Prolate spheroidal hematite particles equatorially belt with drug-carrying layered double hydroxide disks: Ring Nebula-like nanocomposites

Ahmet Nedim Ay, Deniz Konuk, Birgul Zümreoglu-Karan*

Abstract
A new nanocomposite architecture is reported which combines prolate spheroidal hematite nanoparticles with drug-carrying layered double hydroxide [LDH] disks in a single structure. Spindle-shaped hematite nanoparticles with average length of 225 nm and width of 75 nm were obtained by thermal decomposition of hydrothermally synthesized hematite. The particles were first coated with Mg-Al-NO3-LDH shell and then subjected to anion exchange with salicylate ions. The resulting bio-nanohybrid displayed a close structural resemblance to that of the Ring Nebula. Scanning electron microscope and transmission electron microscopy images showed that the LDH disks are stacked around the equatorial part of the ellipsoid extending along the main axis. This geometry possesses great structural tunability as the composition of the LDH and the nature of the interlayer region can be tailored and lead to novel applications in areas ranging from functional materials to medicine by encapsulating various guest molecules.

Introduction
Magnetic iron oxide nanoparticles have attracted extensive attention in biomedicine and nanotechnology areas [1,2]. Among them, hematite (α-Fe2O3) is the oldest known, most stable, and cheapest iron oxide with n-type semiconducting and soft magnetic properties [3]. Since the report of Matijevic and co-workers in the early 1980s [4], much progress has been made toward the synthesis of monodisperse hematite particles with many different shapes that offer promising uses in water splitting, photocatalysis, photoelectrochemistry, magnetic recording media, and other nanodevices [5-7].

For practical applications, magnetic nanoparticles are coated with a protective shell to avoid agglomerization and for chemical stabilization [8]. A nonmagnetic coating is generally employed not only for magnetic core stabilization but also for the integration of biofunctionalization [9]. So far, many spherical core-shell magnetic nanostructures have been reported, while non-spherical core-shell particles with lower symmetries are relatively rare, although they would offer interesting physical properties. Ellipsoidal particles may serve as simple non-spherical models for studying anisotropic optoelectronic effects and drug delivery [10,11]. There has been considerable interest in the synthesis and characterization of non-spherical hybrid nanostructures prepared by coating spindle-shaped hematite particles with gold [12], silica [13], titania [14], and polymeric shells [15].

LDHs have been introduced as alternative inorganic coating materials for magnetic nanoparticles [16]. A number of magnetic core@LDH nanohybrids have been synthesized for catalysis [17,18] and drug delivery [19-21] applications. We have recently reported anti-arthritic agent-carrying, nearly spherical core-shell magnesium ferrite@LDH nanocomposites that have a potential for magnetic arthritis therapy [22]. In this communication, we describe an original morphology of such nanocomposites using spindle-shaped hematite as the core material and salicylate-intercalated Mg-Al-LDH as the shell.

Experimental details
Hematite nanoparticles were obtained by thermal decomposition of iron(III) oxalate in static air. Iron(III) oxalate was prepared hydrothermally by treating aqueous FeCl3 and H2C2O4 at pH 7 (adjusted by ammonia solution) for 48 h at 80°C in a pressure bomb in the
presence of a cationic surfactant (cetyl tributyl ammonium bromide). The product was washed thoroughly several times with water and dried at room temperature. The powder was ground in an agate mortar and calcined at 300°C for 6 h.

Element analysis for metal ions was performed using a Spectro XLP 2000 PRO XRF X-ray fluorescence spectrometer (Spectro Analytical Instruments GmbH) while for carbon and hydrogen on a varioMICRO CHNS instrument (Elementar Analysensysteme GmbH). The water content was determined by thermogravimetry on a DTG-60H (Shimadzu) thermal analysis system at a heating rate of 10°C/min. Powder X-ray diffraction patterns [XRD] were recorded using a D/MAX-2200 (Rigaku) diffractometer equipped with graphite-filtered Cu Kα radiation (λ = 1.54056 Å) from 3° to 70° (2θ) at a scanning rate of 4 min⁻¹. Fourier transform infrared spectra [FTIR] were recorded in the range from 4,000 to 400 cm⁻¹ on a Perkin Elmer Spectrum One instrument using the KBr pellet technique. The morphology and dimension of the synthesized products were observed with a FEI quanta 200 FEG (FEI Company) scanning electron microscope [SEM]. Transmission electron microscopy [TEM] and selected area electron diffraction [SAED] were performed using a FEI Tecnai G2 F30 (FEI Company) instrument operated at 300 or 100 kV. Magnetism of the products was measured at room temperature with a vibrating sample magnetometer (Quantum Designed Physical Property Measurement System (Quantum Design Inc.) in the magnetic field range of ±30 kOe. The electronic spectra were recorded on a Shimadzu UV-3600/UV-VIS-NIR Spectrophotometer (Shimadzu) equipped with a Praying Mantis attachment.

