Sonochemical magnetite encapsulation in silica at low irradiation power

D. Ravelo-Acuña a, J.A. Fuentes-García b,c, H.T. Yee-Madeira a, A.I. Diaz-Cano c, G.F. Goya b, J. Santoyo-Salazar d,*

a Escuela Superior de Física y Matemáticas del Instituto Politécnico Nacional, ESFM-IPN, Building 9, Av. IPN, Zacatenco 07738, Mexico
b Instituto de Nanociencia de Aragón, Departamento de Física de la Materia Condensada, Universidad de Zaragoza, 50018 Zaragoza, Spain
c Unidad Profesional Interdisciplinaria en Ingeniería y Tecnologías Avanzadas del Instituto Politécnico Nacional, UPIITA-IPN, Av. IPN 2580, Ticoman 07340, Mexico
d Departamento de Física, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, CINVESTAV-IPN, Av. IPN 2508, Zacatenco 07360, Mexico

Article info
Article history:
Received 25 February 2019
Received in revised form 10 April 2019
Accepted 18 April 2019
Available online 19 April 2019

Keywords:
Fe3O4@SiO2
Sonochemical
SPIONs
Core-shell

Abstract
Magnetite nanoparticles (Fe3O4 NPs) coated with silicon dioxide [SiO2] defined as Fe3O4@SiO2 core-shells are a viable option for the development of addressable and multifunctional nanotargets; because of their superparamagnetic properties, molecular/biological anchor and biocompatibility in nanomedicine and theragnostics. In this work, we report Fe3O4@SiO2 obtained by Stöber and sonochemical methods combination at low irradiation power (130 W, 1 h) with different volumes of tetraethylorthosilicate (TEOS). Fe3O4@SiO2 results showed effects of diamagnetic silanol (Si-OH) layer as function of concentration over magnetic behavior.

© 2019 Elsevier B.V. All rights reserved.

1. Introduction
Currently, Superparamagnetic Iron Oxide Nanoparticles SPIONs targets have been considered for future applications in cancer hyperthermia therapy and clinical agent diagnosis, due to their magnetic domain orientation and energy exchange [1]. SPIONs can be stimulated by external light excitation and magnetic field as function of frequency in sizes bellow ~20 nm. The main challenge is to control their physical, chemical and biological interactions with cancer cells [2]. SPIONs can be covered by organic links –OH, polyphenols, liposomes, etc. for biological applications. Fe3O4@SiO2 could be potential candidates due to: their local interaction, low-toxicity, biocompatibility, stability and selective targeting [3]. Sonochemistry is an easy route to obtain Fe3O4@SiO2 due to acoustic frequencies produce energy interactions up to 13 eV at 20 KHz–2 MHz [4]. In this work, we report Fe3O4@SiO2, which were tuned with TEOS concentrations; 0.25, 0.50 and 1.00 mL by Stöber method and low ultrasound irradiation. Magnetic response changed as function of shell thickness.

2. Experimental
The reagents used were: iron sulfate heptahydrated (FeSO4-7H2O, reagent ACS ≤ 99.0%), deionized water (Millipore 18.2 MΩ cm), sodium hydroxide (NaOH, reagent grade, ≤98%), tetraethyl orthosilicate (TEOS, 98%), ammonium hydroxide (NH2OH solution 30–32%) and absolute ethyl alcohol (C2H5OH). All purchased from Sigma-Aldrich and used as they received. Ultrasonic Sonics Vibra-cell VCX 130 with titanium tip Ti-6Al-4V was used to generate 130 W of ultrasonic irradiation at 20 KHz in continuous cycle. The lyophilization of samples was done in a LABCONCO FreeZone 2.5 for 24 h.

