Research Article

Synthesis and Characterization of Nontoxic Hollow Iron Oxide (α -Fe₂O₃) Nanoparticles Using a Simple Hydrothermal Strategy

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Hollow spheres of iron oxide (α -Fe₂O₃) were successfully synthesized in a simple one-pot synthesis by using hydrothermal method. Iron salt was dissolved together with glucose in water and then the mixture was heated to 180°C in an autoclave at 12 and 24 hours of synthesis time separately. Carbon spheres were formed with the metal ions into their hydrophilic shell after the hydrothermal approach. Hollow α -Fe₂O₃ spheres of around 200 to 300 nm size were formed after the calcination that lead to the removal of carbon. Size of nanoparticles, surface area, and thickness of the α -Fe₂O₃ shell can be precisely controlled by controlling the ratio of iron and glucose. Increasing the reaction time will decrease the shell thickness. Phase confirmation and crystalline structure of these nanoparticles were done by XRD. Surface morphology was characterized by SEM and TEM analysis showed the hollow spheres inside and a shell of α -Fe₂O₃. Further confirmation was done by EDX and FTIR analysis. Iron content was measured by ICP-OES. Cytotoxicity was done by using CCK-8 assay kit in the Hep G-2 cell line showing the nontoxic behavior of α -Fe₂O₃ nanoparticles. The as-prepared nanoparticles can be exploited in a number of applications in areas ranging from medicine to pharmaceuticals to material science.

1. Introduction

Nanomaterial synthesis has gained attractive increasing attention to their potential applications. The parameters such as size, shape, and structure can influence the physical and chemical properties of the NPs [1]. The properties such as high surface area, monodispersity in the particle size, open and low density structures, optical properties, and nontoxic behaviour are making them an important class of nanomaterials [2, 3].

From the last few decades controlled synthesis of hollow and porous NPs of metal oxides is of particular interest due to potential applications such as drug delivery, controlled release of drugs, catalysis, artificial cells, chemical storage, light weight fillers, adsorptive materials, and chemical sensors [4–6]. Hollow NPs are a unique class in the functional nanomaterials and hollow metal oxide NPs have raised attention due to their thin shell, inner void, and doubled surface area [3, 7] in their applications due to their unique nature and different physicochemical properties and a remarkable

progress has been made in their synthesis until now [8]. Many methodological approaches have been established so far: for example, template methods, Kirkendall effect, spray drying, Ostwald ripening, and self-assembly techniques. Among them, template methods are the most effective way to produce hollow structures and are used typically for the synthesis of core shell structure leading to the coating of desired materials on the templates followed by the removal of templates. Hard and soft templates of different types are being used for instance carbon, acting as hard templates while emulsions, gas bubble, vesicles, and micelles were performing the soft template materials [9]. Template methods are most effective in the formation of hollow structures in accordance with the uniformity [10]. These procedures are expensive and include many steps for the synthesis as well as for the removal of templates that often lead to the breakage of hollow sphere while template is removed [2, 11, 12]. So there is a need of simple, straight forward, and cost effective solution based approaches for the synthesis of hollow iron oxide NPs although there have been many reports on solution based

synthesis of uniform hollow nanostructures [13]. Surface coating of NPs was done by suitable inorganic precursors on the surface and/or controlled layer by layer assembly of polyelectrolyte and inorganic NPs [14].

Removal of core in the core shell NPs is an important parameter to make them hollow structures [15, 16]. The formation of metal oxide hollow NPs is due to the coalescence of cation vacancies formed due to the difference in diffusion rates ($D_{\text{metal}} > D_{\text{oxygen}}$) of metal and oxygen after oxidation of metals while having noncoalesced vacancies after oxidation. Diffusion mechanism of iron oxide NPs from internal pores into shell at elevated temperatures can produce a large occupancy of vacancies in the hollow shells as compared to the solid iron oxide NPs [17]. Hollow iron oxide NPs have also attracted attention due to their attractive applications and physicochemical properties. Biocompatible and water dispersible iron oxide NPs are being used in several applications since the last few years.

