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Synthesis and characterization of nanosized urchin-like α -Fe₂O₃ and Fe₃O₄: Microwave electromagnetic and absorbing properties

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ABSTRACT

Urchin-like α -Fe₂O₃ and Fe₃O₄ nanostructures were prepared from the precursor urchin-like α -FeOOH under reducing atmosphere. The dependence of reduction temperature on their morphology, microstructure, and microwave electromagnetic and absorbing characteristics were systematically studied. It is found that the reduction temperature plays an important role in the microstructure and electromagnetic characteristics of the resulting products. In present study, the urchin-like α -Fe₂O₃ with dual absorption peaks can be formed at the relatively low temperature (e.g. 300 °C). Urchin-like Fe₃O₄ can be obtained just at 350–400 °C, which presents excellent microwave absorption property, with the minimum reflection loss of –29.96 dB and below –20 dB in 3.76–8.15 GHz corresponding to 3–4 mm thickness. The excellent microwave-absorption properties are a consequence of a proper electromagnetic matching and enhanced absorbing abilities resulting from the urchin-like shape and inverse spinel-type crystal structure.

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1. Introduction

With the rapid development of wireless telecommunication systems, electromagnetic interference (EMI) and EM-wave pollution are increasingly deteriorated nowadays. For this purpose, extensive studies have been carried out to exploit new and high efficient absorbents to prevent such phenomena. Among all the contenders, new type nanomaterials with complex nanostructures have attracted considerable attention owing to their unique chemical and physical properties [1–6], especially as microwave absorbing and shielding materials [7–12]. For example, Cao et al. [8] prepared cagelike ZnO/SiO₂ nanocomposites with the maximal attenuation of 10.68 dB at 12.79 GHz. As reported by Yan et al. [9,10] the maximal attenuation values for ZnO nanotrees and 3D spongelike Mn₂O₃ porous network were 42 dB at 3.6 GHz with a thickness of 5.0 mm and 27.1 dB at 3.1 GHz with a thickness of 6.0 mm, respectively. Zou et al. [11] found that the plane antenna absorbent presented an effective bandwidth. Recently, Kang and co-workers [12] observed that FeCo alloy particles/graphite nanoflake composites showed a strong low-frequency absorption of -30.6 dB at 7.4 GHz with a coating thickness of 2.0 mm. Notwithstanding, the aforementioned new-type complex nanostructures display some enhanced electromagnetic characteristics and novel absorption mechanism, the corresponding absorption performances are far from satisfactory for practical application. Thus, it is still a great challenge to find new types of complex nanostructures with relatively light weight, flexible and sound structure, and especially excellent microwave absorbing properties.

Iron oxides (e.g. α -Fe₂O₃ and Fe₃O₄), are generally recognized as most of promising materials because of their low cost, non-toxicity, environmental benignity, and interesting magnetic behaviors, which is of great importance to have potential applications as catalysts, gas sensors, magnetic filters, electrode materials, magnetic storage media, as well as materials for microwave absorbing and shielding research [13–17]. Interestingly, these intrinsic properties of magnetic nanostructures may be tailored by controlling their shape, composition, size, and so forth.

Despite its fundamental and technological importance, the challenge of systematically controlling the morphology, structure, and properties of iron oxides with complex nanostructures have been met with limited success [14,18–21]. Meanwhile, the reported literatures mainly focused on the investigation of the photocatalytic, magnetic, and electrochemical properties of iron oxide complex nanostructures [14,18–21]. To the best of our knowledge, a systematic investigation of microwave electromagnetic and absorbing properties of urchin-like α -Fe₂O₃, especially urchin-like Fe₃O₄ is still unavailable so far. In present study, we developed a facile glucose-guided hydrolyzing-reducing process for the preparation of urchin-like α -Fe₂O₃ and Fe₃O₄, which exhibited excellent microwave absorption properties. Furthermore, structural evolution, electromagnetic characteristics, and microwave absorption mechanism were discussed in detail.

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Fig. 1. (a and b) SEM, (c) XRD pattern and (d) IR spectrum of urchin-like α -FeOOH nanostructures synthesized at 60 °C for 12 h.

