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Synthesis of Fe₃O₄/ZnO Core-shell Nanoparticles for Photodynamic Therapy Applications

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ABSTRACT

The use of nanoparticles as carriers of photosensitizer (PS) molecules for photodynamic therapy (PDT) has attracted much interest on core-shell nanosize structures. Herein, we used a simple aqueous solution method to synthesize Fe₃O₄/ZnO core-shell nanoparticles. X-ray diffraction (XRD) analyses showed the presence of well defined peaks corresponding to Fe₃O₄ and ZnO in as-synthesized nanocrystals. Vibrating sample magnetometer (VSM) measurements showed that these nanoparticles exhibited superparamagnetic behavior of the core with no coercivity nor remanence. X-ray photoelectron spectroscopy (XPS) analyses revealed the presence of Zn^{1/2} and Zn^{3/2} species on the surface of nanocrystals. Photoluminescence measurements showed excitonic emission of ZnO co-existing with a weak and broad defect-related green emission at room temperature. The generation of singlet oxygen was monitored via the photooxidation of diphenyl-1,3-isobenzofuran (DPBF) with different light sources, followed by absorption spectroscopy at 409 nm. The capability of synthesized nanoparticles to generate singlet oxygen has also been verified.

INTRODUCTION

Superparamagnetic iron oxide nanoparticles due to their unique magnetic properties at nanoscale that are highly dependent on size and shape possess promising applications in biomedical science and sensors [1]. Likewise, zinc oxide is an important wide band-gap II-IV semiconductor with direct band-gap of 3.37 eV at room temperature having versatile applications in optoelectronic devices, electrical devices and biomedical sciences [2]. Pursuing multifunctionality, core-shell heterostructured nanoparticles have become an active area of research because of their unique chemical and physical properties; however, the choice of the proper core and shell material depend on the nature of application [3]. In particular, nanocomposite particles consisting of magnetic cores and luminescent shells are receiving increasing attention in biomedical and biological applications such as magnetic separation and detection of cancer cells, bacteria and viruses [4]. The highly efficient luminescence properties of CdSe quantum dots have shown their promises in various field of biology; however, their cytotoxicity is a major concern that limits the use of these visible photoluminescent emitting nanocomposites. Recently, Hong et al. have synthesized Fe₃O₄/ZnO nanoparticles and studied their optical properties [5]. The photocatalytic activity of these nanoparticles also indicates towards their capability of producing reactive oxygen species (ROS) as suggested by Joshi et al. [2]. Yi et al. have synthesized γ -Fe₂O₃-CdSe within silica shell exhibiting efficient luminescent properties and suggesting their use in biomedical applications [6]. Rosenzweig et al. have reported the application of magnetic quantum dots comprising of γ -Fe₂O₃ core and CdSe/ZnS quantum dots for cancer cell separation and optical identification [7]. Gu et. al. have also synthesized bifunctional FePt/CdS nanoparticles showing ferromagnetic nature of nanoparticles with bright blue-green luminescence [8]. Consequently, in the present work we attempted to

synthesize and characterize the biocompatible Fe₃O₄/ZnO nanocomposite core-shell particles for their potential bioapplications, preferably in cancer therapy. The photochemical properties of Fe₃O₄/ZnO nanoparticles for photodynamic therapy (PDT) were investigated in the presence of DPBF as chemical quencher [9].

EXPERIMENT

Materials

Iron (II) Chloride Tetrahydrate FeCl₂·4H₂O, Iron (III) Chloride Hexahydrate, FeCl₃·6H₂O, Sodium Hydroxide NaOH, Sodium Citrate Dihydrate Na₃C₆H₅O₅·2H₂O, Zinc Acetate Dihydrate Zn(OOCCH₃)₂·2H₂O, Lithium Hydroxide Monohydrate LiOH·H₂O, Zinc Nitrate Hexahydrate Zn(NO₃)₂·6H₂O, DPBF 97%, nitric acid ACS reagent 70%, Hydrochloric ACS reagent 37%, Ammonium Hydroxide NH₄OH (14.5 M) were of reagent grade and used without further purification; acetone, methanol (ultrapure HPLC grade, 99.8+%) and ethanol were of chemical grade.