In the present contribution we show the promising simplified and general hydrothermal approach for the synthesis of hollow iron oxide less toxic water dispersible NPs. Our approach limits the multistep process that was being used for the fabrication of hollow spheres of metal oxides. Iron salt addition directly to glucose solution in water via hydrothermal treatment at 12 h and 24 h gives hollow spheres of iron oxides after calcinations at given temperatures and time of reaction. These NPs can be used in various applications in the field of nanoscience and technology.

2. Experimental Procedures

2.1. Chemicals. Glucose (company), $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, AMEM media, and CCK-8 toxicity assay kit were used.

2.2. Synthesis of $\alpha\text{-Fe}_2\text{O}_3$ Nanoparticles. Monodisperse $\alpha\text{-Fe}_2\text{O}_3$ NPs were synthesized by the modified one-pot hydrothermal method [9]. To synthesize the hollow iron oxide NPs, a carbonaceous additive, glucose (5.5 g), was mixed in 20 mL of distilled water and 5 M iron precursor $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 10 mL of distilled water in a ratio of 5:1. Thickness of the shell of hollow nanospheres later on was based on ratio of two solutions mixed. Both solutions were mixed and placed as two separate 45 mL of Teflon lined stainless steel autoclave in an oven at 12 h and 24 h reaction time. After the mentioned time the products were filtered and washed with water several times, first with water and then with ethanol. The products then dried at 60°C for 5 hours in a vacuum oven. Samples were taken out at this stage just to check the carbon and metal nanosphere. To obtain the hollow spheres carbon composites were then calcined in air at 550°C at the heating rate of 4°C/min to remove the carbon core. The as-synthesized NPs are well dispersed in ethanol as well as in water.

2.3. Characterization Techniques. To investigate the morphology and structure SEM (scanning electron microscope) and TEM (transmission electron microscope) images were attained at an accelerating voltage of 200 kV by using Tecnai G2 20 S-TWIN TEM (FEI, USA). X-Ray diffraction patterns

of the particles were recorded and characterized by XRD technique using a D/max-TTR^{III} with Cu K α radiation (Rigaku, Japan) at continuous scanning at 20°–80° with a step size of 0.02° and speed of 2° min^{−1}. Fourier transform infrared spectra (FTIR) were obtained using a Spectrum One Fourier transform infrared spectrometer (Perkin-Elmer Instruments Co. Ltd., USA). By using the KBr pellet technique samples were characterized in the region of 4000–400 cm^{−1}. The concentration of Fe in water dispersible $\alpha\text{-Fe}_2\text{O}_3$ NPs was carried out by ICP-OES Thermo Icap-6300.

2.4. Cytotoxicity Evaluation

2.4.1. Cells Lines and Cell Culture. Hep G2 (human hepatocellular carcinoma cell) cell lines were purchased from American Type Culture Collection (ATCC). Hep-G2 cell line was grown in AMEM medium with 10% FBS, 1% penicillin/streptomycin, 1% HEPES, and 1% NEAA. The cell lines were kept under 5% humidified CO₂ atmosphere at 37°C temperature.

2.4.2. Evaluation of Cell Viability. To evaluate the viability of cells Hep G2 (human hepatic carcinoma cell) cell line was cultured onto 96-well plates having 3×10^3 cells per well in their respective media and maintained at 37°C and 5% humidified CO₂ atmosphere for 12 and 24 h. The culture media were replaced with 100 μL of media containing different concentrations of as-prepared $\alpha\text{-Fe}_2\text{O}_3$ NPs (25 $\mu\text{g}/\text{mL}$, 50 $\mu\text{g}/\text{mL}$, 100 $\mu\text{g}/\text{mL}$, and 200 $\mu\text{g}/\text{mL}$) and maintained at 24 h to check the toxicity level of NPs. The amount of viable cells was evaluated via a CCK-8 kit assay at 450 nm with a microplate reader:

$$\% \text{ Viability} = \frac{A(\text{sample}) - A(\text{Blank})}{A(\text{Control}) - A(\text{Blank})} \times 100. \quad (1)$$

3. Results and Discussion

Hydrothermally treated carbon spheres before calcination are shown by SEM images in Figure 1. Carbon spheres are around a uniform diameter of 200–300 nm in size and impurities are carefully avoided while mixing the iron and glucose solutions together. Dehydration and carbonization are the two main steps involved in the reaction mechanism of carbon sphere formation. Ions of iron and their resulting NPs are predominantly aligned along the hydrophilic shell of carbon particles (Scheme 1). Distribution of O-H and C=O groups and partially dehydrated glucose are responsible for the hydrophilic shell of as-synthesized NPs.