2. Experimental

2.1. Materials

All reagents including D_{+} -glucose ($C_6H_{12}O_6$ - H_2O , AR) and iron (II) sulfate heptahydrate (FeSO₄-7H₂O, AR) were obtained from Shanghai Sinopharm and used without any further purification.

2.2. Preparation

2.2.1. Synthesis of the precursor urchin-like α -FeOOH

The synthesis method-the glucose-guided hydrolyzing approach has been described elsewhere previously in detail [21,22]. In a typical synthesis, certain amount of $D_{-}(+)$ -glucose, FeSO₄.7H₂O, and deionized water were added into a 400 mL three-naked conical flask, and refluxed at 60 °C for 12 h under magnetic stirring and a constant air flow of 1.0 L/min. The urchin-like α -FeOOH precursors were collected by filtrating and washed with deionized water and absolute ethanol for 3 times, respectively, finally dried in a vacuum oven at 90 °C for 12 h.

2.2.2. Synthesis of urchin-like α -Fe₂O₃ and Fe₃O₄

According to the conventional reaction (1) [21,22], the urchin-like α -Fe₂O₃ was obtained after calcinations of the urchin-like α -Fe₂O₄ precursor at 300 °C for 1 h with a heating rate of 5 °C/min. The urchin-like α -Fe₂O₃ conversion to urchin-like Fe₃O₄ was achieved at 350–400 °C for 2 h in H₂/Ar (1:4 volume ratio) mixing gas at a flow of 1.0 L/min. Finally, the system was allowed to cool down naturally to room temperature under the umbrella of N₂.

$$2\alpha \operatorname{FeOOH}_{\Delta} \rightarrow \alpha \operatorname{Fe_2O_3} + \operatorname{H_2O}$$
(1)

2.3. Characterization

The morphologies of the as-prepared samples were observed by a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800), operated at 10.0 kV. The phase analysis of the samples was performed by X-ray diffraction (XRD) on a RIGAKU D/MAX-IIIA diffractometer with CuK α radiation. Fourier-transforming infrared

(FTIR) absorption spectra were captured with a Nicolet FTIR-170SX spectrometer in the range of 4000–400 cm⁻¹ at room temperature with the sample in a KBr disk.

The transmission/reflection method was applied to determine the relative complex permeability and permittivity of the sample-wax composites through an Agilent N5230 vector network analyzer system. The cylindrical toroidal samples with 3.0 mm in inner diameter, 7.0 mm in outer diameter and 3.5 mm in thickness were fabricated by uniformly mixing wax with 50 wt% the absorbents and then pressed into cylindrical compacts. Based on the above relative permeability and permittivity at the given frequency, the reflection loss (R_L) curves were calculated according to transmission line theory [9].

3. Results and discussion

3.1. The morphology and structure of the precursors

Fig. 1a and b shows the low- and high-magnification SEM images of the precursors obtained by a facile glucose-guided hydrolyzing approach. It can be seen that urchin-like aggregates with 0.5–1.0 μ m in diameter consist of sea shuttle fibrous bunches with 40–100 nm in diameter and ca. 200 nm in length, radially growing from a center of the aggregate. Fig. 1c shows that the XRD patterns of the precursors, in which all the characteristic peaks are in good agreement with α -FeOOH (JCPDS card no. 29-0713). This is further confirmed by the FTIR analysis. Observed from Fig. 1d, the sharp peaks at 3178, 892, and 794 cm⁻¹ are attributed to the characteristic vibrations in the FeO-(OH) product [23], while the strong broad peak at 3384 cm⁻¹ and the sharp peak at 1638 cm⁻¹ correspond to the stretching vibration and the bending vibration of hydroxyl groups in the surface-adsorbed molecules [24,25], respectively. Thus the as-obtained precursors are urchin-like α -FeOOH.



Fig. 2. XRD patterns of the products obtained at various *T*_r.

