Magnetite-Silver Core–Shell Nanoparticles: Synthesis, Characterizes, and Optical Properties

Majid Rashidi Huyeh · Saeideh Balouchzehi · Mahdi Shafiee Afarani · Parisa Khajegi

Received: 19 August 2022 / Accepted: 17 October 2022 / Published online: 28 October 2022
© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2022

Abstract

Fe₃O₄ and Fe₃O₄/Ag core–shell nanocomposite powders were synthesized via the co-precipitation method. The structure, microstructure, magnetic, and optical properties of Fe₃O₄/Ag and Fe₃O₄ were studied. XRD patterns and UV–Vis spectra showed that nanostructure Fe₃O₄ and Fe₃O₄/Ag particles were successfully synthesized. AFM and MFM mode micrographs of Fe₃O₄ and Fe₃O₄/Ag powders confirm the formation of Fe₃O₄ particles in the nano-scale range. Both Fe₃O₄ and Fe₃O₄/Ag composite powders represented the superparamagnetic behavior due to the formation of nanosized Fe₃O₄ particles. Furthermore, in-situ synthesis of Ag on the surface of magnetite nanoparticles increased the particle size, resulting in a decrease in saturation magnetization. Moreover, based on the Maxwell-Garnet effective medium theory, a theoretical model was developed to determine the optical properties of suspended core–shell nanoparticles. A very good agreement was found between the theoretical and experimental results. In addition, the local electric field in the particles, evaluated using the numerical finite element method, showed that the electric field in the magnetite core might be amplified up to 20 times at the symmetrical SPR wavelength mode, depending on the silver shell thickness.

Keywords Magneto-plasmonic · Core–shell nanoparticles · Nanofabrication · Effective medium theory

Introduction

Noble metal nanostructures have attracted much attention thanks to their optical properties linked to the surface plasmon resonance (SPR) phenomenon [1]. This phenomenon is related to the coherent oscillation of the free electrons of the metal and results in an exaltation of the local electric field at a wavelength known as SPR wavelength. The SPR wavelength depends on the different parameters, especially on the shape and size of nanoparticles [2]. So these materials were proposed for various applications such as photonic devices [3–5], catalysts [6, 7], and biomedicines [8]. On the other hand, many researchers have been interested in magnetite nanoparticles due to their special properties and environmental compatibility [9–14]. However, their optical applications are limited because of their intrinsic optical properties. Perhaps, suitable nanostructures, including noble metal and magnetite, at the same time have been proposed by many groups to increase the desired properties [15–17]. In particular, the core–shell nanoparticles were studied for their optical and magneto-optical properties [18–20]. Thus, Fe₃O₄/Ag nanoparticles are employed in various application fields, including catalysts [21–23], sensors [24], antibacterial applications [25], cancer detection [26], and magnetic application [27–29].

Fe₃O₄/Ag and Fe₃O₄ can be synthesized by several methods such as solvothermal/hydrothermal [30–32], co-precipitation [33, 34], sol–gel [35], a combination of electrochemical and reduction methods [36], and solution combustion method [37].

The aim of the present study was to synthesize Fe₃O₄/Ag composite nanopowders. First, Fe₃O₄ particles were prepared. Then, Ag particles were in situ-synthesized in the presence of magnetite nanopowders via the precipitation method in the presence of a NaHB₄ reducer agent. The structure, microstructure, magnetic, and optical properties of Fe₃O₄/Ag and Fe₃O₄ were then studied. Moreover, a theoretical model based on the effective medium theory was proposed to determine the optical properties of embedded...
core–shell nanoparticles. This model predicts the symmetrical and antisymmetrical SPR modes linked to the shell silver very well. In addition, the numerical approach, based on the finite element method (FEM) in the frequency domain, was applied to evaluate the local electrical field at the SPR wavelengths.

**Experimental Section/Methods**

Magnetite powders were synthesized by co-precipitation method using iron(III) chloride hexahydrate (FeCl₃·6H₂O, Merck), iron(II) chloride tetrahydrate (FeCl₂·4H₂O, Merck), and silver nitrate (AgNO₃, Merck) as starting materials. Sodium borohydride (NaBH₄, Merck) was also used as a reducing agent.