After the hydrothermal treatment at 12 h and 24 h, filtration and washing step, calcination (4 h at 550°C) was done to get the hollow spheres of $\alpha\text{-Fe}_2\text{O}_3$. Heat treatment in the calcination process shows the loosely adsorbed network of iron oxide along with hollow spheres and removal of carbon content to get the hollow structure inside [10]. Closer look of SEM images reveals rough edges on the surface of hollow spheres and due to aggregation of NPs inherent porosity can also be seen.

SCHEME 1: Schematic illustration of hydrothermally synthesized hollow iron oxide NPs ($\alpha\text{-Fe}_2\text{O}_3$).

FIGURE 1: SEM image of hydrothermally treated noncalcinated nanospheres (glucose + Fe salt).

SEM images of the product show that the synthesized NPs are round in shape and monodisperse, have smooth surface, and are well dispersed in ethanol as well as in water. The EDX mapping shows the purity of Fe element in the as-synthesized nanomaterial (Figures 2(d) and 3(d)). The XRD pattern of hollow spheres of calcinated NPs is shown in Figure 5(a) that indicates the high crystalline form of iron oxide NPs due to the iron precursor used and also due to calcination (to remove the carbon core at high temperature). Before calcinations no crystalline peaks were observed indicating the amorphous structure [9]. XRD peaks can be well indexed to $\alpha\text{-Fe}_2\text{O}_3$ crystals and rhombohedral phase with JCPDS card number 33-0664. Sharp, strong, and well-resolved diffraction peaks reveal the phase purity and crystalline structure of as-prepared nanomaterial [18, 19]. FTIR spectrum analysis of as-synthesized NPs was done for further confirmation. FTIR analysis was recorded by using the KBr pellet for the dried powder in the regions of $3500\text{--}400\text{ cm}^{-1}$. Vibration in $400\text{--}600\text{ cm}^{-1}$ band is attributed to the vibrations of metal and oxide (Fe-O) which confirms the formation of $\alpha\text{-Fe}_2\text{O}_3$ NPs. Vibration around 2300 cm^{-1} , a weak band, may be attributed to atmospheric CO_2 that is obvious in the 24 h hydrothermally treated NPs. Furthermore, bands at 1632 cm^{-1} are attributed to the angular deformation of H_2O and bands around 3436 cm^{-1} show the O-H stretching of H_2O . These findings are in accordance with the available literature [20, 21]. A clear confirmation of hollow structure

was done by TEM characterization (Figure 4). NPs imaged by TEM show the hollow spherical shape of the template colloid. Hollow NPs were obtained after calcination due to the burning of organic matter (glucose). Shell thickness around the ring perimeter of the hollow NPs was calculated by the TEM imaging that is approximately 40 ± 10 of $200\text{--}300\text{ nm}$ for hollow spheres produced at 12 h hydrothermal reaction time while 20 ± 10 of $200\text{--}300\text{ nm}$ produced at 24 h hydrothermal reaction time (Figure 4). Shell thickness at 12 h reaction time is more as compared to the 24 h treatment that might be due to the reaction time variations at given temperature as a lot of parameters influence the structural morphology. As from Figure 6(a) a visible growth pattern and self-polymerization of 24 h hydrothermally treated NPs are shown and from Figure 6(b) broken shells are clearly visible showing hollow spheres from inside and a well-defined shell thickness (SEM micrographs) [14]. Soenen et al. have reported hollow titanium oxide NPs synthesis based on the carbon template casting to achieve the hollow and broken shell hollow NPs [22].

Metal salt concentration to glucose ratio and time of reaction is playing an important role in the variation of shell thickness leading to the calcination process. Calcination is important in the synthesis of hollow structures in a template oriented method. Fe^{3+} ions are evenly dissolved in the hydrophilic shell of carbon NPs or may disperse in the shells as amorphous clusters with no crystalline peaks from XRD before calcinations while during calcination partial oxidation of iron ions was done, producing the crystalline NPs.

