Research Article

Simple Hydrolysis Synthesis of Uniform Rice-Shaped β -FeOOH Nanocrystals and Their Transformation to α -Fe₂O₃ Microspheres

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In the synthesis of nanostructure materials a specific emphasis has been focused on the control of shape and orientation of nanocrystals to obtain prerequisite properties of the materials. Nanorice is a new hybrid nanoparticle prolate geometry of nanoshells with reduced symmetry having new exciting optical behavior. Rice-shaped β -FeOOH nanocrystals have been synthesized by a simple hydrolysis chemical method using ferric aqueous solution and urea as surfactant. The successive calcination of β -FeOOH nanocrystals at 650°C results in the formation of the porous α -Fe₂O₃ (hematite) microspheres. The as-synthesized yield of β -FeOOH nanocrystals was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), and optical spectroscopy. The successive transformation of rice-shaped β -FeOOH nanostructures into porous α -Fe₂O₃ (hematite) microspheres through calcination process was confirmed by XRD, SEM, and EDAX studies. The water contact angle of as-prepared α -Fe₂O₃ microspheres shows hydrophobic behavior of the material.

1. Introduction

The interest in nanomaterials has grown because of their distinct structural, optical, magnetic, electronic, mechanical, and chemical properties compared with those of the bulk materials. Magnetic nanoparticles with a size less than 100 nm represent an important class of nanostructure materials, which allow investigations of fundamental aspects of magnetic ordering phenomena and could lead to new technological applications. Magnetic iron oxides have been used in biomedicine for magnetic resonance imaging (MRI) and drug delivery and as a heating mediator for cancer radiotherapy [1]. In nonsurgical treatments of cancerous tumors, the heating is mainly achieved via magnetization relaxation in superparamagnetic state [2, 3] or hysteresis-loss heating [4]. The sensing capability of iron oxide (especially α -Fe₂O₃ and organic γ -Fe₂O₃ hybrid materials) in different gas sensors is a current research interest of many researchers [5–10]. The most common and interesting class of iron oxide are

magnetite (Fe₃O₄), maghemite (γ -Fe₂O₃), and hematite (α -Fe₂O₃). Iron oxyhydroxide (β -FeOOH) is the most effective and important catalyst and precursor explored in the synthesis of different geometrical nanostructures of iron oxides [11]. Hematite (α -Fe₂O₃) is the most thermodynamically stable structure of iron oxide and has potential applications with different shapes and geometry in nanoregime [12, 13]. Several studies have demonstrated that the fundamental properties of metal nanostructures can be effectively tailored by controlling their size, shape, composition, crystallinity, and structure [14–17]. Magnetic nanostructure materials with novel morphologies and phases are often required for interesting applications. Rice-shaped metal nanoparticles synthesis of silver [17, 18] and iron oxide nanoparticles as templates with thin gold shell [19] to produce rice-shaped gold core-shell nanoparticles has been devised successfully. Various synthesis approaches such as coprecipitation [20–22], hydrothermal synthesis [23–25], thermal decomposition [26, 27], and sol-gel method [28–30] have been used by

FIGURE 1: XRD patterns of (a) as-prepared β -FeOOH nanocrystals and (b) α -Fe₂O₃ microspheres after calcining at 650°C for 2 hrs.

various research groups worldwide for the synthesis of iron-oxide based nanomaterials.

In the present study, we have reported a simple and novel high-yield hydrolysis method to prepare monodisperse rice-shaped β -FeOOH nanocrystals (precursor) and successive transformation of the former into porous α -Fe₂O₃ (hematite) microspheres through calcination process. The as-synthesized products are characterized by XRD, SEM, EDAX, and UV-VIS absorption spectroscopy studies. The hydrophobic properties were measured by contact angle goniometry (Kruss DSA 100 easy drop) using sessile drop method at room temperature.