3.2. The microstructure dependence on reduction temperature

Fig. 2 presents the XRD patterns of the products obtained at various T_r. Compared with the data in JCPDS card no. 24-0072, all peaks denoted by the \blacklozenge sign, from the products obtained at $T_r = 300 \circ C$, can be identified as α -Fe₂O₃ with orthorhombic system. Whereas, all the peaks indicated by the ♥symbol disclose that the products obtained at T_r = 350–400 °C are face centered cubic Fe₃O₄ (JCPDS card no. 65-3107). Owing to the enhanced crystallization and the enlarged crystal size, the intensity of peaks significantly sharpens as the T_r goes up. Known by JCPDS card no. 65-3107 and 06-0696, the products obtained at $T_r = 450 \,^{\circ}$ C may be a mixture of Fe₃O₄ and α -Fe. However, at $T_r = 500 \,^{\circ}$ C the only three peaks denoted by the ∇ symbol can be accurately indexed as (110), (200) and (211) directions of body-centered cubic (bcc) α -Fe, respectively, consistent with the reported data (JCPDS card no. 06-0696). This demonstrates that the chemical activity of H₂ is gradually boosted with the elevated temperature. Hereinto, pure Fe₃O₄ products can be gained just at T_r = 350–400 °C, in which H₂ begins to reduce partially Fe³⁺ into Fe^{2+} as shown in the reaction (2). However, at $T_r = 500 \circ C$ or higher, the chemical activity of H₂ is improved enough to completely revert Fe³⁺ to Fe⁰ (see reaction (3)), resulting in the formation of the pure metallic Fe products.

$$3\alpha - Fe_2O_3 + H_2 \xrightarrow{\Delta} 2Fe_3O_4 + H_2O$$
⁽²⁾

$$\alpha - Fe_2O_3 + 3H_2 \xrightarrow{} 2\alpha - Fe + 3H_2O \tag{3}$$

The average crystal size (δ) and internal strain (ε) of the products are calculated by the Hall–Williamson equation [26,27] and the results are listed in Table 1. It can be clear that varying the T_r from 300 °C to 500 °C, the δ fluctuates at the range of 12.4–104.1 nm and the ε changes at 0.052–0.0083% range. In addition, the δ and ε display an abnormal fluctuation at T_r = 450 °C due to the phase transformation. It indicates that the increasing T_r is conducive to the enhancement of the H₂ chemical activ-

ity and the growth rate of the crystals, resulting in the decrease of the internal strain and the increase of the average crystal size.

3.3. The morphology dependence on reduction temperature

Fig. 3 displays the SEM images of the products obtained at various T_r . The α -Fe₂O₃ samples gained at T_r = 300 °C still keep the initial shapes, namely, sea shuttle fibrous bunches with 20-50 nm in diameter radially spread and assemble into the spherical aggregates of $0.5-1.0 \,\mu\text{m}$ (shown in Fig. 3a). Also, the Fe₃O₄ samples obtained at $T_r = 350-400$ °C exhibit the urchin-like morphology. Interestingly, their building-blocks are not the fibrous bunches but the rod-like nanoparticles with the diameter of 20–50 nm and length of 50-200 nm (Fig. 3b and c). Furthermore, the aspect ratio of the nanorods decreases as the T_r increases (Fig. 3c). This is because at the relatively high reduction temperature, the nanoparticles reduced sharply grow via fusing the neighboring nanoparticles after phase transformation and nucleation, causing the formation of the nanorods. However, the size and the percentage of the urchinlike Fe₃O₄ particles obtained at $T_r = 450 \circ C$ decrease and the rod-like particles begin to appear (Fig. 3d), which can be deduced as α -Fe from the above XRD data. Further increasing the T_r to 500 °C, the urchin-like Fe₃O₄ particles completely disappeared and rod-like α -Fe particles with 20-50 nm in diameter and 50-200 nm in length formed. The aforesaid results demonstrate that the urchin-like α - Fe_2O_3 and Fe_3O_4 are apt to form at the moderate temperature, whereas the only rod-like α -Fe may be obtained at the relatively high temperature.

The above morphological evolution can be interpreted as follows: at the relatively low temperature (e.g. $T_r = 300 \circ C$), the remained morphology is associated with the mild phase transformation from α -FeOOH to α -Fe₂O₃, as well as the same and/or similar crystallographic system. While, at $T_r = 350-400$ °C, the maintenance of the urchin-like structures is mainly ascribed to the FeO₆ coordination octahedrons between the interphases of α -Fe₂O₃ and Fe₃O₄, which interact by sharing their vertices and/or edges. Besides, at $T_r = 450 \,^{\circ}$ C or higher, The morphological evolution from urchin-like to rod-like is relative to the different crystallographic system and the low melting point of Fe nanocrystals. As-reduced Fe nanocrystals automatically depart from the surface of the Fe₃O₄ precursors, causing the decreased size of the urchin-like Fe₃O₄, and subsequently are self-assembled into onedimensional structure under the induced process of the carrier gas flow and the spontaneous magnetization of magnetic nanoparticles [28]. Thus, the phase and morphology can be well tailored by modulation of the T_r .