The percentage cell viability results from CCK-8 assay method are presented to show the biocompatibility of the iron oxide NPs. The calculated values from the assay kit show that the NPs are nontoxic to the hepatocarcinoma cell lines (Hep G-2) at 12 h and 24 h incubation of different concentration of NPs. A normal behavior was shown as higher concentration gives a bit toxic effect (Figure 7). Size, physiochemical properties, and surface area contribute to the cellular toxicity [23, 24]. Nanoparticles and cells interaction is dependent on the surface properties of the nanoparticles whether hydrophobic or hydrophilic, ultimately relying on the adsorption properties and effect on the cellular matrix [25]. It can be assumed that iron oxide nanoparticles can aggregate on the surface of Hep G-2 cells and then get internalized by the endocytosis and then incorporated into

FIGURE 2: SEM images showing the hollow spheres of $\alpha\text{-Fe}_2\text{O}_3$ at 12 h reaction time after calcination process: (a) dispersion in ethanol, (b) dispersion in water, (c) high magnification image of sphere showing $\alpha\text{-Fe}_2\text{O}_3$ shell showing the inherent porosity, and (d) EDX mapping showing the Fe content.

FIGURE 3: SEM images showing the hollow spheres of $\alpha\text{-Fe}_2\text{O}_3$ at 24 h reaction time after calcination: (a) dispersion in ethanol, (b) dispersion in water, (c) high magnification image of sphere showing $\alpha\text{-Fe}_2\text{O}_3$ shell showing the inherent porosity, and (d) EDX mapping showing the Fe content.

the cells and take part in the cell metabolism that is very complicated to elaborate, but according to the study of Villanueva et al. (2009) uptake of nanoparticles and their toxicity was correlated with the dose (increasing the concentration

in return increases the uptake) of the nanoparticles and time of incubation with the nanoparticles [26]. Our findings are in accordance with already cited literature that clearly demonstrates that the internalization of the foreign entities

FIGURE 4: TEM images showing the hollow core and shell of calcinated α -Fe₂O₃ at (a) 12 h and (b) 24 h.

FIGURE 5: Hollow iron oxide NPs after calcination at 550°C for 4 h: (a) X-ray diffraction (XRD) patterns and (b) FTIR patterns.

such as nanoparticles can be incorporated and internalized into the cells *via* cell mechanism endocytosis. Other cell types also intake the foreign entities by the process of endocytosis. Overall as-synthesized spherical hollow NPs of around 200 nm size exhibit very low toxicity that is also dose dependent, thus showing biocompatibility to the living cellular environment. This is in accordance with the toxicity due to size as more than 40 nm sized NPs exhibit low toxicity that diminishes cellular internalization [27, 28]. These NPs can be exploited in a wide range of biomedical applications.

4. Conclusion

In summary, we have synthesized hollow iron oxide nanoparticles by a simple and straight forward hydrothermal

approach and by the economical use of chemicals like iron salt and glucose. In the as-synthesized nanoparticles spheres were synthesized containing carbon core prior to calcination step that ultimately produce the hollow spheres containing iron oxide round shell. Iron oxide nanoparticles are nontoxic to the human cell lines that indicate the safe use in the biomedical applications. The hollow iron oxide nanoparticles are homogenous and monodisperse in the aqueous medium and nontoxic to the cells and can be exploited in a range of applications.

Abbreviations

NPs: Nanoparticles
 α -Fe₂O₃: Alpha-iron oxide
 TEM: Transmission electron microscope

FIGURE 6: SEM images showing the growth of hollow spheres of $\alpha\text{-Fe}_2\text{O}_3$ at 24 h reaction time and after calcination: (a) dispersion in ethanol showing the growth mechanism of hollow NPs and (b) hollow NPs showing the pores or broken shell confirming the hollow structure inside the $\alpha\text{-Fe}_2\text{O}_3$ porous shells.