Fe3O4@SiO2 samples were analyzed by X-Ray diffraction (XRD) RIGAKU-Smart Lab (λ = 1.542 Å, steps of 0.02° from 20 to 90° in 2θ). Shells were identified in a spectrophotometer FT-IR NICOLET 6700 from 4000 to 400 cm−1. Core-shell configuration was observed by transmission electron microscope (TEM) JEOL JEM ARM200F (200 kV) and Scanning Transmission Electron Microscopy (STEM), plus energy-dispersive X-ray spectroscopy (EDS). Magnetic properties were measured in a superconducting quantum interference device (SQUID) magnetometer (accuracy of 5 × 10−8 emu) at room temperature from −40 to 40 kOe. Elemental surface composition was analyzed in a K-alpha X-ray photoelectron spectrometer (XPS) system by Thermo Fisher Scientific Company with a monochromatic Al Kα X-ray source, survey and high-resolution spectra were collected at energies among 20 and 200 eV.

2.1. Fe3O4 synthesis
Fe3O4 NPs were prepared with 90 mL of aqueous FeSO4·7H2O (8 mM) and sonicate at 130 W. After irradiation by 15 min, 10 mL...
of 3 N NaOH solution were injected as reducing agent. This solution was sonicated by 60 min to obtain Fe$_3$O$_4$ NPs. The black solution was precipitated with a magnet and the supernatant was removed, washed with distilled water and dispersed in ultrasonic bath until pH = 7. Finally, particles were dispersed in water and dried for 24 h.

2.2. Fe$_3$O$_4$@SiO$_2$ processing

50 mg of Fe$_3$O$_4$ NPs in powder were dispersed in 90 mL of ethanol/water solution (60/40 v/v) using ultrasonic irradiation by 10 min (130 W). After, TEOS series were prepared by volume addition from 0.25, 0.50 to 1.00 mL in order to modify SiO$_2$ shell thickness. These Fe$_3$O$_4$ NPs were sonicated 10 min for the different solutions.

TEOS hydrolyzation began after 15 mL of NH$_3$OH was incorporated to the solution and sonicated 1 h for SiO$_2$ polymerization. Each sample was precipitated and centrifuged at 40,000 RPM, during 2 min to recover Fe$_3$O$_4$@SiO$_2$. Finally, samples were washed 5 times with ethanol, dried at room temperature and powders were stored.

2.3. Reaction kinetics of Fe$_3$O$_4$@SiO$_2$

The ultrasonic method confines periodic regions by compression and expansion until formation, growth and collapse of acoustic cavitation. The air molecules are dissolved into the solution by bubbles at high pressure cycle, which compress radicals and ions. This process continues until the external pressure gets over and the bubbles collapse. The pressure and temperature during cavitation reached more than 1000 atm and 500 K respectively. The collapse is promoted at $10^{10}$ K/s, with energy of 13 eV [5].

3. Results

3.1. XRD and FT-IR

A cubic inverse spinel structure (JCPDS 65-3107) was detected by XRD from Fe$_3$O$_4$ NPs with lattice parameter $a = 8.396$ Å; Fig. 1(a). Fe$_3$O$_4$@SiO$_2$ samples prepared with TEOS showed amorphous surface contribution from SiO$_2$ scattering. Fe$_3$O$_4$ signals decreased due these large and short interactions from the SiO$_2$ coating.

Fe$_3$O$_4$ vibrational bands were in 1635 and 583 cm$^{-1}$ by FTIR, Fig. 1(b). While 3437 cm$^{-1}$ was attributed to –OH layers due to NaOH reduction. Other modes as 1128, 885, 500 and 400 cm$^{-1}$ came from Fe–O interactions and Fe$^{2+}$ vacancies as maghemite, Fig. 1(c).

Fe interactions were reduced as SiO$_2$ volume is increased. SiO$_2$ normal modes correspond to 1220 cm$^{-1}$ in asymmetric stretch, 1081 cm$^{-1}$ in symmetric stretch vibration and 460 cm$^{-1}$ to vibration of (Si–O–Si) bonds 8–11. 3437 cm$^{-1}$ corresponds to (–OH) modes. At 960 cm$^{-1}$, to silanol group (Si–OH) is more defined in 0.50 and 1.00 mL samples. Si–OH and –OH modes are over Fe$_3$O$_4$ surface as result of intermediate alkoxides during the SiO$_2$ formation.