2. Materials and Methods

2.1. Materials Preparation. All the chemicals used in the research work were of analytical grade and used without further purification. In a typical experimental procedure, in the first step, a designated molar ratio of iron chloride (FeCl₃·6H₂O) and urea [CO(NH₂)₂] was dissolved in deionized water for the preparation of β -FeOOH nanocrystals (precursor). The mixture was vigorously stirred for 1 hr at 90°C to form a homogenous solution and then cooled down to room temperature. Finally, the produced precipitates were collected by centrifugation, filtered and washed several times with deionized water followed by ethanol, and then dried at 70°C for 4 hrs. The as-prepared dry powder was further heated at 250°C for 1 hr, resulting in the formation of β -FeOOH nanocrystals. In the next step, the as-prepared product (β -FeOOH nanocrystals precursor) was annealed in a tube furnace at 650°C for 2 hours in air to get α -Fe₂O₃ phase microspheres. The resultant products β -FeOOH nanocrystals and α -Fe₂O₃ microspheres were used for further characterization.

2.2. Characterization Techniques. The phase of the samples was examined by X-ray powder diffraction (XRD) using a Bruker, D8 Advance X-ray diffractometer with CuK α radiation (1.5406 Å) over the 2θ range 20–70°. The morphology of the synthesized powders was investigated by scanning electron microscopy (SEM) with EDX analysis to investigate the details of their microstructure and composition. The instrument UV-VIS Spectrophotometer (Hitachi U-3400) was used to measure the absorption spectra of sample. Absorption measurements were performed in the wavelength spectral range 400–700 nm. Sessile drop method was employed to measure the water droplet contact angle by using contact angle goniometry (Kruss DSA 100 easy drop) to confirm the hydrophobic nature. The average contact angle was determined by dropping the distilled deionized water droplets at different positions on the α -Fe₂O₃ surface coating using a microsyringe.

3. Results and Discussion

3.1. X-Ray Diffraction (XRD) Studies. The phase of as-prepared β -FeOOH nanocrystals and their transformation to α -Fe₂O₃ phase was investigated by XRD. Figure 1 shows the XRD patterns of as-prepared β -FeOOH nanocrystals and α -Fe₂O₃ microspheres. All the diffraction peaks in Figure 1(a) are assigned to the tetragonal β -FeOOH phase according to JCPDS card number 34-1266, confirming the formation of well crystalline β -FeOOH structure heated at 250°C in air. Absence of other characteristic peaks of α -Fe₂O₃ and γ -Fe₂O₃ in the XRD pattern (Figure 1(a)) confirms the formation of β -FeOOH nanocrystals without any impurities whereas the clarity and sharpness of the all peaks indicate the good crystallization of as-prepared sample.

The as-prepared sample was calcined at 650°C for 2 hours to transform the β -FeOOH nanocrystals to α -Fe₂O₃

FIGURE 2: SEM micrograph of (a) as-prepared β -FeOOH nanocrystals and (b) α -Fe₂O₃ microspheres after calcining at 650°C for 2 hrs.

(hematite) phase as can be seen from XRD pattern reported in Figure 1(b). All diffraction peaks in Figure 1(b) are assigned to the rhombohedral α -Fe₂O₃ (hematite) phase according to JCPDS card number 33-0664, confirming the transformation of crystalline β -FeOOH to α -Fe₂O₃ (hematite) phase after calcining the former at 650°C in air. The α -Fe₂O₃ microspheres show good crystallinity with strong preferential orientations along (104) and (110) planes at 2θ values around 33.19° and 35.68°, respectively, showing a prospective in photocatalytic application due to the good conductivity for fast electron transfer in α -Fe₂O₃ [31]. Furthermore, the intense and sharp peaks in XRD (Figure 1(b)) are indicative of good crystalline nature of the sample without producing any impurities and mixing of other phases of iron oxide. The XRD results are consistent with the recent research work reported by various workers on iron oxides [11, 31, 32].

The peak broadening in all the XRD patterns of the samples clearly indicates the formation of crystals of small size. The crystallite size (D) has been estimated by using the following Scherrer formula [33]:

$$D = \frac{k\lambda}{\beta \cos \theta}, \quad (1)$$

where λ is the wavelength used ($\lambda = 1.54 \text{ \AA}$), β is the full width half maximum (FWHM) of a particular diffraction peak in radians, θ is the Bragg angle, and k is a constant equal to 0.9. The peak broadening at lower angle is more meaningful for the calculation of particle size; therefore the size of β -FeOOH and α -Fe₂O₃ samples was calculated using high intensity peak (112) and (104) in XRD patterns of β -FeOOH and α -Fe₂O₃, respectively. The calculated size is found to be 16.09 nm and 22.06 nm for β -FeOOH and α -Fe₂O₃, respectively. This increment in the crystal size further reveals phase transformation from β -FeOOH to α -Fe₂O₃ after calcining at 650°C.