**Synthesis of Fe₃O₄ Nanoparticles**

Magnetite powders were synthesized based on the work of Tahmasebi and Yamini [38]. Synthesis of Fe₃O₄ particles were carried out in a 500 ml three-necked round glass flask under N₂ atmosphere together with reflux condition. First, 8.48 g iron(III) chloride hexahydrate and 2.25 g iron(II) chloride tetrahydrate were dissolved in 400 ml of deionized water under magnetic stirring at 80 °C. Then 20 ml of chloride tetrahydrate were dissolved in 400 ml of deionized water under magnetic stirring at 80 °C. Then 20 ml of diluted ammonia (25 vol.%, Merck) was added drop-wise to the solution for 30 min until a dark olive green precipitate was obtained. Then 50 ml of aBH₄ (3.172 molars) was added drop-wise to the solution for 5 min. until a black precipitate was obtained. Then, the synthesized powders were washed with deionized water several times. Finally, the powders were dried in an electric oven at 70 °C for 2 h.

**Synthesis of Fe₃O₄/Ag Nanocomposite Particles**

First, 1 g of synthesized magnetite was added to 20 ml of AgNO₃ (0.885 molar) solution and agitated (1000 rpm) for 30 min. Then 50 ml of NaBH₄ (3.172 molars) was added drop-wise to the solution for 30 min until a dark olive green precipitate was obtained. Then, the synthesized powders were washed with deionized water several times and dried in an electric oven at 70 °C for 2 h.

In some cases, Ag particles were synthesized solely by removing nano magnetite particles from the reactor flask.

Structural characterization of the samples was performed using the X-ray diffraction (XRD, Bruker Advance D8) technique. The mean magnetite crystallite diameter ($d_{\text{Scherrer}}$) was determined from the half-height width ($\beta$) of the (311) diffraction peak of magnetite using the Scherrer equation ($d_{\text{Scherrer}} = 0.9 \lambda / \beta \cos \theta$). One T80 UV–Vis spectrophotometer (PG Instruments Ltd) was applied to measure UV–visible absorption spectra. Scanning probe microscope with atomic force and magnetic force modes (AFM/ MFM, Ara Research Co. Iran) were used for topographic and fly phase of magnetic characterizations. The magnetic behavior of powders was characterized using the vibration sample magnetometer (VSM, Meghnatis Daghigh Kavir Co., Kashan, Iran).

**Results and Discussion**

Figure 1a, b show the XRD patterns of Fe₃O₄ and Fe₃O₄/Ag nanopowders. As illustrated, magnetite (card no. 01–076-1849) is the dominant phase for Fe₃O₄ powders. Moreover, Fe₃O₄/Ag contained magnetite and silver (card no. 01–087-0717) phases. Since Ag was synthesized on the surface of the Fe₃O₄ particles, the magnetite peak intensities decreased considerably. The broadening of magnetite peaks is due to the nanocrystalline nature of the magnetite powders, with a mean crystallite size of 10.1 nm.

AFM and MFM mode micrographs of Fe₃O₄ and Fe₃O₄/Ag powders are shown in Figs. 2a-d. The dark arrows in Fig. 2a, b indicate the magnetite nanoparticles. Consideration of the AFM mode micrograph of Fe₃O₄ powders (bright areas in Fig. 2a) confirms the formation of Fe₃O₄ particles in the nano-scale range. Correspondingly, the magnetic nature of these particles can be observed in the MFM mode micrograph (dark areas in Fig. 2b). Moreover, in-situ synthesis of Ag on the surface of magnetite nanoparticles increased particle dimensions (Fig. 2c) and so resulted in a decrease in magnetic behavior (Fig. 2d). These magnetic behaviors were studied by VSM measurements.

The magnetization of Fe₃O₄ and Fe₃O₄/Ag powders as a function of the applied magnetic field at room temperature is shown in Fig. 3. As illustrated, both samples show superparamagnetic behavior due to the formation of nanosized Fe₃O₄ particles. Moreover, saturation magnetization values of the Fe₃O₄ and Fe₃O₄/Ag powders at 15 kOe field were about 30 and 20 emu·g⁻¹, respectively. These values are accorded to the results reported by Pastula et al. [39] As expected, the covering of Fe₃O₄ powders with Ag resulted in a decrease in saturation magnetization.