FIGURE 7: Effect of iron oxide NPs on the growth of liver cell lines (Hep G-2). Cells are grown into 96-well plate and incubated with different concentrations of $\alpha\text{-Fe}_2\text{O}_3$ NPs at 12 h and 24 h maintained at 37°C. % cell viability is determined by CCK-8 cytotoxicity kit assay. Data is represented as means $\pm$ SD of triplicate experiments.

SEM: Scanning electron microscope
 XRD: X-ray diffraction pattern
 FTIR: Fourier transform infrared spectrum
 Hep G-2: Hepatocarcinoma cells.

Competing Interests

There is no conflict of interests declared by the authors regarding the publication of the manuscript.

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References

- [1] A. P. Alivisatos, "Semiconductor clusters, nanocrystals, and quantum dots," *Science*, vol. 271, no. 5251, pp. 933–937, 1996.
- [2] Y. Li and J. Shi, "Hollow-structured mesoporous materials: chemical synthesis, functionalization and applications," *Advanced Materials*, vol. 26, no. 20, pp. 3176–3205, 2014.
- [3] Z. Wang, Z. Wang, H. Wu, and X. W. Lou, "Mesoporous single-crystal $\text{CoSn}(\text{OH})_6$ hollow structures with multilevel interiors," *Scientific Reports*, vol. 3, article 1391, 2013.
- [4] F. Caruso, "Hollow capsule processing through colloidal templating and self-assembly," *Chemistry*, vol. 6, no. 3, pp. 413–419, 2000.
- [5] Z. Y. Zhong, Y. D. Yin, B. Gates, and Y. N. Xia, "Preparation of mesoscale hollow spheres of TiO_2 and SnO_2 by templating against crystalline arrays of polystyrene beads," *Advanced Materials*, vol. 12, no. 3, pp. 206–209, 2000.
- [6] C. Z. Yu, J. Fan, B. Z. Tian, and D. Y. Zhao, "Morphology development of mesoporous materials: a colloidal phase separation mechanism," *Chemistry of Materials*, vol. 16, no. 5, pp. 889–898, 2004.
- [7] Y. Yin, R. M. Rioux, C. K. Erdonmez, S. Hughes, G. A. Somorjal, and A. P. Alivisatos, "Formation of hollow nanocrystals through the nanoscale Kirkendall effect," *Science*, vol. 304, no. 5671, pp. 711–714, 2004.
- [8] M.-M. Titirici, M. Antonietti, and A. Thomas, "A generalized synthesis of metal oxide hollow spheres using a hydrothermal approach," *Chemistry of Materials*, vol. 18, no. 16, pp. 3808–3812, 2006.
- [9] J. Zhou, H. Song, X. Chen et al., "Carbon-encapsulated metal oxide hollow nanoparticles and metal oxide hollow nanoparticles: a general synthesis strategy and its application to lithium-ion batteries," *Chemistry of Materials*, vol. 21, no. 13, pp. 2935–2940, 2009.
- [10] A. Saha, P. Bharmoria, A. Mondal, S. C. Ghosh, S. Mahanty, and A. B. Panda, "Generalized synthesis and evaluation of formation mechanism of metal oxide/sulphide@C hollow spheres," *Journal of Materials Chemistry A*, vol. 3, no. 40, pp. 20297–20304, 2015.
- [11] Z. Li, M. Li, Z. Bian, Y. Kathiraser, and S. Kawi, "Design of highly stable and selective core/yolk-shell nanocatalysts—a review," *Applied Catalysis B: Environmental*, vol. 188, pp. 324–341, 2016.
- [12] A. Carné-Sánchez, I. Imaz, M. Cano-Sarabia, and D. Maspoch, "A spray-drying strategy for synthesis of nanoscale metal-organic frameworks and their assembly into hollow superstructures," *Nature Chemistry*, vol. 5, no. 3, pp. 203–211, 2013.

