BNL-213511-2020-JAAM

Water as the Solvent in the Stober Process for Forming Ultrafine Silica Shells on Magnetite Nanoparticles

P. Furlan, K. Kisslinger

To be published in "ACS SUSTAINABLE CHEMISTRY & ENGINEERING"

August 2019

Center for Functional Nanomaterials

Brookhaven National Laboratory

U.S. Department of Energy

USDOE Office of Science (SC), Basic Energy Sciences (BES) (SC-22)

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Water as the Solvent in Stober Process for Forming Ultrafine Silica Shells on Magnetite Nanoparticles

Ping Y. Furlan[†], Alexander Y. Furlan[†], Kim Kisslinger[‡], Michael E. Melcer[†], David W. Shinn[†], John B. Warren[‡]*

† Math & Science Department, United States Merchant Marine Academy, 300 Steamboat Road, Kings Point, New York 11024, United States

‡ Center for Functional Nanomaterials, Brookhaven National Laboratory, 735 Brookhaven Avenue, Upton, New York 11973, United States

*Email: Furlanp@usmma.edu

KEYWORDS

Magnetite, oxidation, thin silica shell, Stober, core-shell, magnetic, green solvent

ABSTRACT: Silica coating of magnetite nanoparticles (MNPs) is of great importance since it offers MNPs stability against oxidation, water dispersity, and a tailorable surface for functionalities, allowing a wide range of applications in areas such as water pollutant removal and targeted drug delivery. In this work, a simple and green procedure has been developed using water, instead of traditional alcohols, as the solvent in the Stober method to produce well-dispersed MNPs coated with ultrathin (< 5 nm) silica outer shells. The resultant core-shell structures possess superparamagnetic properties, high magnetization value of 59 emu/g, and excellent resistance to oxidation when exposed to ultrasonic accelerated oxidation. The oxidation stability of the coated

MNPs is shown to extend to their functionalized product. All syntheses are carried out under ambient conditions using commonly available chemicals and equipment. The Fe_3O_4@SiO_2 core-shell structures are characterized using FTIR-ATR spectroscopy, Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDS), and a Vibrating Sample Magnetometer (VSM).

INTRODUCTION

In recent years, extensive research has been centered on the preparation of superparamagnetic nanoparticles due to their immense technological applications. Examples include their potential use as an effective tool for magnetically assisted water pollutant removal, biochemical sensing, NMR imaging, and targeted drug delivery.[1-3] Across the realm of known superparamagnetic particles, magnetite (Fe_3O_4) nanoparticles (MNPs) have received the greatest attention due to their unique magnetic properties and ease of preparation.[4-8] Since iron(II) ions are highly susceptible to oxidation, magnetite is readily transformed to the much less magnetic goethite, FeO(OH), and/or iron(III) oxide, Fe_2O_3, in the presence of oxygen, greatly reducing MNPs' responsiveness to magnetic fields. A protective coating is thus essential for the successful incorporation of MNPs in many medical and environmental applications which often associate with oxidative aqueous environments.

Among the available coatings, silica has proven ideal since it not only offers chemical stability and biocompatibility to the dispersed superparamagnetic MNPs but also sites for surface functionalization with a wide range of chemicals, organic and inorganic alike, due to its Si-OH rich surface. Among the known methods of coating MPNs with silica, Stober's sol-gel method has been adopted most widely for its advantages including relatively mild reaction conditions, thinner

coating results, low cost, and ease of synthesis.[9-12] The Stober-based methods employ alcohols as the solvent for the synthesis and relies on the use of tetraethyl orthosilicate (TEOS) as the silica source. The molecular precursor TEOS first reacts with water in an alcoholic solution to form silanol groups. The resulting molecules combine via condensation, either between the silanol groups or between the silanol groups and ethoxy groups, creating siloxane bridges (Si–O–Si) that produce the silica-network structure, effectively encapsulating MNPs. Ammonia works as a basic catalyst in this reaction; the hydrolysis is initiated by the attacks of hydroxyl anions on TEOS molecules. The general reactions of TEOS that lead to the formation of silica can be written as[13]:

Hydrolysis: $Si(OC_2H_5)_4 + H_2O \rightarrow Si(OC_2H_5)_3OH + C_2H_5OH$ [1]

Water condensation: $\equiv Si{-}O{-}H + H{-}O{-}Si\equiv \rightarrow \equiv Si{-}O{-}Si\equiv + H_2O$ [2]

Alcohol condensation: $\equiv Si{-}OC_2H_5 + H{-}O{-}Si\equiv \rightarrow \equiv Si{-}O{-}Si\equiv + C_2H_5OH$ [3]

Most papers have adopted the Stober process with varied concentrations in different alcohols and/or varied temperatures to control the formation of silica-coated MNPs in terms of coating thickness, morphology, and size of the particles produced. Some require anhydrous alcohol and others introduce binding agents or surfactants such as polyvinyl pyrolidone (PVP) to MNPs prior to silica coating to improve the MNPs' stability in alcohol.[9-10] Most of these procedures still produce relatively thick silica shells with thicknesses greater than 5-10 nm, resulting in somewhat large particles that may limit their potential functionalities, especially in biomedical fields.[5] Lu *et al.*[11] coated MNPs with silica at 40 ^{o}C by adding MNPs at the appropriate time during the hydrolysis and condensation of TEOS, and obtained 5-nm coatings 30 seconds after the MNPs were introduced to the Stober process; the coating thickness, however, increased in time and reached 80 nm in 12 h. Abbas *et al.*[9] reported an attractive approach using a PVP pre-coating step and absolute alcohol that yielded 5-nm shell thicknesses. Wang *et al.*[12] also reported a method for