Synthesis of Fe₃O₄@ZnO core/shell nanoparticles

Fe₃O₄ superparamagnetic cores were synthesized by co-precipitation [10] of FeCl₃·6H₂O and

FeCl₂·4H₂O at the 2:1 molar ratio of Fe³⁺ and Fe²⁺, and they were dissolved in deionized water.

After stirring for 10 min, calculated amount of NH₄OH was added to the solution. The Fe₃O₄ precipitates were separated out using centrifuge and washed rigorously with deionized water. Fe₃O₄/ZnO core/shell nanoparticles were synthesized using previously reported method [5] with minor modifications. The as-prepared magnetite sample was dispersed into deionized water and the pH value was regulated to 5.0. Then, Zn(NO₃)₂ dissolved in deionized water was dripped into the solution with a molar ratio of magnetite to zinc source adjusted to 1:2. After 1 hour of contact, the pH value was increased up to 9.0 at 80 °C in order to promote the dehydration and atomic rearrangement involved with the formation of ZnO on the surface of magnetite. At the end of the contact stage, the solids were magnetically collected, washed with ethanol and abundant deionized water and dried.

Determination of singlet oxygen

The direct generation of ROS by synthesized Fe₃O₄/ZnO nanoparticles was monitored through an indirect assay using DPBF. Photooxidation reaction involves the formation of singlet oxygen via energy transfer from the excited nanoparticle to ground state

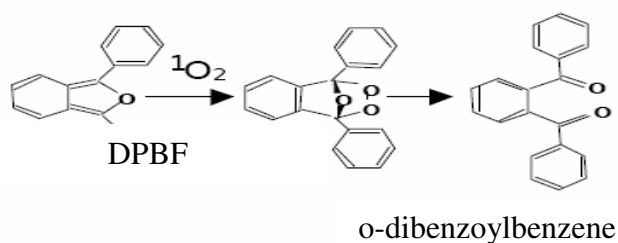


Figure 1. Photooxidation mechanism of DPBF by singlet oxygen.

molecular oxygen. DPBF is oxidized via 1, 4-addition by singlet oxygen to give the endoperoxide, which decomposes at room temperature to give o-dibenzoylbenzene (figure 1). In this mechanism, DPBF is singlet oxygen trapping agent and light is necessary for the photooxidation reaction. Accordingly, two milliliters of the 7×10^{-5} M $\text{Fe}_3\text{O}_4/\text{ZnO}$ nanoparticle suspension was contacted with one milliliter of 6.0×10^{-5} M DPBF solution in methanol in a quartz cuvette in the dark. The mixture was then excited at a wavelength 350 nm using a UV-lamp, and quenching in the absorption spectra of DPBF at 409 nm was monitored.

Characterization

X-Ray Diffraction (XRD) measurements were carried out with a Siemens Diffractometer D5000 using $\text{Cu-K}\alpha$ radiation with $\lambda=0.154315\text{nm}$. A UV-vis spectrophotometer (DU 800, Beckman Coulter) was used to study the optical absorption and singlet oxygen generation capability of core-shell nanoparticles. Luminescence properties were investigated by photoluminescence (PL) spectroscopy, using a spectrofluorometer FluoroMax-2 at room temperature with a 150mW continuous ozone-free Xe lamp. XPS spectra were recorded on samples in a PHI 5600 Multisystem, equipped with an Al source and a neutralizer at a base pressure of 5×10^{-10} torr. The magnetic properties were measured at room temperature with a Vibrating Sample Magnetometer (VSM, Lakeshore 7400).

DISCUSSION

XRD analyses of the as-synthesized isolated and combined solids confirmed the development of the crystalline phases of cubic magnetite and hexagonal ZnO wurzite phases (figure 2).