Results and discussion

Figure 1a shows the powder X-ray diffraction pattern of the as-prepared hematite sample. The pattern indicates single phase of α-Fe₂O₃ with characteristic sharp reflections at d values of 3.66 Å (012), 2.69 Å (104), 2.51 Å (110), 2.20 Å (113), 1.83 Å (024), 1.69 Å (116), 1.48 Å (214), and 1.45 Å (300), matching with the JCPDS file 13-534. The FTIR spectrum confirmed the hematite structure with two characteristic bands located at 547±13-534. The FTIR spectrum confirmed the hematite (214), and 1.45 Å (300), matching with the JCPDS file (110), 2.20 Å (113), 1.83 Å (024), 1.69 Å (116), 1.48 Å (214), and 1.45 Å (300), matching with the JCPDS file. The measured saturation magnetization values for α-Fe₂O₃@NO₃-LDH (0.7 emu/g) and α-Fe₂O₃@SAL-LDH (0.6 emu/g) were lower than that of the naked hematite (9.6 emu/g). The decreased saturation magnetization should be attributed to the presence of the nonmagnetic material around the magnetic core and is related to the amount of the shell. α-Fe₂O₃@SAL-LDH was formulated as Fe₂O₃@4[Mg₀.68Al₀.32(OH)₂]C₆H₄O₃₃(NO₃)₀.0₁H₂O according to the chemical and thermogravimetric analysis data. The core content of the nanocomposite is 26 wt.% and the drug content 28 wt.%.

The effect of LDH coating on the optical properties of the hematite core is illustrated in Figure 4. Related to the change in morphology, ligand-to-metal charge transfer transition of the uncoated spindle hematite at 358 nm showed a red shift, while the shoulder due to the

Nedim Ay et al. Nanoscale Research Letters 2011, 6:116
http://www.nanoscalereslett.com/content/6/1/116
Figure 1 Powder X-ray diffraction patterns, SEM and TEM images of the as-prepared samples. XRD patterns of uncoated, NO₃-LDH-coated, and SAL-LDH-coated hematite (A). SEM images of uncoated (B) and SAL-LDH-coated hematite (C). TEM images of uncoated (D) and SAL-LDH-coated hematite (E). SAED pattern of SAL-LDH-coated hematite (F).

Figure 2 Morphological resemblance of the as-prepared nanocomposite to The Ring Nebula. TEM image of α-Fe₂O₃@SAL-LDH (end-on view) (A). The Ring Nebula (end-on view; Credit: Hubble Heritage, http://www.nasa.gov) (B).
ligand field transition around 520 nm did not shift. This typical behavior for anisotropic hematite agrees with recent reports [26,27].

**Conclusion**

In conclusion, we present here the first example of a non-spherical magnetic core@LDH shell architecture. This new structural feature is similar to that of the Ring Nebula, displaying a unique resemblance of nano to macro. The reported anisotropic nanohybrid possesses a great structural tunability and may show unprecedented properties in shape-sensitive drug delivery/release [28] and nanophotonics applications.

---

**Figure 3** Room temperature magnetization curves of uncoated and coated hematite particles. Uncoated (A), NO3-LDH-coated (B), and SAL-LDH-coated hematite (C).

**Figure 4** Effect of LDH coating on the optical properties of hematite core. Diffuse reflectance UV/Vis spectra of uncoated hematite (A), NO3-LDH-coated hematite (LDH peak at 218 nm) (B), and SAL-LDH-coated hematite (LDH and SAL peaks at 224, 240, and 319 nm) (C).

**Acknowledgements**

We thank Prof. A. Temel for XRD analysis and H.U. SNTG for magnetization measurements.

**Authors’ contributions**

ANA and DK carried out synthesis and characterization studies. ANA and BZK performed data analysis and discussion of the results. BZK conceived of the study and wrote the manuscript. All authors read and approved the final manuscript.

**Competing interests**

The authors declare that they have no competing interests.