UV–visible absorption spectra of Ag, Fe₃O₄, and Fe₃O₄/Ag powders are shown in Fig. 4. Fe₃O₄ absorbance decreases gradually with the wavelength, which confirms the formation of Fe₃O₄ in nano-scale dimensions [40]. As illustrated, the Ag absorbance spectrum (red curve) presents a maximum value at 400 nm of wavelength. This peak is associated with the surface plasmon resonance effect of Ag nanoparticles [41]. Also, the Fe₃O₄/Ag spectrum (blue curve) presents two peaks at 435 and 780 nm of wavelengths, attributed to asymmetric and symmetric surface plasmon resonance, respectively [42, 43].
Model

The optical properties of suspended core–shell magnetite-silver nanoparticles were studied using the Maxwell-Garnet effective medium theory. This approximation is valid for a negligible scattering nanocomposite material, including the low volume fraction of nanoparticles embedded in a host medium as the following:

\[ \varepsilon = \frac{\varphi}{\varepsilon_d} \]

where \( \varphi \), \( \varepsilon_d \), and \( \varepsilon_p \) are nanoparticle volume fraction, dielectric function of host medium, and the core–shell magnetite-silver nanoparticle, respectively. This earlier may be given using the effective medium theory for sphere multilayer [44]:

\[ A_1 = \frac{(\varepsilon_c - \varepsilon_{sh})(1 - \delta) + \varepsilon_{sh}}{\varepsilon_{sh}} \]  

\[ A_2 = \frac{[A_1 \varepsilon_{sh} + (\varepsilon_c - \varepsilon_{sh})\delta]}{\varepsilon_{sh}} \]

where \( \varepsilon_c \) and \( \varepsilon_{sh} \) are the dielectric function of the magnetite core and that of the silver shell, and \( \delta = (R_c/R_{sh})^3 \) represents the volume ratio of the magnetite core to the particle volume. The absorbance then may be given as:

\[ \alpha = \frac{4\pi}{\lambda} \text{Im} \left( \sqrt{\varepsilon_{\text{eff}}} \right) \]
The model was applied to evaluate the optical properties of the core–shell magnetite-silver nanoparticle suspended in the water. The magnetite particle radius was considered 10 nm for the different silver shell thicknesses of 2, 5, and 10 nm. Based on the model, the absorbance spectra of different core–shell magnetite-silver nanoparticles are depicted in Fig. 5. The absorbance of the magnetite and silver nanoparticles suspended in the water is also shown in Fig. 5. The magnetite nanoparticle absorbance is magnified by a factor of 50. As illustrated, the absorbance of suspended magnetite NPs regularly decreases by wavelength, while the suspended silver NPs show a maximum value at about 400 nm of wavelength. This maximum is related to the surface plasmon resonance phenomena [2]. As can be observed, the absorbance of the core–shell magnetite-silver NPs presents two maxima. These maxima are linked to the combination of the dark and bright modes of SPR[39, 40, [45]. Indeed, the first pic of SPR, located at the shorter wavelength, is due to the antisymmetrical combination of the dark and bright mods. In contrast, the second SPR pic, located at the longer wavelength, is related to the symmetrical combination of the dark and light mods. A very good agreement may be seen between the experimental results (Fig. 4) and the theoretical ones (Fig. 5). Figure 6 represents the symmetrical and antisymmetrical combination of dark and bright modes schematically. The finite element method was also used for the study of the absorption cross-section as well as the electrical field in the nanoparticle according to reference 2.
The local field in the particle for symmetrical and antisymmetrical SPR modes is depicted in Fig. 7 for different shell thicknesses. The local field in the core for the symmetrical mode is much higher than that of the antisymmetrical mode for each particle. This behavior can also explain the higher amplitude of the symmetrical mode compared to the antisymmetrical one. By increasing the shell thickness, the first maximum, located at the low wavelength, presents a slightly red-shift displacement, whereas the second one, located at the longer wavelength, reveals an important blue-shift. Indeed, for a very thin shell thickness, there is a high electric coupling between the dark and bright modes of SPR. By increasing the silver shell thickness, the distance between the inner and outer of the silver shell surfaces increases. Therefore, the electric coupling becomes weaker. As the magnetite core size is considered the same for different shell thicknesses, the first SPR mode is slightly affected by the shell thickness. In addition, the SPR amplitude increases by increasing the shell thickness.