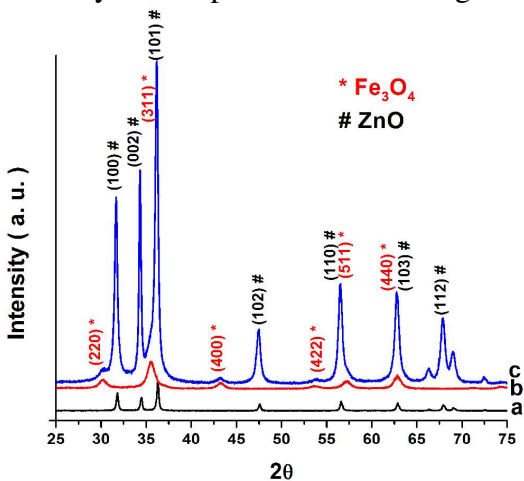


Figure 2: X-ray diffraction patterns of ZnO (a), Fe_3O_4 (b) and $\text{Fe}_3\text{O}_4/\text{ZnO}$ nanoparticles (c).

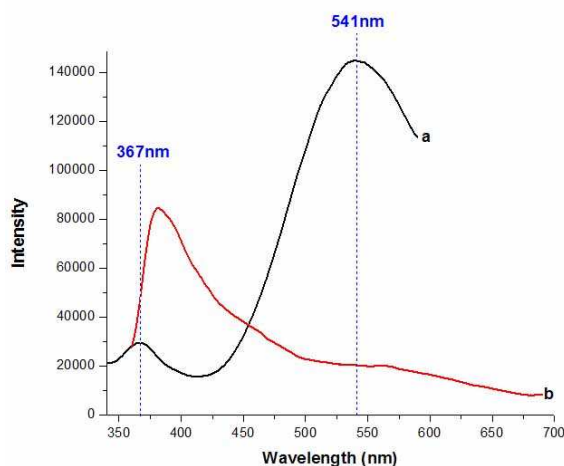


Figure 3: Photoluminescence spectra for ZnO (a) and $\text{Fe}_3\text{O}_4/\text{ZnO}$ (b) nanoparticles.

The broadness of the diffraction peaks evidenced the formation of nanosize phases. The XRD pattern corresponding to the ZnO synthesized in presence of magnetite seeds (figure 2-c) indicate the possible formation of core-shell structure. The average crystallite size for magnetite and $\text{Fe}_3\text{O}_4/\text{ZnO}$ nanoparticles, estimated by Scherrer's equation, were 9.424 nm and 15.107 nm, respectively, suggesting an approximate shell thickness of 2.7 nm.

The photoluminescence spectra of the $\text{Fe}_3\text{O}_4/\text{ZnO}$ core-shell nanoparticles with excitation wavelength of 350 nm were recorded and are shown in figure. 3. Pure ZnO nanoparticles display

a strong defect-related emission at 541 nm along with weak excitonic emission at 367 nm [12]. On the other hand pure Fe_3O_4 nanoparticles did not exhibit any luminescence. Interestingly $\text{Fe}_3\text{O}_4/\text{ZnO}$ nanoparticles revealed a very strong emission at 380 nm with a very weak defect-related emission of ZnO suggesting the rearrangement of electronic configuration in those core-shell structures. It could be explained in the framework of spatial confinement of electron and hole wavefunctions that migrate towards nanocrystal periphery with increasing semiconducting shell thickness and thus tuning their overlapping with magnetic core giving rise to reduction in band gap according to the tight binding model [13]. This effect can be seen in figure 3 in the form of red shift in the excitonic emission of ZnO from 367 to 380 nm.

Figure 4 shows the MH loops of the pure Fe_3O_4 and as-synthesized $\text{Fe}_3\text{O}_4/\text{ZnO}$ nanoparticles. The M-H loop for $\text{Fe}_3\text{O}_4/\text{ZnO}$ nanoparticles was well saturated and reported a saturation magnetization of 15.64 emu/g (figure 4-a). This magnetization is below the value for superparamagnetic magnetite nanoparticles, (59.87 emu/g, figure 4-b) and can be attributed to the presence of diamagnetic zinc oxide layer that may surround the magnetic cores.