3.2. Scanning Electron Microscopy (SEM) and EDAX Studies. Field Emission Scanning Electron Microscope (FEI, Quanta 200F) with EDX analysis is used to study the microstructure and chemical composition of samples. Figure 2 shows the high magnification image of β -FeOOH nanocrystals and α -Fe₂O₃ microspheres. Figure 2(a) shows the formation of uniform rice-shaped nanocrystals of β -FeOOH precursor with maximum length of about 300 nm.

Figure 2(b) shows the high magnification image of α -Fe₂O₃ microspheres after calcining at 650°C for 2 hrs. As shown in this SEM image, it is clear that the calcination at 650°C affects the shape, size, and uniformity of the α -Fe₂O₃ microspheres. The rice-shaped nanocrystals of β -FeOOH precursor were congregated and fused to form aggregated irregular microspheres of α -Fe₂O₃ with a maximum diameter of around 200 nm. The higher surface area (due to porosity) of α -Fe₂O₃ microstructures is much desirable because the intercalation capacities and affinities for Li⁺ to have potential use of hematite in lithium ion batteries [34].

The SEM coupled EDAX technique was used to highlight the different chemical element present in the synthesized powder of β -FeOOH nanocrystals and α -Fe₂O₃ microstructures. Elemental composition of rice-shaped nanocrystals of β -FeOOH precursor and α -Fe₂O₃ microstructures was verified using EDAX as shown in Figure 3. The Atomic% of constituents of respective sample is shown in the underneath tables of Figure 3. The presence of Fe and O components in EDAX confirms the formation of desired material. EDX analysis has also shown the presence of C and Cl addition to Fe and O in both samples. The existence of the carbon peak at about 0.2 KeV in EDX spectrum is due to the carbon tape that was used in holding the sample during the SEM and EDX measurements. The peak of Cl in both samples is attributed to the chemical component present in synthesis materials (from the used FeCl₃·6H₂O). The average atomic percentage

FIGURE 3: EDAX spectrum of (a) as-prepared β -FeOOH nanocrystals and (b) α -Fe₂O₃ microspheres after calcining at 650°C for 2 hrs.

formation of Fe and O in β -FeOOH precursor is 23.88% and 46.57%, respectively, while the average atomic percentage formation of Fe and O in α -Fe₂O₃ microspheres is 29.45% and 43.19%, respectively. The underneath table of Figure 3(b) reveals that the O/Fe atomic percentage ratio of the α -Fe₂O₃ analyzed is 1.47, which is relatively consistent with the theoretical O/Fe atomic ratio of 1.50 for the α -Fe₂O₃. The energy dispersive X-ray analyses of both β -FeOOH precursor and α -Fe₂O₃ microstructures show the Fe and O composition to be that of β -FeOOH and α -Fe₂O₃, respectively.

3.3. Absorption Spectra. The optical absorption behavior of rice-shaped β -FeOOH nanocrystals was investigated at room temperature using a UV-VIS Spectrophotometer (model: HITACHI U-3400) as shown in Figure 4. The absorption spectra show that the optical absorption coefficient increases sharply and significantly with decreasing the wavelength, which signify the narrower size distribution (uniformity) of the rice-shaped β -FeOOH nanocrystals. The absorption spectra show a blue shift from the corresponding absorption data for β -FeOOH bulk material due to well-known quantum confinement effect in nanomaterials. The optical band gap of as-prepared β -FeOOH nanocrystals was determined using absorption spectra by the following well-known Tauc relation:

$$\alpha h\nu = A(h\nu - E_g)^n, \quad (2)$$

FIGURE 4: Absorption spectra of as-prepared β -FeOOH nanocrystals. Inset shows the plot of $(\alpha h\nu)^2$ versus $h\nu$ for determination of optical band gap.

where α is the absorption coefficient, $h\nu$ is photon energy, A is a constant, E_g is the optical energy band gap of the material, and exponent n depends on the nature of optical transition and $n = 1/2$ for allowed direct transition. The various types of transitions give rise to different frequency dependencies on absorption coefficient near the fundamental absorption edge.