**Conclusion**

The present work aimed to synthesize Fe₃O₄ and Fe₃O₄/Ag composite nanopowders via the co-precipitation method. The structure, microstructure, magnetic, and optical properties of Fe₃O₄/Ag and Fe₃O₄ were studied. Moreover, a theoretical model was proposed to determine the optical properties of core–shell nanoparticles embedded in a host medium. Also, numerical FEM was used for the study of the electric local field in the particle. The main results can be concluded as follows:

1. XRD patterns and UV–vis spectra showed that nanostructure Fe₃O₄ and Fe₃O₄/Ag particles could be successfully synthesized.
2. AFM and MFM mode micrographs of Fe₃O₄ and Fe₃O₄/Ag powders confirm the formation of Fe₃O₄ particles in the nano-scale range.
3. Both Fe₃O₄ and Fe₃O₄/Ag composite powders represented the superparamagnetic behavior due to the formation of nano-sized Fe₃O₄ particles. In-situ synthesis of Ag on the surface of magnetite nanoparticles increased particle sizes, resulting in a decrease in magnetic behavior.
4. The theoretical model predicts well two modes of symmetry and asymmetry SPRs. By increasing the silver shell thickness, the symmetrical mode presents a blueshift, and its amplitude increases.
5. Electric local field, calculated by FEM, showed amplification of the electric local field in the particle at the symmetric SPR wavelength mode depending on the silver shell thickness.

**Acknowledgements** The authors would like to thank Mohammad Azari Nadaf Abad from the Karlsruhe Institute of Technology and Anh Van Le from the University of Tuebingen for their scientific comments.

**Author Contribution** All authors contributed to the study’s conception and design. Material preparation, data collection, and analysis were performed by Majid Rashidi Huyeh, Saeideh Balouchzahi, Mahdi Shafiee Afarani, and Parisa Khajegi. The first draft of the manuscript was written by Majid Rashidi Huyeh and Mahdi Shafiee Afarani, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.
Funding This work was supported by the University of Sistan and Baluchestan, Iran. The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

Data Availability The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Declarations

Conflict of Interest The authors declare no competing interests.