- [13] F. Caruso, R. A. Caruso, and H. Möhwald, "Nanoengineering of inorganic and hybrid hollow spheres by colloidal templating," *Science*, vol. 282, no. 5391, pp. 1111–1114, 1998.
- [14] D. Walsh and S. Mann, "Fabrication of hollow porous shells of calcium carbonate from self-organizing media," *Nature*, vol. 377, no. 6547, pp. 320–323, 1995.
- [15] N. Kawahashi and E. Matijevic, "Preparation of hollow spherical particles of yttrium compounds," *Journal of Colloid and Interface Science*, vol. 143, no. 1, pp. 103–110, 1991.
- [16] R. Nakamura, G. Matsubayashi, H. Tsuchiya, S. Fujimoto, and H. Nakajima, "Transition in the nanoporous structure of iron oxides during the oxidation of iron nanoparticles and nanowires," *Acta Materialia*, vol. 57, no. 14, pp. 4261–4266, 2009.
- [17] H.-B. Fan, D.-F. Zhang, and L. Guo, "Fabrication, formation mechanism and the photocatalytic properties of hierarchical porous hematite networks," *Acta Physico-Chimica Sinica*, vol. 28, no. 9, pp. 2214–2220, 2012.
- [18] A. Dong, N. Ren, Y. Tang et al., "General synthesis of mesoporous spheres of metal oxides and phosphates," *Journal of the American Chemical Society*, vol. 125, no. 17, pp. 4976–4977, 2003.
- [19] A. Azam, A. S. Ahmed, M. Oves, M. S. Khan, S. S. Habib, and A. Memic, "Antimicrobial activity of metal oxide nanoparticles against Gram-positive and Gram-negative bacteria: a comparative study," *International Journal of Nanomedicine*, vol. 7, pp. 6003–6009, 2012.
- [20] M. Arshad, A. Azam, A. S. Ahmed, S. Mollah, and A. H. Naqvi, "Effect of Co substitution on the structural and optical properties of ZnO nanoparticles synthesized by sol-gel route," *Journal of Alloys and Compounds*, vol. 509, no. 33, pp. 8378–8381, 2011.
- [21] Y. Xia and R. Mokaya, "Hollow spheres of crystalline porous metal oxides: a generalized synthesis route via nanocasting with mesoporous carbon hollow shells," *Journal of Materials Chemistry*, vol. 15, no. 30, pp. 3126–3131, 2005.
- [22] S. J. Soenen, P. Rivera-Gil, J.-M. Montenegro, W. J. Parak, S. C. De Smedt, and K. Braeckmans, "Cellular toxicity of inorganic nanoparticles: common aspects and guidelines for improved nanotoxicity evaluation," *Nano Today*, vol. 6, no. 5, pp. 446–465, 2011.
- [23] A. Verma and F. Stellacci, "Effect of surface properties on nanoparticle-cell interactions," *Small*, vol. 6, no. 1, pp. 12–21, 2010.
- [24] S. J. H. Soenen and M. De Cuyper, "Assessing cytotoxicity of (iron oxide-based) nanoparticles: an overview of different methods exemplified with cationic magnetoliposomes," *Contrast Media and Molecular Imaging*, vol. 4, no. 5, pp. 207–219, 2009.
- [25] A. Gholami, S. Rasoul-Amini, A. Ebrahiminezhad, S. H. Seradj, and Y. Ghasemi, "Lipoamino acid coated superparamagnetic iron oxide nanoparticles concentration and time dependently enhanced growth of human hepatocarcinoma cell line (Hep-G2)," *Journal of Nanomaterials*, vol. 2015, Article ID 451405, 9 pages, 2015.
- [26] A. Villanueva, M. Căete, A. G. Roca et al., "The influence of surface functionalization on the enhanced internalization of magnetic nanoparticles in cancer cells," *Nanotechnology*, vol. 20, no. 11, Article ID 115103, 2009.
- [27] C. Wilhelm, C. Billotey, J. Roger, J. N. Pons, J.-C. Bacri, and F. Gazeau, "Intracellular uptake of anionic superparamagnetic nanoparticles as a function of their surface coating," *Biomaterials*, vol. 24, no. 6, pp. 1001–1011, 2003.
- [28] C. Rivière, C. Wilhelm, F. Cousin, V. Dupuis, F. Gazeau, and R. Perzynski, "Internal structure of magnetic endosomes," *The European Physical Journal E*, vol. 22, no. 1, pp. 1–10, 2007.