FIGURE 5: Contact angle image of $\alpha\text{-Fe}_2\text{O}_3$ microspheres surface after dropping the distilled deionized water droplet on the $\alpha\text{-Fe}_2\text{O}_3$ surface coating.

The optical band gap was obtained by extrapolating the linear portion of $(\alpha h\nu)^2$ versus $h\nu$ plot as shown in inset of Figure 4 and comes out as 2.86 eV. The higher value of optical band gap than bulk band gap 2.12 eV [35] was obtained which may be attributed to the nanocrystalline nature of $\beta\text{-FeOOH}$.

3.4. Hydrophobic Properties. The study of hydrophobic materials with their wetting-dewetting tendency, with a water contact angle (θ_w) larger than 90° , has been the focus of various researchers. The water contact angle is based on the water repellent performance of the material. In general, the coating of low surface energy molecules on the rough surface enhances the hydrophobic nature of the materials. The wettability on the surface was first studied by Young [36] who proposed a minimization model of three interfacial surface energies: solid-vapor (γ_{sv}), solid-liquid (γ_{sl}), and liquid-vapor (γ_{lv}) phase by using the following equation:

$$\cos \theta_w = \frac{(\gamma_{sv} - \gamma_{sl})}{\gamma_{lv}}, \quad (3)$$

where θ_w is water contact angle. If $\theta_w > 90^\circ$, the surface is hydrophobic, otherwise hydrophilic. Sessile drop method was employed to measure the water droplet contact angle by using contact angle goniometry and comes out as 113° which confirms the hydrophobic nature of $\alpha\text{-Fe}_2\text{O}_3$ surface. The contact angle image of $\alpha\text{-Fe}_2\text{O}_3$ microspheres is shown in Figure 5. The above Young equation has dispersive and polar components as described in Owens-Wendt and Wu methods. The details of these two components of surface energy (Owens-Wendt and Wu methods) are discussed elsewhere [37]. Calculated solid-vapor (γ_{sv}) surface energy with dispersive (γ_{sv}^D) and polar (γ_{sv}^P) components of $\alpha\text{-Fe}_2\text{O}_3$ surface (contact angle θ_w : 113°) is listed in Table 1. The value of dispersive (γ_{sv}^D) component of solid-vapor (γ_{sv}) surface energy is minimum and follows the same trend as calculated by both methods. The surface modification of $\alpha\text{-Fe}_2\text{O}_3$ microspheres may lead to an extraordinary superhydrophobic behavior,

TABLE 1: Calculated solid-vapor (γ_{sv}) surface energy with dispersive (γ_{sv}^D) and polar (γ_{sv}^P) components of $\alpha\text{-Fe}_2\text{O}_3$ (contact angle θ_w : 113°).

Parameter	Owens-Wendt method	Wu method
γ_{sv} (m N/m)	6.91	13.39
γ_{sv}^D (m N/m)	3.08	6.52
γ_{sv}^P (m N/m)	3.86	6.87

implying extensively new perspectives in practical applications of iron oxides [38].

3.5. Possible Formation Mechanism. The possible formation mechanism of rice-shaped $\beta\text{-FeOOH}$ nanocrystals and their transformation to $\alpha\text{-Fe}_2\text{O}_3$ microspheres has been proposed and schematically illustrated in Figure 6. The complete process includes nucleation of iron hydroxide (particle formation) by hydrolysis of iron complexes, growth regulation, nanorice formation due to urea decomposition, and dehydration due to calcination process. Initially, crystal nucleation of $\beta\text{-FeOOH}$ starts from the solution and tends to be regulated eventually in the form of anisotropic nanorice due to increases in temperature and shape directing molecules of urea [32]. The shape of the nanoparticles may be tuned by controlling many experimental parameters such as concentration of the precursor, reducing agents, and stabilizers with reaction conditions like temperature, ambient environment, and time. The exact role of these parameters in determining the morphology of the crystals is not yet fully understood and it has been proposed that synergistic effect of each one of these parameters has substantial influence on the final shape of the nanocrystal [39]. The anisotropic growth of $\beta\text{-FeOOH}$ nanostructure material in the shape of nanorice might be mainly owing to the surfactant (urea) used in the synthesis. The complete decomposition of urea at 250°C results in the inclusive formation of rice-shaped $\beta\text{-FeOOH}$ nanocrystals. Finally, the calcination of as-prepared $\beta\text{-FeOOH}$ nanocrystals at 650°C for 2 hrs releases the H_2O molecules in the structure of $\beta\text{-FeOOH}$ [11] and ultimately rice-shaped $\beta\text{-FeOOH}$ nanocrystals transform to mesoporous $\alpha\text{-Fe}_2\text{O}_3$ microspheres.