coating 5-nm silica shells on MNPs which required pre-stabilization of the MNPs with tetramethylammonium hydroxide (TMA) and large quantities of alcohol. For instance, coating 1 g of MNPs required more than 14 liters of alcohol. Wang *et al.* investigated effects of alcohol types and reported that only particles produced in methanol yielded the thinnest 5-nm silica coating. As the carbon chain of the alcohol became longer, particle agglomeration increased. 1-butanol resulted in heavily agglomerated particles with thick silica coatings. Deng *et al.*[14] reported silica thicknesses of ~12 nm on MNPs by using ethanol, and with the decrease of alcohol polarity (i.e., from methanol to ethanol to isopropanol to propanol), the morphology of the silica-coated MNPs became more irregular, even resulting in large clusters of silica-coated magnetite particles. In Wang and Deng's reports, the polarity of the reaction media was found to affect the zeta potential of the MNPs: MNPs with higher zeta potential in more polar media would disperse more readily, favoring the formation of silica-coated MNPs exhibiting more regular morphology. This agreed with Stober's early research[15] which showed that high polarity of the reaction media slowed down the condensation rates and led to small silica particle formation. These trends suggest that the use of the most polar protic solvent, water, in the Stober process, may allow the most consistent dispersion of MNPs in the reaction media and the slowest condensation rates of TEOS, favoring the formation of ultrafine, or < 5 nm thick, silica coatings on MNPs.

In this work we demonstrate, for the first time, the use of water instead of alcohol in the Stober process to achieve a uniform sub-5-nm thick silica coating on MNPs. Considering the solvent is a major component of the reaction, replacing flammable, toxic, and more expensive alcohols (especially methanol) with water, the first-choice green solvent, allows the popular Stober process to be much cheaper, safer, easier to operate, and more eco-friendly. Additionally, the proposed procedure does not require the use of absolute alcohol, surfactants, and/or elevated

temperatures, thus further enhancing the operation by reducing the cost, reaction time, energy consumption, and environmental impact, all important when large-scale production is involved.

EXPERIMENTAL SECTION

Chemicals. Concentrated hydrochloric acid (HCl, 36.5-38.0%), iron(II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), concentrated ammonia (NH_3, 26-30%), and ethanol (90-95% ethanol, denatured) were purchased from VWR International (Radnor, PA, USA). Tetraethyl orthosilicate (TEOS) and polyvinyl pyrolidone (PVP, MW=50,000) were purchased from Aesar (Haverhill, MA, USA) and neodymium magnets from Applied Magnets (Plano, TX, USA). All chemicals were used as received without any further purification and all syntheses were carried out under ambient conditions.

Synthesis of Fe_3O_4 nanoparticles. The synthesis of MNPs was done based on our previous reported work.[6-8] Briefly, 40 mL of 1.0 M $FeCl_3$ was mixed with 10 mL of 2.0 M $FeCl_2$ (both solutions were prepared from the corresponding hydrate salts). While stirring, 350 mL of 1.4 M NH_3 or NH_4OH was added dropwise over 5-8 min to the mixture. The as-synthesized MNPs were washed with deionized water 3 times, collected with a magnet and dried at 60 ^oC for 1 h.

Synthesis of Fe_3O_4@SiO_2 core-shell structures. The MNPs were coated with silica using the modified Stober method. In particular, water was used as the solvent by replacing the traditional alcoholic reaction media. Since the molecular precursor, tetraethyl orthosilicate (TEOS), has a very limited solubility in water, a small amount of ethanol may be used to help better disperse it in water, leading to its more frequent interaction with Fe_3O_4 nanoparticles. For a typical synthesis, 0.100 g of MNPs was added to 100 mL of deionized water, followed by adding 5 mL of concentrated NH_3 that results in a mixture having a pH of 11. 2 mL of tetraethyl orthosilicate

(TEOS), dissolved in 2 mL of ethanol (optional), was then added to the mixture. The dispersion was homogenized during the first hour by alternating between manual shaking for 10-20 min, followed by a brief sonication for 3-10 s. After this, the reaction was allowed to continue for 24 h in a shaker shaking at 250 rpm. The product was washed with deionized water several times, collected with a magnet and dried at 60 ^{o}C for 1 h. If not indicated, the results in this manuscript are based on the optional use of 2 mL ethanol for the dissolution of TEOS. These results are later compared to those without using ethanol in the discussion section.

Characterization of Fe_3O_4@SiO_2 core-shell structures. The as-prepared samples were investigated via Fourier transform infrared spectroscopy (FT-IR; Bruker Alpha II Platinum spectrometer) using the ATR accessory equipped with a single reflection diamond crystal. Spectra were collected at a resolution of 4 cm^{-1} with 24 scans from 400 to 4000 cm^{-1}. Particle sizes and morphology were characterized via transmission electron microscopy (TEM), with the images obtained through a JOEL 1400 TEM operated at 120 kV, after diluted dispersions of the particles were dropped onto 200-mesh carbon-coated copper grids. The chemical compositions of the samples were analyzed by energy-dispersive X-ray spectroscopy (EDS) which was coupled with the TEM. The elemental maps of the samples were also obtained by scanning electron microscopy (SEM; Coxem CX-Plus 200) - EDS using the Aztec Live model by Oxford. The samples for SEM were prepared by dropping dilute dispersions of the particles on pieces of carbon tap attached to aluminum stabs and allowing the particles to dry. The images taken for EDS were at a 15 cm working distance using 15 kV. A vibrating-sample magnetometer (VSM; Tech Weistron) was used with an applied field between -10 MG to +10 MG at room temperature to study the magnetic properties of both the MNPs and silica-coated MNPs.