Results are coherent with the increment of SiO$_2$ shell. (Fe–O) interactions can be masking by (Si–O–H) interactions or overlap of normal vibration mode frequencies.

3.2. TEM and STEM

Fe$_3$O$_4$ NPs distribution was 9.6 ± 1.8 nm, Fig. 2(a,b). HRTEM showed crystalline Fe$_3$O$_4$, Fig. 2(c,d). Fe$_3$O$_4$@SiO$_2$ TEOS 0.25, 0.50 and 1.00 mL show shells of 60, 98 and 120 nm respectively. Well-defined core-shells were observed in 0.25 and 0.50 mL. TEOS ~1.00 mL was not an optimal condition for encapsulation, Fig. 3(a-c).

STEM and linear EDS analysis are showed in Fig. 3(d,e) for sample 0.25 mL with elemental K$_x$ signals at: 0.525 KeV of O, 1.740 KeV of Si and 6.405 KeV of Fe.

3.3. XPS

X-ray photoelectron spectroscopy (XPS) showed layer analysis from Fe$_3$O$_4$@SiO$_2$ samples TEOS 0.50 and 1.00 mL, Fig. 4. Carbon C binding energy was centered ~282 eV (C–C) from XPS correction. Oxygen O 1s centered ~531 eV, corresponds to O–Si–O binding in accordance to bulk SiO$_2$, silicon Si 2s centered ~152 eV and Si 2p binding energy centered ~101 eV corresponding to silica. XRD, XPS, TEM and EDS are agreement with Fe$_3$O$_4$@SiO$_2$ configuration.

3.4. MSV

Hysteresis loops showed magnetization from Fe$_3$O$_4$@SiO$_2$ samples and references. SiO$_2$ contributes with diamagnetic behaviour. Meanwhile, Fe$_3$O$_4$ NPs magnetization, $M_s = 70.4$ emu/g and coercive field, $H_c = 83.91$ Oe. Close loops indicate that sonochemical route is able to produce addressable SPIONs targets.

Fe$_3$O$_4$@SiO$_2$ TEOS: 0.25, 0.50 and 1.00 mL reported $M_s$: 2.53, 0.24, 0.04 emu/g and $H_c$: 88.16, 104.43, 47.23 Oe respectively, Fig. 5(b). The random ordering from SiO$_2$ atoms ($\mu = 0.55$) over Fe$_3$O$_4$ surface induces a molecular barrier and slight tendency that resembles diamagnetic behaviour.
Fig. 2. Fe₃O₄ NPs TEM: (a-b) sizes distribution; (c) HRTEM; and (d) electron diffraction.

Fig. 3. Fe₃O₄@SiO₂ STEM: TEOS (a) 0.25; (b) 0.50; (c) 1.00 mL; (d) EDS analysis for 0.25 mL; and (e) core-shell elements.
4. Conclusions

Fe$_3$O$_4$@SiO$_2$ with TEOS hydrolysis and condensation were done with reaction time ~1 h. $M_s$ is reduced as function of SiO$_2$ thickness layer. Enhancement, $M_s$ was obtained with TEOS 0.25 mL as 2.53 emu/g. This works contributes with an easy processing to obtain Fe$_3$O$_4$@SiO$_2$ as controlled nanomaterials for future biomedical application due to functional groups over hydroxyl surface.

Conflict of Interest

None.

Acknowledgements

This work was supported partially by CONACYT and Marcos Moshinsky Foundation 2018. Thanks to Eng. Marcela Guerrero by her XRD technical support. CONACYT by the financial support for D. Ravelo-Acuña (Ph.D.) and J.A. Fuentes-García (Postdoc Fellow).

References