4. Conclusions

In the present study, uniform rice-shaped $\beta\text{-FeOOH}$ nanocrystals were successfully synthesized by a simple hydrolysis chemical method in presence of urea. The $\alpha\text{-Fe}_2\text{O}_3$ microspheres were consecutively and straightforwardly prepared by calcining rice-shaped $\beta\text{-FeOOH}$ nanocrystals precursor at 650°C . XRD patterns and SEM images demonstrated the phase transformation of as-prepared $\beta\text{-FeOOH}$ nanocrystals to $\alpha\text{-Fe}_2\text{O}_3$ microspheres. No other phases of iron oxide (e.g., Fe_2O_4 and $\gamma\text{-Fe}_2\text{O}_3$) were observed in the XRD patterns of the samples. The optical and hydrophobic properties were also studied. The possible formation mechanism of rice-shaped $\beta\text{-FeOOH}$ nanocrystals and their transformation to $\alpha\text{-Fe}_2\text{O}_3$ microspheres was proposed. The achieved new hybrid prolate

FIGURE 6: Schematic illustration of the possible formation mechanism of rice-shaped $\beta\text{-FeOOH}$ nanocrystals and their transformation to $\alpha\text{-Fe}_2\text{O}_3$ microspheres.

nanorice geometry of $\beta\text{-FeOOH}$ nanostructures and porous architecture of $\alpha\text{-Fe}_2\text{O}_3$ (hematite) microspheres may have potential in new exciting optical behavior and sensing applications.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

- [1] H. Aono, H. Hirazawa, T. Naohara, T. Maehara, H. Kikkawa, and Y. Watanabe, "Synthesis of fine magnetite powder using reverse coprecipitation method and its heating properties by applying AC magnetic field," *Materials Research Bulletin*, vol. 40, no. 7, pp. 1126–1135, 2005.
- [2] R. E. Rosensweig, "Heating magnetic fluid with alternating magnetic field," *Journal of Magnetism and Magnetic Materials*, vol. 252, pp. 370–374, 2002.
- [3] J.-P. Fortin, C. Wilhelm, J. Servais, C. Ménager, J.-C. Bacri, and F. Gazeau, "Size-sorted anionic iron oxide nanomagnets as colloidal mediators for magnetic hyperthermia," *Journal of the American Chemical Society*, vol. 129, no. 9, pp. 2628–2635, 2007.
- [4] M. Kishimoto, M. Minagawa, H. Yanagihara, T. Oda, N. Ohkuchi, and E. Kita, "Synthesis and magnetic properties of platelet $\gamma\text{-Fe}_2\text{O}_3$ particles for medical applications using hysteresis-loss heating," *Journal of Magnetism and Magnetic Materials*, vol. 324, no. 7, pp. 1285–1289, 2012.
- [5] K. Suri, S. Annapoorni, A. K. Sarkar, and R. P. Tandon, "Gas and humidity sensors based on iron oxide-polypyrrole nanocomposites," *Sensors and Actuators B: Chemical*, vol. 81, no. 2-3, pp. 277–282, 2002.
- [6] L. Geng and S. Wu, "Preparation, characterization and gas sensitivity of polypyrrole/ $\gamma\text{-Fe}_2\text{O}_3$ hybrid materials," *Materials Research Bulletin*, vol. 48, no. 10, pp. 4339–4343, 2013.
- [7] Z. Sun, H. Yuan, Z. Liu, B. Han, and X. Zhang, "A highly efficient chemical sensor material for H_2S : $\alpha\text{-Fe}_2\text{O}_3$ nanotubes fabricated using carbon nanotube templates," *Advanced Materials*, vol. 17, no. 24, pp. 2993–2997, 2005.