Oxidation Stability Test. The oxidative stability of the samples was evaluated using an ultrasonic-accelerated oxidation method. In a typical procedure, 0.050 g of the magnetic particles were mixed with 10 mL of deionized water in a 50-mL beaker. The beaker was then placed in a sonicator and sonication was carried out at room temperature for selected periods of time.

RESULTS AND DISCUSSION

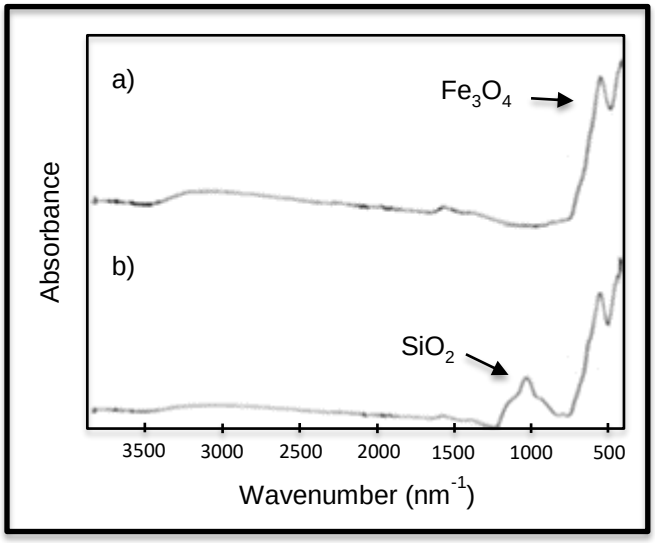


Figure 1. FTIR Spectra of a) as synthesized Fe_3O_4 nanoparticles; b) the Fe_3O_4@SiO_2 nanocomposite.

Characterization of Fe_3O_4@SiO_2 core-shell structures. The procedure for making Fe_3O_4@SiO_2 nanocomposites produced consistent yields. For five repeated trials, the mass conversions from 0.100±0.002 g MNPs yielded 0.120±0.002 g Fe_3O_4@SiO_2. Figure 1 shows the FTIR-ATR spectra of MNPs and Fe_3O_4@SiO_2. The absorption peak at around 540 cm^{-1} is assigned to the Fe-O vibration,[9] a characteristic peak of Fe_3O_4 and observed for both samples. A broad band at around 1060 cm^{-1} with a visible high-frequency shoulder at around 1160 cm^{-1} appeared in the spectrum of Fe_3O_4@SiO_2. Assigned to the asymmetric Si-O-Si bond vibration,[9] these bands provided

spectroscopic evidence for the presence of SiO_2 component which contains the Si-O-Si linkages and, thus, evidence for the formation of Fe_3O_4@SiO_2 core-shell structures. The additional absorption peaks at around 900 cm^{-1} were assigned to the stretching vibrations of Si-OH.[9]

The structural morphology of the nanomaterials was observed through TEM with 120 kV e-beams and the elemental analysis was performed using EDS (Figure 2). Figure 2a is the TEM image of the as-synthesized MNPs, which had well-defined spherical shapes of sizes ranging from 5-40 nm. Figure 2b shows the spatial distributions of the elements iron (red) and oxygen (purple) in a micro-sized particle, which resulted from nanoparticle aggregation. The elemental analysis gave the formula of $Fe_{3.0}O_{3.9}$, agreeing well with the expected Fe_3O_4 formula for magnetite. As shown in Figure 2c, the TEM image confirmed that the silica was successfully coated onto MNPs to form core-shell nanostructures, which could be clearly identified by the two different contrasts observed for MNP (dark) and silica (light). The procedure successfully produced relatively uniform silica shells of 2-4 nm in thickness, resulting in core-shell structures of 10-50 nm. The element mapping of several micro-sized aggregates, as shown in Figure 2d, clearly illustrated the presence of silicon (blue), in addition to iron and oxygen. In particular, the spatial distribution of Si matches that of Fe and O, providing direct evidence that the silicon is homogeneously coated onto the MNPs. This coating gives rise to the product's resistance to oxidation.

The magnetic behavior of the synthesized MNPs and the silica-coated MNPs are shown in Figure 3. The measurements were conducted at room temperature using a Vibrating Sample Magnetometer (VSM) in an external magnetic field ranging from -10 MG to +10 MG. The magnetization versus applied field curves showed no hysteresis and was completely reversible at room temperature. Neither coercivity nor remanence were observed, indicating the superparamagnetic nature of both MNPs and silica-coated MNPs. The saturation magnetization

value, M_s, extracted from the corresponding hysteresis loop at ±10 MG for the as-prepared MNPs, was 73 emu/g. The value was decreased to 59 emu/g when a 2-4 nm thick silica layer was coated on the MNPs. This decrease in M_s was attributed to the weight contribution of the nonmagnetic silica shells surrounding the magnetic magnetite cores. The possible formation of chemical bonds such as (Fe-O-Si), as a consequence of surface reactions, may also contribute to the reduction in M_s. The relatively high magnetization value of 59 emu/g reported here is favorable in many applications such as water pollutant removal and targeted drug delivery which require high magnetic moments for easy control and manipulation.