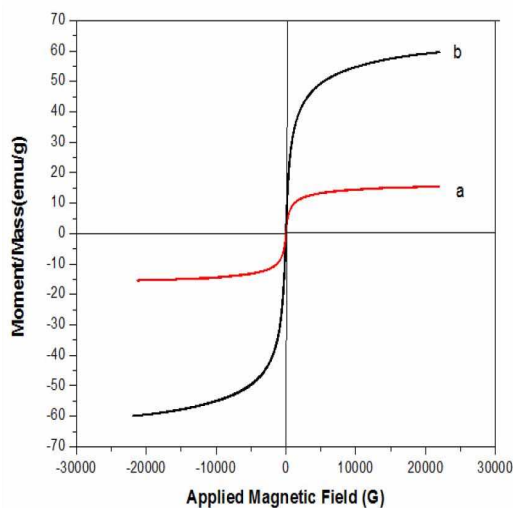


Fig. 4 M-H curve for Fe_3O_4 (b) and $\text{Fe}_3\text{O}_4/\text{ZnO}$ nanoparticles (a).

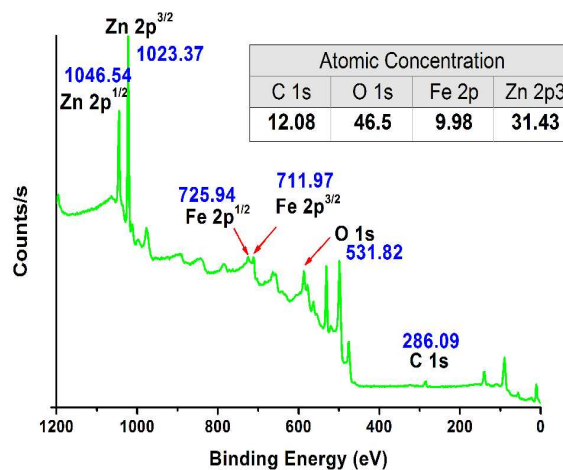


Fig. 5 Surface analysis for $\text{Fe}_3\text{O}_4/\text{ZnO}$ nanoparticles.

The composition of $\text{Fe}_3\text{O}_4/\text{ZnO}$ core-shell nanoparticles was further determined by XPS analysis. The two characteristic peaks of ZnO located at 1046.54 and 1023.37 eV binding energies of $\text{Zn } 2p^{1/2}$ and $\text{Zn } 2p^{3/2}$ respectively are shown in figure 5 which demonstrate the presence of Zn on the surface of the magnetic seed at this shell thickness [14]. The peaks corresponding to O 1s and C 1s are shown as reference.

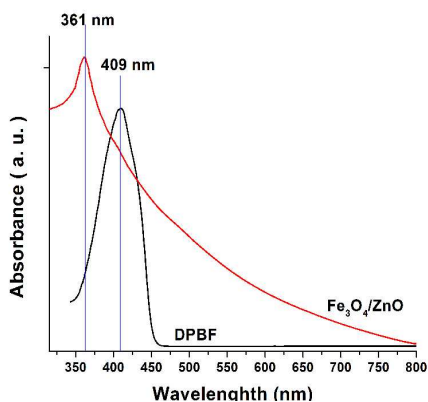


Figure 6: Absorption spectra of DPBF and $\text{Fe}_3\text{O}_4/\text{ZnO}$.

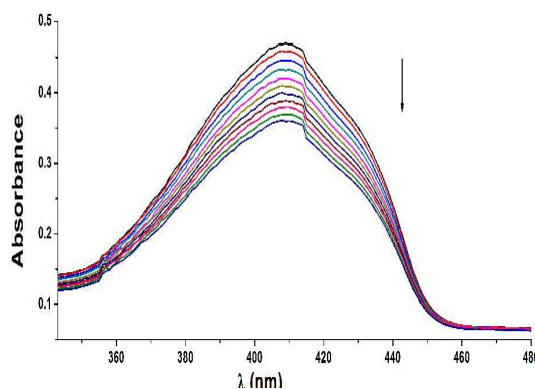


Figure 7: Quenching in absorbance of DPBF at 409 nm in presence of 1.0×10^{-5} M solution of $\text{Fe}_3\text{O}_4/\text{ZnO}$.