3.4. The permittivity dependence on reduction temperature

Fig. 4 shows the frequency dependence of real (ε') and imaginary (ε'') parts of the relative complex permittivity for the wax-composites including 50 wt% samples obtained at various T_r . In general, α -Fe₂O₃ with corundum structure is an n-type semiconductor with relatively low ε' and ε'' [20]. Seen from Fig. 4, the ε' value of the urchin-like α -Fe₂O₃ obtained at T_r = 300 °C is about

Table 1

Average crystal size (δ), internal strain (ε), and microwave absorption properties of the as-obtained products at various reduction temperatures (T_r).

<i>T</i> _r (°C)	Crystallite size δ (nm)	Strain € (%)	Minimum R _L value (dB)	$f_{\rm m}$ (GHz) (minimum $R_{\rm L}$)	$\frac{d_{\rm m}(\rm mm)}{(R_{\rm L} < -20\rm dB)}$	Frequency range (GHz) (R _i < -20 dB)
300	12.4	0.052	-9.20	16.4	1	/
350	30.5	0.015	-24.89	4.4	3-4	4.20-6.40
400	67.2	0.014	-29.96	5.2	3-4	3.76-8.15
450	51.7	0.017	-21.22	8.4	3	7.89-8.23
500	104.1	0.0083	-19.07	13.2	1	



Fig. 3. SEM images of the samples obtained at different T_r of: (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C, and (e) 500 °C. The bars in (a)–(e) are 200 nm and the bar in (f) is 2 μ m.

5.0, and the ε'' value is about 0.5. It indicates that the urchinlike α -Fe₂O₃ possesses enhanced dielectric loss. The permittivity originates from orientation polarization, atomic polarization, and electronic polarization [7,29], and the dielectric loss may be classified in conductance loss (tg δ_e), dielectric relaxation loss (tg δ_{rel}), resonance loss (tg δ_{res}), and other [30]. They are strongly dependent on the composition, dimension, morphology, conductivity, and polarization model [31]. In this study, the improvement of the dielectric characteristics for α -Fe₂O₃ is mainly attributed to the enhanced orientation and interface polarization in the urchin-like



Fig. 4. (a) Real part ε' and (b) imaginary part ε'' of the permittivity for the wax-composites including 50 wt% samples obtained at various $T_{\rm r}$.



Fig. 5. (a) Real part μ' and (b) imaginary part μ'' of the complex permeability for the wax-composites including 50 wt% samples obtained at various $T_{\rm r}$.

structures [9], which is different from the rod-like and spherical particles.

By contrast, urchin-like Fe₃O₄ obtained at $T_r = 350$ °C exhibits significantly increasing ε' and ε'' , suggesting the higher storage and loss capability of the electric energy owing to the enhanced electrical conductivity of Fe₃O₄ arising from its inverse spinel-type crystal structure. Formally, it is written as Fe_A^{A+}[Fe²⁺, Fe³⁺]_BO₄²⁻ to show that the first (A type) Fe³⁺ is tetrahedrally coordinated, whereas the bracketed Fe²⁺ and Fe³⁺ ions occupy (B type) octahedrally coordinated sites. At room temperatures, hopping of the minority-spin "extra" electron between the B site Fe²⁺ and Fe³⁺ ions enhances the electronic conductivity σ [32,33]. On the one hand, known from tg $\delta_c = 1.8 \times 10^{10} (\sigma/f\varepsilon_r)$ [34], the enhanced electrical conductivity σ is good for the elevation of the conductance loss (tg δ_c). On the other hand, the space charge polarizations stemming from both the inverse spinel-type crystal and urchin-like structure cause the significant increase of the dielectric relaxation loss (tg δ_{rel}).