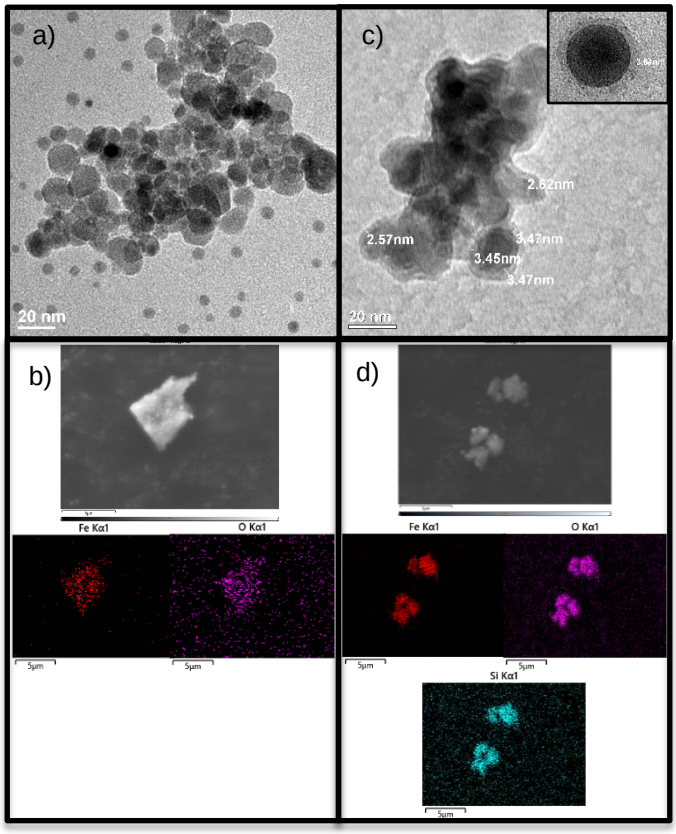


Figure 2. a) TEM image of the as-synthesized Fe_3O_4 nanoparticles; b) SEM image and EDS element maps of the as-synthesized Fe_3O_4 nanoparticles; c) TEM images of the Fe_3O_4@SiO_2 nanocomposite; d) SEM image and EDS element maps of the Fe_3O_4@SiO_2 nanocomposite.

Oxidation Stability Test. Since the oxidation stability of the MNPs-based-nanocomposite is very important for practical applications, the oxidation stability of our nanomaterials in water was investigated. We employed an ultrasonic-accelerated method in this study since ultrasound is known to considerably accelerate oxidation of various organic and inorganic systems, including oxidizing magnetite to the much less magnetic goethite, the main component of rust, in water.[16,17] The enhanced and accelerated oxidation is attributed to the oxygen within the ultrasonic cavitation bubbles being highly activated during the collapse of these bubbles.[17] The accelerated oxidation tests were carried out by sonicating 50 mg of the uncoated MNPs and 50 mg of the coated MNPs (Fe_3O_4@SiO_2), in 10 mL of deionized water for up to 60 min. The uncoated MNPs, after being sonicated in water for 1 min, were found to be much less responsive to a magnet, while the silica-coated MNPs demonstrated an unaltered response to the magnet, even after 60 min of sonication. Figure 4a shows the results of the accelerated oxidation tests of these samples after 1 min and 60 min of sonication at room temperature. While the solution containing silica-coated MNPs turned clear immediately after being placed on a magnet, the one containing uncoated, native MNPs was reddish brown, and the color darkened more if the native MNPs were exposed to longer sonication. The reddish brown color was associated with iron(III) oxide or goethite particles, or oxidation products of magnetite.[17] Figure 4a also shows the photos of the recovered MNPs and the silica coated MNPs after undergoing 5 days of sonication. The color of the MNPs visibly changed to reddish brown while that of the silica-coated MNPs remained distinctly black with metallic luster. It was clearly evident that the silica coating greatly enhanced the stability of the MNPs by preventing them from being oxidized by the dissolved oxygen in water.

The oxidation stability successfully extended to other functionalized products. As an example, the magnetic core-shell structure was functionalized by adding a silver coating to the

silica shell, then covering the silver with another silica shell, only this time, with meso-sized channels. The product, referred to as Fe_3O_4@SiO_2@Ag@mSiO_2, was designed for effective water disinfection while controlling the release of silver, the antimicrobial agent, at levels less than the 0.1 ppm recommended by the Environmental Protection Agency (EPA). As shown in Figure 4b, the magnetic responsiveness of this final product remained strong after being sonicated for 100 min: the nanocomposites, initially well-dispersed in water, instantaneously attracted to the magnet that was brought near to their solution, following the motion of the magnet and moving up out of the water solution, leaving the solution clear and transparent within a few seconds. When the magnet was removed, the nanocomposite particles were easily re-dispersed with light agitation. This work will be described in a later paper.

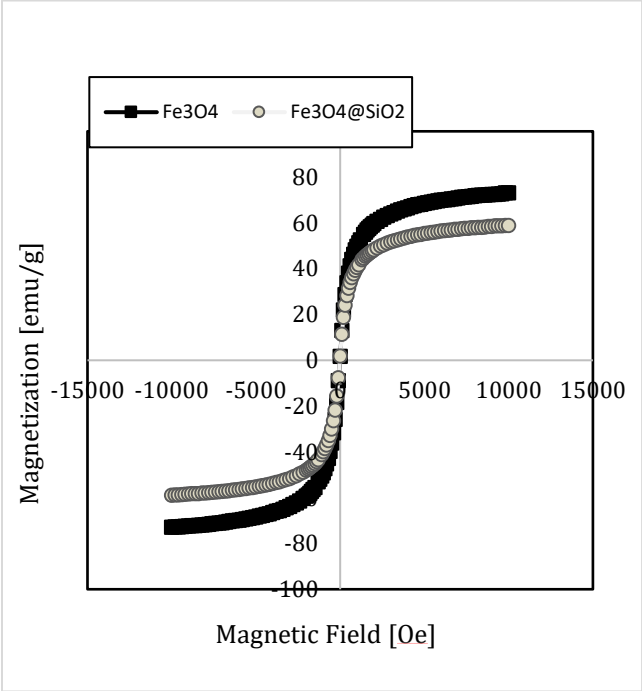


Figure 3. The magnetization curves for both Fe_3O_4 nanoparticles and Fe_3O_4@SiO_2 nanocomposite measured using a Vibrating Sample Magnetometer (VSM) at room temperature.