the variation of the DPBF absorption intensity with irradiation time (the arrow indicates increase in time of irradiation) when contacted with $\text{Fe}_3\text{O}_4/\text{ZnO}$ nanoparticles. The drop in the absorption intensity of DPBF can be attributed to its oxidation by generated singlet oxygen. Triplet state oxygen dissolved in methanol solution reacts with the excited triplet state nanoparticle to produce singlet oxygen or other ROS. The nanoparticle returns to its singlet ground state transferring its energy to the oxygen dissolved and produces singlet oxygen, which reacts rapidly with unsaturated carbon-carbon bonds in DPBF [15].

CONCLUSIONS

We have successfully synthesized $\text{Fe}_3\text{O}_4/\text{ZnO}$ core-shell heterostructured nanoparticles at room temperature through a simple and non-toxic aqueous route. XRD results confirmed the formation of nanosize crystalline magnetite and $\text{Fe}_3\text{O}_4/\text{ZnO}$. The photoluminescence measurements revealed the feasibility in the band gap engineering as a result of ZnO shell formation onto Fe_3O_4 cores. The formation of core-shell arrangement also evidenced through the weak defect-related emission and strong blue emission. The possibility and capability of the $\text{Fe}_3\text{O}_4/\text{ZnO}$ nanoparticles to generate singlet oxygen has also been verified through the continuous oxidation of DPBF. These nanoparticles could find application in photodynamic therapy for cancer.

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REFERENCES

- [1] Y. Jun, J. Choi, J. Cheon, *Chem. Commun.* (2007) 1203-1214.
- [2] P. Joshi, S. Chakraborti, P. Chakrabarti, D. Haranath, V. Shanker, Z. A. Ansari, Surinder P. Singh, V. Gupta, *J. Nanoscience and Nanotechnology* (2009) 9:6427-33.
- [3] C. Lin, Y. Li, M. Yu, P. Yang, J. Lin, *Adv. Funct. Mater.* (2007) 17:1459.

- [4] Wang K., Tan W., He X., Proceedings of the **2005** IEEE, Engineering in Medicine and Biology 27th Annual Conference, Shanghai, China, September 1-4.
- [5] R.Y. Hong, S.Z. Zhang, G.Q. Di, H.Z. Li, Y. Zheng, J. Ding, D.G. Wei, *Mat. Res. Bull.* (**2008**) 43:2457-2468.
- [6] Yi D. K., Selvan S. T., Lee S. S., Papaefthymiou G. C., Kundaliya D., Ying J. Y., *J. Am. Chem. Soc.* (**2005**)127:4990-1.
- [7] Wang D. S., He J., Rosenzweig N., Rosenzweig Z., *Nano Lett.* (**2004**) 4:409-13.
- [8] Gu H., Zheng R., Zhang X., Xu B., *J. Am. Chem. Soc.* (**2004**) 126:5664-5.
- [9] Zare R. N., Spencer B. H., Springer D. S., Jacobson M. P., “*Laser Experiments for beginners*”, University Science Books: Sausalito CA., **1995**, page 196.
- [10] K. D. Kim, S. S. Kim, Y-H. Choa, H. T. Kim, *J. Ind. Eng. Chem.*, (**2007**) 13:1137-1141.
- [11] B. Liu, D. Wang, W. Huang, M. Yu, A. Yao, *Mat. Res. Bull.* (**2008**) 43:2904-2911.
- [12] L. Spanhel, M. Anderson, *J. Am. Chem. Soc.* (**1991**) 113:2826-2833.
- [13] D. Bussian, S. Crooker, M. Ying, M. Brynda, A. Efros, V. Klimov, *Nature Mater.* (**2009**) 8, 35–40.
- [14] C. Y. Lee, T. Y. Tseng, S. Y. Li, P. Lin, *Tamkang J. Sci. Eng.* (**2003**) 6(2):127-132.
- [15] DeRosa M., Crutchley R, *Coordination Chemistry Review.* (**2002**) 234:351-377.