Received: 25 July 2010 Accepted: 3 February 2011 Published: 3 February 2011

**References**

1. Laurent S, Forge D, Port M, Roch A, Robic C, Vander Elst L, Muller RN: Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations and biological applications. *Chem Rev* 2008, 108:2064.
2. Lu AH, Salabas EL, Schuth F: Magnetic nanoparticles: synthesis, protection, functionalization and applications. *Angew Chem Int Ed Engl* 2007, 46:1222.
3. Cornell RM, Schwertmann U: *The Iron Oxides. Structure, Properties, Reactions, Occurrences and Uses* Weinheim: Wiley-VCH; 2003.
4. Hsu WP, Matijevic E: Optical properties of monodisperse hematite hydrosols. *Appl Optics* 1985, 24:1623.
5. Chinta M, Grozescu I: Fe2O3-nanoparticles, physical properties and their photochemical applications. *Chem Bull Polytechnica Univ Timisoara* 2009, 54:1.
6. Eggleston CM: Toward new uses for hematite. *Science* 2008, 320:184.
7. Hu X, Yu JC: Continuous aspect-ratio tuning and fine-shape control of monodisperse α-Fe2O3 nanocrystals by a programmed microwave-hydrothermal method. *Adv Funct Mater* 2008, 18:880.
8. Wu W, He Q, Jiang C: Magnetic iron oxide nanoparticles: synthesis and surface functionalization strategies. *Nanoscale* 2008, 3:397.
9. Tartaj P, Del Puerto Morales MS, Veenenmillas-Verdaguer T, Gonzales-Carrero C, Sema J: The preparation of magnetic nanoparticles for applications in biomedicine. *J Phys D: Appl Phys* 2003, 36:R182.
10. Glotzer SC, Solomon MJ: Anisotropy of building blocks and their assembly into complex structures. *Nat Mater* 2007, 6:557.
11. Yang SH, Kim SH, Lim JM, Yi GR: Synthesis and assembly of structured colloidal particles. *J Mater Chem* 2008, 18:2177.
12. Wang H, Brandi DW, Le F, Nordlander P, Halas NJ: Nanorice: a hybrid plasmonic structure. *Nano Lett* 2006, 6:827.
13. Sacanna S, Rossi L, Kupers BM, Philips AP: Fluorescent monodisperse silica ellipsoids for optical rotational diffusion studies. *Langmuir* 2006, 22:1832.
14. Lou XW, Archer LA: A general route to non-spherical anatase TiO2 hollow colloids and magnetic multifunctional particles. *Adv Mater* 2008, 20:2008.
15. Xuan S, Fang Q, Hao L, Jiang W, Gong X, Hu Y, Chen Z: Fabrication of spindle Fe2O3/polypyrrole core/shell particles by surface-modified hematite templating and conversion to spindle polypyrrole capsules and carbon capsules. *J Colloid Interface Sci* 2007, 314:502.
16. Rives V, EdB: Layered Double Hydroxides: Present and Future. *New York: Science Publishers;* 2003.
17. Zhang H, Qi R, Evans DG, Duan X: Synthesis and characterization of a novel nano-scale magnetic solid base catalyst involving a layered double hydroxide supported on a ferrite core. *J Solid State Chem* 2004, 177:772.
18. Li J, Feng Y, Li Y, Zhao W, Shi J: Fe2O3 core/layered double hydroxide shell nanocomposite: versatile magnetic matrix for anionic functional materials. *Angew Chem* 2009, 121:6002.
19. Zhang H, Zou K, Sun H, Duan X: A magnetic organic-inorganic composite: synthesis and characterization of magnetic 5-aminosalicylic acid intercalated layered double hydroxides. *J Solid State Chem* 2005, 178:3485.
20. Carja G, Chiriac H, Lupu N: New magnetic organic-inorganic composites based on hydrotalcite-like anionic clays for drug delivery. *J Magn Magn Mater* 2007, 311:26.
21. Zhang H, Pan D, Zou K, He J, Duan X: A novel core-shell structured magnetic organic-inorganic nanohybrid involving drug-intercalated layered double hydroxides coated on a magnesium ferrite core for magnetically controlled drug release. J Mater Chem 2009, 19:3069.

22. Ay AN, Zümreoglu-Karan B, Temel A, Rives V: Bioinorganic magnetic nanocomposites carrying anti-arthritic agents: intercalation of ibuprofen and glucuronic acid into Mg-Al-layered double hydroxides supported on magnesium ferrite. Inorg Chem 2009, 48:8871.

23. Namduri H, Nasrazadani S: Quantitative analysis of iron oxides using Fourier transform infrared spectrophotometry. Corros Sci 2008, 50:2493.

24. Higgs GA, Salmon JA, Henderson B, Vane JR: Pharmacokinetics of aspirin and salicylate in relation of inhibition arachidonate cyclooxygenase and anti-inflammatory activity. Proc Natl Acad Sci USA 1987, 84:1417.

25. Jiles DC: Introduction to Magnetism and Magnetic Materials. 2 edition. New York: Chapman & Hall; 1998.

26. Fan HM, You GJ, Li Y, Zheng Z, Tan HR, Shen ZX, Tang SH, Feng YP: Shape-controlled synthesis of single-crystalline Fe2O3 hollow nanocrystals and their tunable optical properties. J Phys Chem C 2009, 113:9928.

27. Sivula K, Zboril R, Le Formal F, Robert R, Weidenkaff A, Tucek J, Frydrych J, Gratzel M: Photoelectrochemical water splitting with mesoporous hematite prepared by a solution based colloidal approach. J Am Chem Soc 2010, 132:7436.

28. Champion JA, Mitragotri S: Role of target geometry in phagocytosis. Proc Natl Acad Sci USA 2006, 103:4939.

doi:10.1186/1556-276X-6-116
Cite this article as: Nedim Ay et al: Prolate spheroidal hematite particles equatorially belt with drug-carrying layered double hydroxide disks: Ring Nebula-like nanocomposites. Nanoscale Research Letters 2011 6:116.