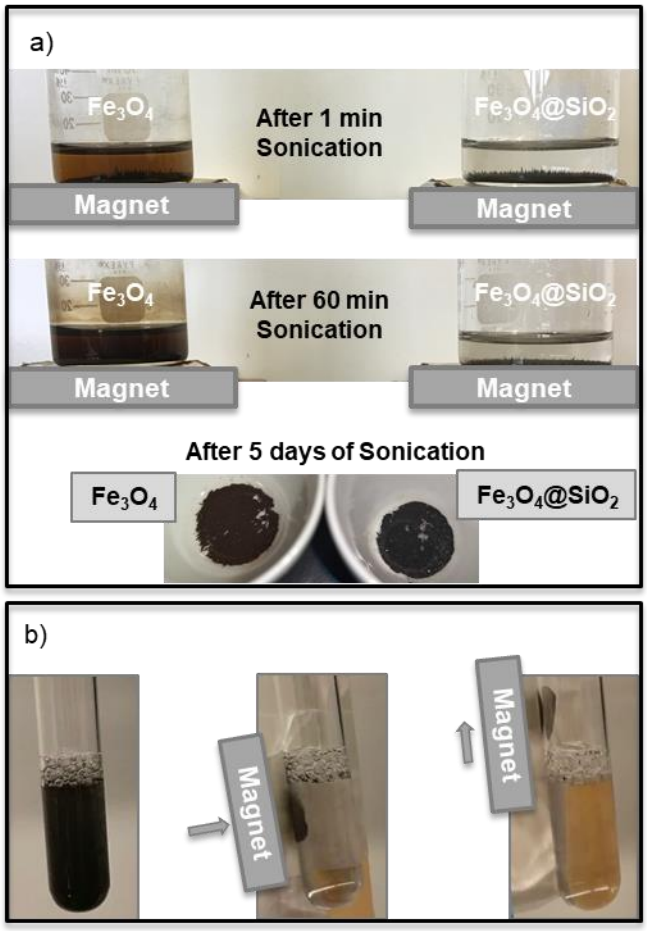


Figure 4. a) Results of the accelerated oxidation test: after being sonicated in water for 1 min and 60 min, respectively, the MNPs control (left) became much less responsive to a magnet under the beaker, while the Fe_3O_4@SiO_2 nanocomposites (right) demonstrated an instantaneous and unaltered response to the magnet. After 5 days of sonication, the color of the recovered MNPs changed to reddish brown, a color associated with iron(III) oxide or goethite, while that of the silica-coated MNPs remained distinctly black with metallic luster. b) The magnetic responsiveness of Fe_3O_4@SiO_2@Ag@mSiO_2 nanocomposites remain strong after being sonicated for 100 min.

Synthesis Conditions. In this study, we investigated several reaction parameters including using a) polyvinyl pyrrolidone (PVP) vs. non-PVP stabilization prior to coating silica on MNPs, b) ethanol vs. water as the solvent, c) shaker vs. magnetic stirring during the reactions, and d) the reaction time on the quality of the process based on 1) how well the as-prepared Fe_3O_4@SiO_2 core-shell structures resist sonication-induced oxidation; 2) the amount of colloidal SiO_2 remaining in the final reaction mixture; and 3) the apparent reaction yield.

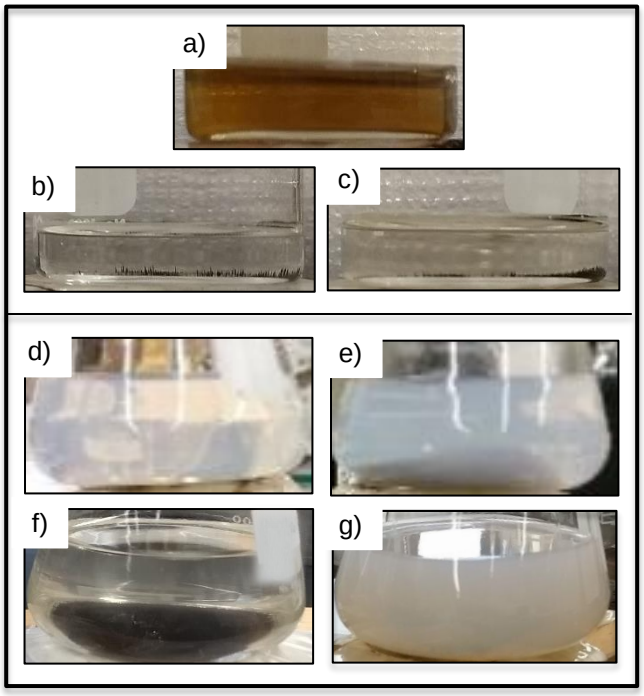


Figure 5. The response of the magnetic particles to a magnet in water after being sonicated in water for 45 min: a) the uncoated MNPs, the as-prepared Fe_3O_4@SiO_2 using PVP stabilization with b) water or c) ethanol as the solvent. The amount of colloidal SiO_2 left in the final reaction mixtures using d) water as solvent with PVP stabilization; e) ethanol as solvent with PVP stabilization; f) water as solvent without PVP stabilization; and g) ethanol as solvent without PVP. Observations were made immediately after the solution was placed on top of a magnet.

