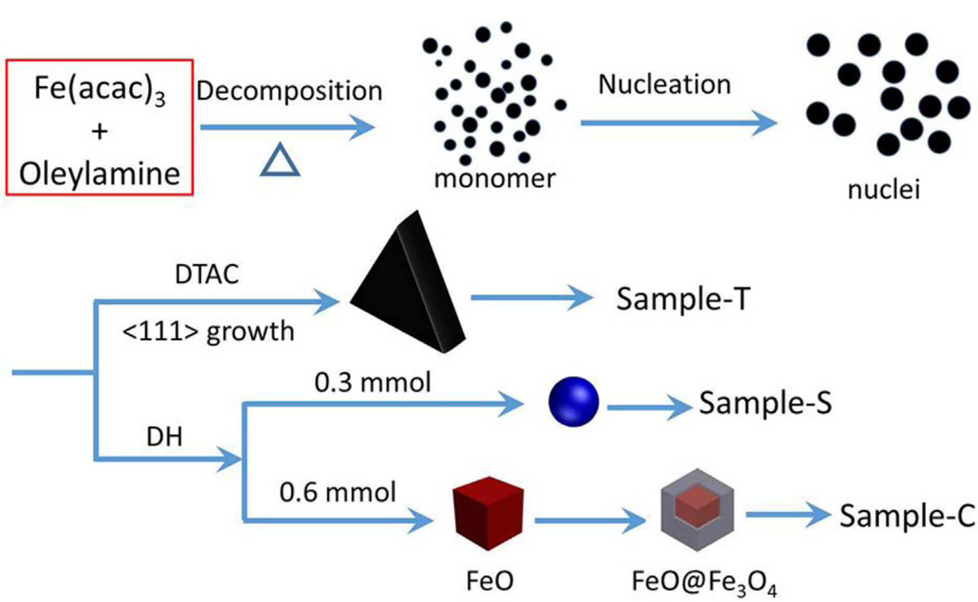

Fig. 1. Schematic illustration for the formation of iron oxide nanocrystals with different shapes.