- [8] H.-J. Song, X.-H. Jia, H. Qi, X.-F. Yang, H. Tang, and C.-Y. Min, "Flexible morphology-controlled synthesis of monodisperse α -Fe₂O₃ hierarchical hollow microspheres and their gas-sensing properties," *Journal of Materials Chemistry*, vol. 22, no. 8, pp. 3508–3516, 2012.
- [9] W. S. Choi, H. Y. Koo, Z. B. Zhongbin, Y. Li, and D.-Y. Kim, "Templated synthesis of porous capsules with a controllable surface morphology and their application as gas sensors," *Advanced Functional Materials*, vol. 17, no. 11, pp. 1743–1749, 2007.
- [10] N. S. Arul, D. Mangalaraj, P. N. Kumar, E. Kim, P. Devi, and J. In Han, "Synthesis and characterization of α -Fe₂O₃ Micro-/Nanorods-modified glassy carbon electrode for electrochemical sensing of nitrobenzene," *Ceramics International*, vol. 41, no. 4, pp. 5568–5573, 2015.
- [11] H. J. Song, X. Zhang, T. Chen, and X. Jia, "One-pot synthesis of bundle-like β -FeOOH nanorods and their transformation to porous α -Fe₂O₃ microspheres," *Ceramics International*, vol. 40, no. 10, pp. 15595–15602, 2014.
- [12] S. B. Wang, Y. L. Min, and S. H. Yu, "Synthesis and magnetic properties of uniform hematite nanocubes," *The Journal of Physical Chemistry C*, vol. 111, no. 9, pp. 3551–3554, 2007.
- [13] X. L. Gou, G. X. Wang, J. S. Park, H. Liu, and J. Yang, "Monodisperse hematite porous nanospheres: synthesis, characterization, and applications for gas sensors," *Nanotechnology*, vol. 19, no. 12, Article ID 125606, 2008.
- [14] Z. L. Wang, "Structural analysis of self-assembling nanocrystal superlattices," *Advanced Materials*, vol. 10, no. 1, pp. 13–30, 1998.
- [15] S. J. Oldenburg, R. D. Averitt, S. L. Westcott, and N. J. Halas, "Nanoengineering of optical resonances," *Chemical Physics Letters*, vol. 288, no. 2–4, pp. 243–247, 1998.
- [16] C. J. Orendorff, T. K. Sau, and C. J. Murphy, "Shape-dependent plasmon-resonant gold nanoparticles," *Small*, vol. 2, no. 5, pp. 636–639, 2006.
- [17] H. Liang, H. Yang, W. Wang, J. Li, and H. Xu, "High-yield uniform synthesis and microstructure-determination of rice-shaped silver nanocrystals," *Journal of the American Chemical Society*, vol. 131, no. 17, pp. 6068–6069, 2009.
- [18] B. J. Wiley, Y. Chen, J. M. McLellan et al., "Synthesis and optical properties of silver nanobars and nanorice," *Nano Letters*, vol. 7, no. 4, pp. 1032–1036, 2007.
- [19] H. Wang, D. W. Brandl, F. Le, P. Nordlander, and N. J. Halas, "Nanorice: a hybrid plasmonic nanostructure," *Nano Letters*, vol. 6, no. 4, pp. 827–832, 2006.
- [20] W. Yu, T. Zhang, J. Zhang, X. Qiao, L. Yang, and Y. Liu, "The synthesis of octahedral nanoparticles of magnetite," *Materials Letters*, vol. 60, no. 24, pp. 2998–3001, 2006.
- [21] I. Nedkov, T. Merodiiska, L. Slavov, R. E. Vandenberghe, Y. Kusano, and J. Takada, "Surface oxidation, size and shape of nano-sized magnetite obtained by co-precipitation," *Journal of Magnetism and Magnetic Materials*, vol. 300, no. 2, pp. 358–367, 2006.
- [22] A. Azhari, S. M. Sharif, F. Golestanifard, and A. Saberi, "Phase evolution in Fe₂O₃/MgO nanocomposite prepared via a simple precipitation method," *Materials Chemistry and Physics*, vol. 124, no. 1, pp. 658–663, 2010.
- [23] V. Sreeja and P. A. Joy, "Microwave-hydrothermal synthesis of γ -Fe₂O₃ nanoparticles and their magnetic properties," *Materials Research Bulletin*, vol. 42, no. 8, pp. 1570–1576, 2007.