For the same phase structure, the ε' and ε'' of urchin-like Fe₃O₄ obtained at $T_r = 400 \degree C$ decrease. The change can be interpreted as following two aspects: One is the decreased dipoles. It is well known that the dipoles will contribute to the dielectric loss [35,36]. However, an increase in the T_r will lead to a decrease in the dipoles. This is because the number of surface atoms with unsaturated bonds decreases with the increasing crystalline size and the decreasing internal strain [37]. The other is the variation of the urchin-like structure. The urchin-like nanostructure can enhance the dielectric characteristics due to the special orientation and interface polarization. However, the above characteristics are closely relative with its structure parameters, such as crystal size, diameter, surface area, and aspect ratio of the nanorod. Therefore, the decreased aspect ratio with the increasing T_r may induce the weakened orientation polarization. Further, elevating the T_r from 450 °C to 500 °C, the ε' and ε'' of the as-prepared products further decrease owing to the disappearance of urchin-like Fe₃O₄ and appearance of the rod-like α -Fe. This further confirms the above results.

In addition, two strong peaks of 6–10 GHz and 11–16 GHz can be observed in the ε'' plots, implying a resonance behavior. Also, the similar multiresonance behaviors have been reported in the others literatures, which are ascribed to the existence of polarizable Fe²⁺ ions [38], the heterogeneous structure of the composite [39], the vacancy and space-charge polarization [40], respectively. Therefore, the general dispersive behaviors of dielectric response rely heavily on the composition, morphology, and microstructure of the samples. Seen from Fig. 4b, the resonance peaks are obviously enhanced after the appearance of the urchin-like Fe₃O₄ and weakened after the disappearance of the one. So we may deduce that electronic spin and charge polarization originating from the urchin-like Fe₃O₄ may be responsible for the above resonance. The result reveals that the permittivity resonance behavior reported here is the intrinsic characteristic of our urchin-like material.

3.5. The permeability dependence on reduction temperature

Fig. 5 presents the complex permeability of the wax composites with 50 wt% samples obtained at various T_r . As for the urchin-like α -Fe₂O₃ gained at T_r = 300 °C, the μ' and μ'' values are around 1.0 and 0.25, respectively. This suggests the presence of the weak ferromagnetic behavior and magnetic loss. Usually, α -Fe₂O₃ is an antiferromagnetic material below Morin temperature ($T_{\rm M}$ = 260 K) and exhibits weak ferromagnetic behavior (called parasitic ferromagnetism) when the temperature is between 260 and 955 K (Néel temperature). In this study, the oxygen vacancies inside the urchin-like α -Fe₂O₃ may destroy the balance of antiferromagnetic behavior, resulting in the extremely weak ferromagnetism and magnetic loss [41]. However, for the urchin-like Fe₃O₄ obtained at $T_r = 350-400$ °C, the μ'' significantly increases, suggesting the enhanced magnetic loss. This arises from its inverse spinel-type crystal structure, in which the incomplete cancellation of the two B site magnetic moments by the antiparallel A site cation moment results in ferrimagnetism and enhanced magnetic loss [32]. Meanwhile, the μ' and μ'' fluctuate at the range of 0.85–1.25 and 0.05–0.35, respectively, and slightly increase as the T_r increases as a result of the morphology and microstructure variation.

It is worthy of notice that the two sharp resonance peaks of the μ' and μ'' curves appear at 2–7 GHz and 14–18 GHz, respectively. Usually, for ferromagnetic materials the occurrences of two types of magnetic resonance are ferromagnetic and spin resonances. The former normally emerges at low frequency region (<2 GHz) owing to domain wall motion; while, the latter appears at high frequency region thanks to spin rotational component [42]. However, in our studies, the first resonance peak (around 7 GHz) may be related with the "exchange mode" resonance as a result of the small size effect, surface effect, and spin wave excitations. Whereas the second resonance peak (around 16 GHz) may be associated with natural resonance. This indicates that the multi-resonance behavior of the ferromagnetic matter is very sensitive to its composition, size, and morphology.

