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Supporting Information

Ultrathin Silica-Coated Iron Oxide Nanoparticles: Size-Property Correlation

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SUPPORTING INFORMATION

Materials and Methods. All chemicals used in this study were purchased from Sigma Aldrich. DLS characterizations (diameter and zeta potential) were performed in water using Malvern Zetasizer Nano. For TEM, Hitachi HF-8100 Transmission Electron Microscope (TEM) was used. The size distribution was determined by the statistical averaging using Digital Micrograph 3.4. SQUID analyzer (Quantum Design, MPMS, San Diego, CA) was used to obtain the hysteresis of the samples at room temperature with the applied external field ranging from -2 Tesla to 2 Tesla. To measure transverse (T_1) and longitudinal (T_2) relaxation time, 1.41 T (60 MHz) Bruker mq 60 NMR analyzer with the Minispec V2.51 Rev.00/NT software (Billerica, MA) was used. Carr-Purcell-Meiboom-Gill (CPMG) and spin-echo pulse sequences were used to measure transverse relaxation times and inversion-recovery pulse sequence was used to measure the longitudinal relaxation times at 37 ^{o}C.

Synthesis of MNSs. Iron oxide nanoparticle of different sizes were synthesized using the method reported by Park et al., with some modification.[1] According to that method, first iron-oleate complex was prepared followed by its thermal decomposition at elevated temperature using high boiling point solvents over various time spans yielding different size iron oxide nanoparticle. In brief, approximately 30 g Iron oleate complex was prepared by dissolving 10.8 g of Iron Chloride Hexahydrate ($FeCl_3.6H_2O$) and 36.5 g Sodium oleate ($C_{18}H_{33}O_2Na$) in 80 ml ethanol, 60 ml of water and 140 ml of hexane followed by reflux at 60 °C for 4 hours. After the reaction, iron oleate complex being soluble in hexane is extracted in it, dehydrated (by Na_2SO_4) and hexane is evaporated, giving a black waxy liquid. To obtain different sized MNSs, 5 g of iron oleate complex and 600 mg of oleic acid were dissolve in 50 g of octadecene and the reaction mixture was heated at 320^{o}C for variable time. For 9 nm, 12 nm, 16 nm, 20 nm MNSs the solution was heated for 25 min, 35 min, 45 min and 1hr respectively. After the reaction, oleate stabilized MNSs were purified by precipitation with ethanol subsequently separated by permanent magnet. The 7 nm MNS was prepared by using the synthesis protocol as directed by Xu et al, with minor modifications.[2] Approximately 3 mmol $Fe(acac)_3$ complex was dissolved in 15 mL of olaylamine. Then this solution was dehydrated at about 110^{O}C for 1 hr, under inert nitrogen atmosphere.

This was followed by quick heating up to 300^{O}C for another 1 hr. When the reaction is complete, it was cooled down to room temperature. The nanoparticles were extracted under 50 mL ethanol followed by centrifugation, and was stored under nonpolar solvent hexane.

Phase transfer of MNSs. Hexane soluble MNSs was phase transferred to water using octahedral silica compound POSS or Octakis(tetramethylammonium) pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane-1,3,5,7,11,13,15-octakis(yloxide) hydrate. Stoichiometrically, 50 mg of each of the synthesized MNSs in hexane, was added with 500 mg of POSS and the mixture was stirred vigorously for 24 h. For separation of the two layers of solvent, excess of hexanes was added to the mixture. Aqueous layer was collected and dialyzed against distilled water to remove free excess POSS. The concentration of MNSs were measured by ICP-AES by estimating the concentration of iron.

[1] J. Park, K. An, Y. Hwang, J.G. Park, H.J. Noh, J.Y. Kim, J.H. Park, N.M. Hwang, T. Hyeon, *Nat. Mater.* **2004**, *3*, 891.

[2] Z. Xu, C. Shen, Y. Hou, H. Gao, S. Sun, *Chem. Mater.* **2009,** *21*, 1778-1780.