- [24] T. J. Daou, G. Pourroy, S. Bégin-Colin et al., "Hydrothermal synthesis of monodisperse magnetite nanoparticles," *Chemistry of Materials*, vol. 18, no. 18, pp. 4399–4404, 2006.
- [25] J. Ma, J. Lian, X. Duan, X. Liu, and W. Zheng, " α -Fe₂O₃: hydrothermal synthesis, magnetic and electrochemical properties," *Journal of Physical Chemistry C*, vol. 114, no. 24, pp. 10671–10676, 2010.
- [26] K. Simeonidis, S. Mourdikoudis, M. Moulla et al., "Controlled synthesis and phase characterization of Fe-based nanoparticles obtained by thermal decomposition," *Journal of Magnetism and Magnetic Materials*, vol. 316, no. 2, pp. e1–e4, 2007.
- [27] W. Zhou, K. Tang, S. Zeng, and Y. Qi, "Room temperature synthesis of rod-like FeC₂O₄·2H₂O and its transition to maghemite, magnetite and hematite nanorods through controlled thermal decomposition," *Nanotechnology*, vol. 19, no. 6, Article ID 065602, 2008.
- [28] J. Hu, G. Chen, and I. M. C. Lo, "Removal and recovery of Cr(VI) from wastewater by maghemite nanoparticles," *Water Research*, vol. 39, no. 18, pp. 4528–4536, 2005.
- [29] X. Q. Liu, S. W. Tao, and Y. S. Shen, "Preparation and characterization of nanocrystalline α -Fe₂O₃ by a sol-gel process," *Sensors and Actuators B: Chemical*, vol. 40, no. 2-3, pp. 161–165, 1997.
- [30] J. Zhang, A. Thurber, C. Hanna, and A. Punnoose, "Highly shape-selective synthesis, silica coating, self-assembly, and magnetic hydrogen sensing of hematite nanoparticles," *Langmuir*, vol. 26, no. 7, pp. 5273–5278, 2010.
- [31] X. Wen, S. Wang, Y. Ding, Z. L. Wang, and S. Yang, "Controlled growth of large-area, uniform, vertically aligned arrays of α -Fe₂O₃ nanobelts and nanowires," *The Journal of Physical Chemistry B*, vol. 109, no. 1, pp. 215–220, 2005.
- [32] A. A. Ayachi, H. Mechakra, M. M. Silvan, S. Boudjaadar, and S. Achour, "Monodisperse α -Fe₂O₃ nanoplatelets: synthesis and characterization," *Ceramics International*, vol. 41, no. 2, pp. 2228–2233, 2015.
- [33] H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, John Wiley and Sons, New York, NY, USA, 2nd edition, 1954.
- [34] S. Zeng, K. Tang, T. Li et al., "Facile route for the fabrication of porous hematite nanoflowers: its synthesis, growth mechanism, application in the lithium ion battery, and magnetic and photocatalytic properties," *Journal of Physical Chemistry C*, vol. 112, no. 13, pp. 4836–4843, 2008.
- [35] A. F. White, "Heterogeneous electrochemical reactions associated with oxidation of ferrous oxide and silicate surfaces," *Reviews in Mineralogy and Geochemistry*, vol. 23, no. 1, pp. 467–509, 1990.
- [36] T. Young, "An essay on the cohesion of fluids," *Philosophical Transactions of the Royal Society*, vol. 95, pp. 65–87, 1805.
- [37] A. Sanger, A. Kumar, S. Chauhan, Y. K. Gautam, and R. Chandra, "Fast and reversible hydrogen sensing properties of Pd/Mg thin film modified by hydrophobic porous silicon substrate," *Sensors and Actuators B: Chemical*, vol. 213, pp. 252–260, 2015.
- [38] Z. Hu and W. Li, "Preparation of superhydrophobic Fe₂O₃ nanorod films with the tunable water adhesion," *Journal of Colloid and Interface Science*, vol. 376, no. 1, pp. 245–249, 2012.
- [39] P. R. Sajanlal, T. S. Sreeprasad, A. K. Samal, and T. Pradeep, "Anisotropic nanomaterials: structure, growth, assembly, and functions," *Nano Reviews*, vol. 2, article 5883, 2011.