PVP stabilization was done by preparing Solutions A and B: Solution A was prepared by mixing 4 g of PVP with 55 mL of deionized water for 5 min using a magnetic stirrer; Solution B by mixing 0.100 g MNPs with 15 mL of deionized water for 5 min. Both Solutions A and B were then mixed together using a magnetic stirrer for 2 h. After this, the mixture was separated magnetically and the resultant PVP-stabilized MNPs were introduced to 100 mL of water, if water was used as the solvent, or 100 mL of ethanol, if ethanol was the solvent. The ammonia and the TEOS dissolved in ethanol were added to the reaction mixture as in a typical procedure, and the reaction mixture was mixed either in a shaker (250 rpm) or using a magnetic stirrer for 24 h.

Mixing the reactants using a magnetic stirrer, regardless of the solvent used or PVP or non-PVP stabilization involved, resulted in the least magnetically responsive particles and also yielded the characteristic reddish-brown rust or iron (III) oxide color. This was due to the fact that a large amount of the MNPs were naturally attracted and attached to the magnetic bar during stirring. A high percentage of the particles were likely not coated or only partially coated by the silica and their prolonged exposure to the dissolved oxygen in the reaction media resulted in pronounced oxidation.

Table 1. Yields from coating 0.100 g MNPs using a) PVP vs. Non-PVP as a stabilizer and b) ethanol vs. water as the solvent

	Ethanol	Water	% Increase
PVP	0.051 g	0.078 g	53
Non-PVP	0.101 g	0.120 g	19

The Fe_3O_4@SiO_2 nanocomposites prepared using either water or ethanol as the solvent, or with PVP or without PVP stabilization, all yielded magnetically responsive particles, and all demonstrated dramatic improvement in resistance to sonication-induced oxidation relative to the native MNPs. However, slightly better resistance to oxidation was observed when water was used as the solvent. Figures 5a-c show the response of the magnetic particles to a magnet after being sonicated in water for 45 min for the uncoated MNPs, and the as-prepared Fe_3O_4@SiO_2 using PVP stabilizer with either water or ethanol as the solvent. It can be seen that the solution containing the coated MNPs prepared in water turned clear immediately after being placed on a magnet, while the one containing the coated MNPs prepared in ethanol remained slightly reddish-brown: both were markedly clearer than the solution containing the uncoated, native MNPs.

The solvent choice was found to greatly affect the amount of colloidal SiO_2 left in the final reaction mixtures and the reaction yields, as shown in Figures 5d-g and Table 1. When ethanol was employed as the solvent, whether PVP stabilizer was used or not, a larger amount of colloidal silica remained in the solution, as evidenced by the increased turbidity. This indicated that substantial amount of silica could not form around the MNPs, possibly due to the poor dispersion of the MNPs in the less polar solvent ethanol, leading to the formation of irregular silica-coated aggregates of MNPs[14] as well as colloidal silica as a stand-alone product. In contrast, the greater polarity of water not only allowed the MNPs to disperse in the reaction media more readily, but also facilitated a slow condensation rate of TEOS to allow an effective and uniform silica coating on the MNPs. The greater dispersion of the MNPs in water also produced a larger total particle surface per volume relative to the TEOS amount, encouraging the silica growth on the surface of the MNPs that greatly suppressed the formation of the separate silica colloids.

Water as an optimal reaction media was further supported by the reaction yields. For coating 0.100 g MNPs, the yields of Fe_3O_4@SiO_2 increased ranging from 20% to 50% when reaction occurred in water relative to ethanol, depending on whether the PVP stabilizer was used, as shown in Table 1. The barely noticeable reddish-brown color of the aqueous reaction solution in Figure 5f was likely due to early oxidation of the MNPs during the brief sonication periods employed to promote uniform dispersion. This oxidation may be minimized if oxygen is first removed from the water solvent and the sonication is carried out in an inert environment.

Many procedures in the literature utilized a thin layer such as PVP to improve the dispersion of the MNPs in alcohol where the classical Stober process was performed.[9] In our work, the extra 2 h employed for adsorbing PVP onto MNPs prior to silica coating did not seem to improve the dispersion of the MNPs in the reaction media, whether in water or alcohol, since the

amount of colloidal SiO_2 left in the final reaction mixture did not seem to be reduced as shown in Figures 5d-g. On the other hand, the 2 h of PVP coating in aqueous environment resulted in the loss of magnetic particles due to oxidation, causing reduced and inconsistent product yields. As shown in Table 1, the reduction in yield ranged from 35% in water and 50% in ethanol when employing PVP stabilization. Our different results may be due to the fact that we used PVP with a molecular weight of 50,000 while others in the literature with 40,000 or less. The longer PVP chains may have produced partial coatings and irregular coating thicknesses, making the MNPs vulnerable to oxidation and difficult for silica shell to grow on them.

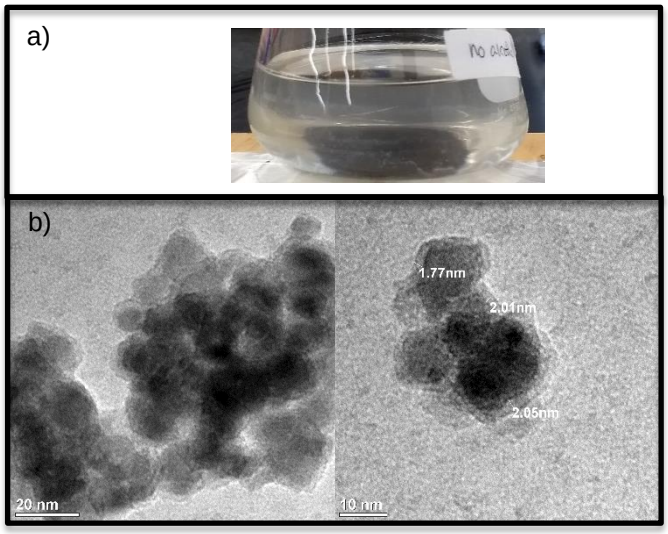


Figure 6. a) The amount of colloidal SiO_2 left in the final reaction mixture using water as solvent with no use of alcohol or PVP stabilizer. Observation was made immediately after the solution was placed on top of a magnet. b) TEM images of the Fe_3O_4@SiO_2 core-shell nanocomposite prepared with no ethanol or PVP stabilizer.