3.6. The absorption property dependence on reduction temperature

Fig. 6 shows a typical relationship between the calculated R_L and frequency for the wax composites containing 50 wt% samples obtained at various T_r . The entire curves present a similar variation trend and the R_L are found to be dependent sensitively on the coating thickness. On the one hand, R_L peaks gradually shift to the lower frequency with increasing coating thickness. On the other hand,



Fig. 6. Reflection loss curves of the as-prepared products obtained at various T_r.

the minimum $R_{\rm L}$ value changes with the coating thickness. This is in accord with $f_{\rm m} = (c/4d_{\rm m})(1/\sqrt{\varepsilon'\mu'})(1+(1/8)\tan^2\delta_{\rm M})^{-1}$ [43], where $d_{\rm m}$ is matching thickness, $f_{\rm m}$ is the matching frequency, and c is the velocity of light. Therefore, the best matching and absorbing performance can be achieved via adjusting the coating thickness and electromagnetic parameters.

The EM-wave absorption properties of the wax composites containing 50 wt% samples obtained at various T_r are summarized in Table 1. As shown in Fig. 6a and Table 1, as for the urchin-like α -Fe₂O₃ obtained at $T_r = 300$ °C, the absorbing peaks of 4–13 GHz and 14–18 GHz can be observed, respectively, with a minimum $R_{\rm L}$ value of -9.2 dB and coating thickness between 1.0 and 5.0 mm. However, the absorption properties of urchin-like Fe₃O₄ obtained at $T_r = 350-400 \circ C$ are significantly enhanced. Among them, urchinlike Fe₃O₄ obtained at $T_r = 400 \,^{\circ}\text{C}$ exhibits the optimal absorption properties, with a minimum $R_{\rm L}$ value of $-29.96\,\rm dB$ and below -20 dB in 3.76–8.15 GHz corresponding to 3–4 mm thickness. It is worth noting that the R_L values (below -20 dB in the 3.76-8.15 GHz frequency range) are broader frequency ranges than those reported in the literatures, i.e. carbon fibers coated by Fe₃O₄ nanoparticles [15], Fe₃O₄ nanoparticles [39], Fe₃O₄-carbon sphere composite [44]. Further increasing the T_r leads to a decrease in the number of urchin-like Fe₃O₄ and an increase in the number of rod-like α -Fe. Consequently, the absorbing intensity reduces and the effective bandwidth (below -20 dB) pinched down from 3.39 GHz to 0 GHz (see Table 1 and Fig. 6d and e).

Apparently, the mechanism for the microwave attenuation of urchin-like nonmaterial is different from that of conventional microwave absorbing materials due to the especially geometrical morphology. As can be seen from the aforesaid figures, urchin-like samples demonstrate diverse electromagnetic characteristics from the sphere-like and rod-like samples: (1) enhanced value of all parameters, especially for permittivity; (2) extra multi-resonance behaviors. Additionally, the following facts are well worth considering for the microwave attenuation of urchin-like nonmaterial: When the urchin-like samples are filled in the wax matrix, some urchin-like nanostructures interconnect and form the continuous micronetwork. This may generate the microcurrent network on a large scale, resulting in the enhancement of conductive loss [8]. Whereas, others with discontinuous networks can form isotropic quasi-antennas, which favors the electromagnetic wave to penetrate the composites containing the urchin-like iron oxide nanostructures. The above EM energy further is induced into a dissipative current and then consumed in the discontinuous networks [10]. However, to clarify the mechanism, further experimental and theoretical work will be carried out in the future.

4. Conclusions

Urchin-like α -Fe₂O₃ and Fe₃O₄ were synthesized after calcination of the urchin-like α -FeOOH precursors at diverse temperatures under reducing atmosphere, respectively; and the urchin-like α -FeOOH precursors were obtained by a glucose-guided hydrolyzing approach. The phase, morphology, and microstructure of the urchin-like nanomaterials can be well controlled and carried out via modulation of the temperature, which resulted in well controlled the electromagnetic characteristics correspondingly. Excellent microwave absorbing performances have been observed in urchin-like Fe₃O₄ obtained at 400 °C, with a minimum $R_{\rm L}$ value of -29.96 dB and below -20 dB in 3.76-8.15 GHz corresponding to 3-4 mm thickness. Our results give a novel insight of the absorption mechanism of urchin-like α -Fe₂O₃ and Fe₃O₄ for the first time. The urchin-like magnetic nanostructures would find applications in a variety of fields, such as catalysis, energy conversion, electromagnetic devices, electrode materials, sensors, biomedicine, and microwave absorbing and shielding materials, etc.

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