References

1. Palpant B (2012) in Gold nanoparticles for physics, biology and chemistry, edited by Louis C and Pluchery O. (Imperial College Press, London, 2012), pp. 75–102. https://doi.org/10.1002/anie.201309908
2. Parisa K, Huyeh MK (2021). IJOP. https://doi.org/10.52547/ijop.15.1.41
3. Lesniak W, Bielinska AU, Sun K, Janczak KW, Shi X, Baker JR, Balogh LP (2005). Nano Lett. https://doi.org/10.1021/nl051077u
4. Liu CH, Zhou ZD, Yu X, Lv BQ, Mao JF, Xiao D (2005). Anal. Chem. https://doi.org/10.1021/acs.analchem.040940
5. Li K, Zhengtao Xu, Hanhui Xu, Carroll PJ, Fettigner JC (2006). Inorg Chem. https://doi.org/10.1021/ic051135e
6. Endo T, Yomokazu T, Esumi K (2005). J Colloid Interface Sci. https://doi.org/10.1016/j.jcis.2005.01.057
7. Tan LL, Wei M, Shang L, Yang YW (2021). Adv Funct Mater. https://doi.org/10.1002/adfm.202007277
8. Yang X, Yang M, Pang Bo, Vara M, Xia Y (2015). Chem Rev. https://doi.org/10.1021/cr500195m
9. Arturo M, Lopez Q, Jose R (1993) J Colloid Interface Sci. https://doi.org/10.1006/jcis.1993.1277
10. Chiang CL, Wang CS (2006). J Magn Magn Mater. https://doi.org/10.1016/j.jmmm.2005.08.022
11. Aoshima K, Wang SX (2003). J Appl Phys. https://doi.org/10.1063/1.1588633
12. Morton SA, Waddill GD, Kim SI, Schuller K, Chambers SA, Tobin JG (2002) Surf Sci. https://doi.org/10.1016/s0039-6028(02)01824-1
13. Shebanova ON, Lazor P (2013) J Chem Phys. https://doi.org/10.1063/1.4804594
14. Schrupp D, Sing M, Tsunekawa M, Fujiiwara H, Kasi S, Sekiyama A, Suga S, Muro T, Brabers VAM, Claessen R (2005). Europhys Lett. https://doi.org/10.1209/epl/i2005-10045-9
15. Huang ZB, Tang FQ (2004) Preparation, structure, and magnetic properties of polystyrene coated by Fe3O4 nanoparticles. J Colloid Interface Sci. https://doi.org/10.1016/j.jcis.2003.12.065
16. Cui YL, Hu DD, Fang Y, Ma JB (2001) Sci China Ser B. https://doi.org/10.1007/BF02879815
17. Shimizu T, Kitayama Y, Kodama T (2001). Energy fuels. https://doi.org/10.1021/ef000200w
18. León Félix L, Coaquira JA, Martinez MA, Goya GF, Mantilla J, Sousa MH, Valladares LL, Barnes CH, Morais PC (2017) Scientific reports. https://doi.org/10.1038/srep41732
19. Salehizadeh H, Hekamatian E, Salehighi M, Kennedy K (2012). J Nanobiotechnol. https://doi.org/10.1186/1477-3155-10-3
20. Brullot W, Valev VK, Verbiest T (2012) Nanomedicine: NBM. https://doi.org/10.1016/j.nano.2011.09.004
21. Wang G, Li F, Li L, Zhao J, Ruan X, Ding W, Cai J, Ang Lu, Pe Y (2020). ACS Omega. https://doi.org/10.1021/acsomega.0c00437
22. Khedkar CV, Khupse ND, Thombare BR, Dusane PR, Lole G, Devan RS, Deshpande AS, Patil SI (2020). Chem Phys Lett. https://doi.org/10.1016/j.cplett.2020.137131
23. Jiang W, Zhou Y, Zhang Y, Xuan S, Gong X (2012). Dalton Trans. https://doi.org/10.1039/C2DT12307J
24. Chen Q, Wang H, Wang Q, Pan Y (2018) J Plasmonics. https://doi.org/10.1015/1-s3c201911801002
25. Amarjargal A, Tijing LD, Ik-Tae I, Kim CS (2013) Chemical Engineering Journal. https://doi.org/10.1016/j.cej.2013.04.054
26. Benvidi A, Jahanbani S (2016) J Electroanalytic Chem. https://doi.org/10.1016/j.jelechem.2016.02.038
27. Liu CH, Zhou ZD, Xiao D (2008) Inorganic materials. https://doi.org/10.1134/S002068580803014X
28. Ghazanfari M, Johar F, Yazdani A (2014) Journal of ultratine grained and nanostructured materials. https://doi.org/10.7589/jufgnsma.2014.02.006
29. Bankole OM, Nyokong T (2016). New J Chem. https://doi.org/10.1039/C6NJ01511E
30. Shan Y, Yang Y, Caoab Y, Huang Z (2015). RSC Adv. https://doi.org/10.1039/C5RA17606A
31. Gai K, Qi H, Zhu X, Wan M (2019) EJS Web Conf. https://doi.org/10.1051/econf/201911801002
32. Pan L, Tang J, Chen Y (2013). Sci China Chem. https://doi.org/10.1007/s11426-012-4763-y
33. Amarjargal A, Tijing LD, Cheol I-T, Kim S (2013). Chem Eng J. https://doi.org/10.1016/j.cej.2013.04.054
34. Khalil MI (2015). Arab J Chem. https://doi.org/10.1016/j.ajch.2015.02.008
35. Wang G, Li F, Li L, Zhao J, Ruan X, Ding W, Cai J, Ang Lu, Pei Y (2020). ACS Omega. https://doi.org/10.1021/acsomega.0c00437
36. Fajaroh F (2017) IOP Conf. Ser.: Mater Sci Eng. https://doi.org/10.1088/1757-899X/202/1012064
37. Ianoś R, Táculescu A, Pácurariu C, Lazáu I (2012) J Am Ceram Soc. https://doi.org/10.1111/j.1551-2966.2012.05159.x
38. Tahmasebi E, Yamin Y (2012) Anal Chim Acta. https://doi.org/10.1016/j.aca.2012.10.040
39. Patsula V, Kosinová L, Lovrič M, Ferhatovic Hamzić L, Rabýk M, Konela R, Paruzel A, Šlouf M, Herynek V, Gajović S, Horák D (2016) ACS Appl Mater & Interf. https://doi.org/10.1021/acsami.5b12720
40. Villegas VRA, Isaías De León Ramírez J, Hernandez Guevara E, Sicairos SP, Hurtado Ayala LA, Sanchez BL (2020) J Saudi Chem Soc. https://doi.org/10.1016/j.jscs.2019.12.004
41. Hashemi Zadeh S, Rashidi-Huyeh M, Palpant B (2017) J Appl Phys. https://doi.org/10.1063/1.4997276
42. Prodan E, Radloff C, Halas NJ, Nordlander P (2003) Science. https://doi.org/10.1126/science.1089171
43. Prodan E, Nordlander P (2004). J Chem Phys. https://doi.org/10.1063/1.1647518
44. Voschinnikov NV, Mathis JS (1999) Astrophys J 526:257–264
45. Levin CS, Hofmann C, Ali TA, Kelly AT, Morosan E, Nordlander P, Whittmore KH, Halas NJ (2009) ACS Nano. https://doi.org/10.1021/nn900118a

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.