The effect of reaction time from 2 h to 24 h was also investigated. Although the initial magnetic response of all products appeared similar, the ones prepared in 6 h or less became noticeably less magnetic after 5 min of sonication. This suggests that the silica coating detached upon vibration due to incomplete condensation and poor mechanical stability associated with the

short segments rather than an entire silica network structure. The products prepared in 18 h or longer, however, remained magnetic after much longer sonication. This indicates at least 18 h were needed to achieve a desirable degree of condensation.

The results above are based on the optional use of 2 mL ethanol which helps TEOS better disperse in water. The effect of the 2 mL of ethanol was investigated by repeating the synthetic procedure without the use of any alcohol and repeating the testing and characterization procedures on the resultant product. Some of the results are shown in Figures 6a-b. Comparing to the suspension in Figure 5f (with 2 mL ethanol), the suspension in Figure 6a (without using ethanol) is slightly cloudier, indicating a slightly greater amount of colloidal silica remaining in the final reaction mixture. As expected, the small amount of ethanol facilitated a better interaction between the MNPs and the TEOS and promoted the silica growth on the MNP surface, rather than as a separate product. Since slightly more silica particles were left behind free from the magnetic nanocomposite, the reaction yield and the silica amount were expected to be slightly less for the product prepared with no ethanol, which agreed with the observed results: the yield was found to be about 1% less than that prepared with ethanol, and the silica coating thickness, as revealed by the TEM results shown in Figure 6b, was slightly thinner, 1.5-3 nm (without ethanol) vs. 2-4 nm (with ethanol). Most importantly, the silica coating remained uniform, as shown in Figure 6b, even when ethanol was not used. Equally important, the product prepared without ethanol demonstrated the same level of superior resistance to sonication-induced oxidation.

Biomimetic Method. Biomimetics is an approach to innovation that seeks sustainable solutions to human challenges by emulating nature's time-tested patterns and strategies. In recent years, a mild method was reported for coating nanoparticles including MNPs with silica shells by imitating biosilicification found in diatoms and glass sponges.[18] The naturally-occurring silica structures

occur under ambient conditions at slightly acidic pH values and the process is considered to be "green" since no harsh chemical or high temperatures are needed. However, to prepare and convert nanoparticle systems to conditions so they can simulate the naturally-occurring, silica-forming peptides and thus biosilicification can occur requires the use of multiple steps, complicated procedures, sophisticated equipment, and at least 12 organic chemical reagents including solvents such as dimethylformamide (DMF), methylene chloride, methanol, and hexane. Since MNPs are more stable in basic environments and tend to dissolve or oxidize in acidic media, the biosilicification conditions may also not be ideal to preserve the structural integrity of MNPs before coating occurs. Our approach here therefore represents a remarkable success for converting the age-old Stober method into a more sustainable process.

CONCLUSION

We have replaced alcohol with water, Earth's greenest solvent, in the Stober process, and successfully formed uniform, ultrafine, 1.5-4 nm silica shells on magnetite nanoparticles. The resultant Fe_3O_4@SiO_2 core-shell structures have demonstrated superparamagnetic properties, high magnetization of 59 emu/g, and excellent resistance to oxidation when exposed to ultrasonic accelerated oxidation. The oxidation stability of the coated MNPs is shown to extend to their functionalized products as well. Unlike other Stober approaches, our eco-friendly method also requires no absolute alcohol, no stabilizers, and no elevated temperatures; hence, it provides substantial advantages in terms of simplicity, safety, time, energy, material cost, and environmental impact.

AUTHOR INFORMATION

Corresponding Author

*furlanp@usmma.edu

Present Addresses

†AYF's current address: 8000 York Rd, Towson, MD 21252

Author Contributions

PYF and AYF conceived and designed the experiments. AYF and PYF developed the procedures of and performed the synthesis and oxidation stability measurements. DWS and MEM performed FTIR measurements. KK, JBW, and PYF performed transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) experiments. PYF wrote the manuscript. All authors evaluated data, reviewed and approved the manuscript.

Notes

The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results. The authors declare that the views expressed in this article are the authors' own and not those of the U.S. Merchant Marine Academy, the Maritime Administration, the Department of Transportation or the United States government.

ACKNOWLEDGMENT

We acknowledge the Center for Functional Nanomaterials at Brookhaven National Laboratory for supporting the project under the U.S. DOE Contract No. DE-SC0012704. We thank the USMMA Math & Science Department, the Dean's Office, and the Superintendent's Office for their support and encouragement. We also thank Dr. Bright Emenike of SUNY Old Westbury for experimental assistance with FTIR.

REFERENCES

1. Lee, D.; Fatima, H.; Kim, K. Preparation of silica coated magnetic nanoparticles for bioseparation, *J. Nanosci. Nanotechnol*. **2018**, *18* (2), 1414-1418.
2. Andrade, A. L.; Souza, D. M.; Pereira, M. C.; Fabris, J. D.; Domingues, R. Z. Synthesis and characterization of magnetic nanoparticles coated with silica through a sol-gel approach, Cerâmica **2009**, *55*, 420-424.
3. Gupta, N.; Pant, P.; Gupta, C.; Goel, P.; Aain, A.; Anand, S.; Pundir, A. Engineered magnetic nanoparticles as efficient sorbents for wastewater treatment: a review, *Mater. Res. Innov*., **2017** https://doi.org/10.1080/14328917.2017.1334846
4. Hong, R.; Li, J.; Zhang, S.; Li, H.; Zheng, Y.; Ding, J.; Wei, D. Preparation and characterization of silica-coated Fe_3O_4 nanoparticles used as precursor of ferrofluids, *Appl. Surf. Sci.* **2009**, *255*, 3485–3492
5. Foglia, S.; Ledda, M.; Fioretti, D.; Iucci, G.; Papi, M.; Gapellini, G.; Lolli, M. G.; Grimaldi, S.; Rinaldi, M.; Lisi, A. *In vitro* biocompatibility study of sub-5 nm silica-coated magnetic iron oxide fluorescent nanoparticles for potential biomedical application. *Sci. Rep.* **2017**, *7*, 46513; doi: 10.1038/srep46513.
6. Furlan, P.Y.**;** Fisher, A.J.; Furlan, A.Y.; Melcer, M.E.; Shinn, D.W.; Warren, J.B. Magnetically recoverable and reusable antimicrobial nanocomposite based on activated carbon, magnetite nanoparticles, and silver nanoparticles for water disinfection. *Inventions* **2017**, *2*, 10; doi:10.3390/inventions2020010

7. Furlan, P.Y.; Melcer, M.E. Removal of aromatic pollutant surrogate from water by recyclable magnetite-activated nanocomposite: An experiment for general chemistry. *J. Chem. Educ.* **2014**, *91*, 1966–1970.

8. Furlan, P.Y.; Ackerman, B.M.; Melcer, M.E.; Perez, S.E. Reusable magnetic nanocomposite sponges for removing oil from water discharges. *J. Ship Prod. Des.* **2016**, *32*, 1–10.

9. Abbas, M; Torati, S.R.; Lee, C.S.; Rinaldi, C.; Kim, C. Fe_3O_4/SiO_2 core/shell nanocubes: novel coating approach with tunable silica thickness and enhancement in stability and biocompatibility, *J. Nanomed. Nanotechnol.* **2014**, *5* (6), 1-8.

10. Sharafia, Z.; Bakhshib, B.; Javidic, J.; Adrangia, S. Synthesis of silica-coated iron oxide nanoparticles: preventing aggregation without using additives or seed pretreatment *Iran. J. Pharm. Res.* **2018**, *17* (1), 386-395.

11. Lu, Z.; Dai, J.; Song, X.; Wang, G.; Yang, W. Facile synthesis of Fe_3O_4/SiO_2 composite nanoparticles from primary silica particles *Colloids Surf. A Physicochem. Eng. Asp.* **2008**, *317*, 450–456.

12. Wang, H.; Nakamura, H.; Yao, K.; Maeda, H.; Abe, E. Effect of solvents on the preparation of silica-coated magnetic particles *Chem. Lett*. **2001**, *11*, 1168-1169.

13. Rahman, I. A.; Padavettan, V. Synthesis of silica nanoparticles by sol-gel: size-dependent properties, surface modification, and applications in silica-polymer nanocomposites - a review *J. Nanomater*., **2012**, *2012*, Article ID 132424, 15 pages. https://doi.org/10.1155/2012/132424.

14. Deng, Y.; Wang, C.; Hu, J.; Yang, W.; Fu, S. Investigation of formation of silica-coated magnetite nanoparticles via sol-gel approach, *Colloids Surf. A Physicochem. Eng. Asp.* **2005**, *262*, 87–93.

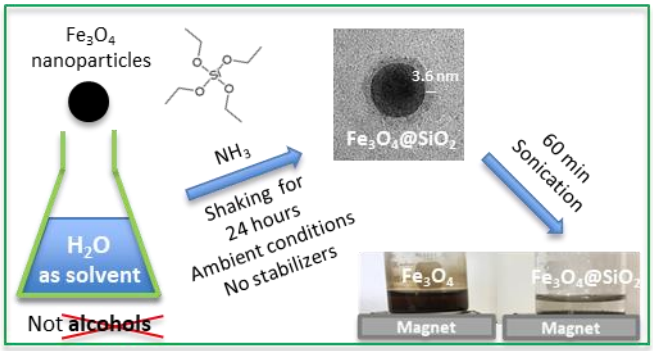
15. St¨ober, W.; Fink, W. Controlled growth of monodisperse silica spheres in the micro size range. *J. Colloid Interface Sci.* **1968**, *26*, 62-69.

16. Orozco, F.D.A; Sousa, A.C.; Domini, C.E.; Araujo, M.C.U.; Band, B.S.F. An ultrasonic-accelerated oxidation method for determining the oxidative stability of biodiesel, *Ultrason. Sonochem*., **2013**, *20* (3), 820-825.

17. Enomoto, N.; Akagi, J.; Nakagawa, Z. Nakagawa Sonochemical powder processing of iron hydroxides. *Ultrason. Sonchem.*, **1996**, *3*, S97-S103.

18. Kang, S.M.; Kim, W.; Choi, I.S. Biomimetic approach to the formation of magnetic nanoparticle/silica core/shell structures. *J. Nanosci. Nanotechnol.* **2008**, *8*, 5347–5350.

Table of Content (TOC)/Abstract Graphic



Synopsis. Less than 5-nm coating, water rather than alcohols as the solvent, ambient conditions, and no stabilizers well reflect the Green Chemistry Principles 1, 2, 3, 5, 6, 8, and 12.