Controlling Silica Encapsulation of Iron Oxide Magnetic Nanoparticles via Modified Stöber Strategies

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Key Finding
Neat iron oxide magnetic nanoparticles (MNPs) possess several inherent stability issues leading to inconsistent encapsulation efforts. Through an initial surface functionalization via citric acid ligand addition, the stability of the MNPs can be increased, allowing for a more consistent silica encapsulation reaction with smaller particle sizes and lower polydispersities.

Motivation
• Synthesis of nanoparticles such as functionalized MNPs has shown immense potential in the field of advanced separations and processes, providing an opportunity to address global issues centered around obtaining water security.

• Larger surface area to volume ratio, low mean coordination number and superparamagnetic behavior are a few of the characteristics that can be exploited to obtain more reactive and responsive materials for advanced processes.

• To overcome inherent issues with neat MNPs (e.g., agglomeration, solubility limitations, oxidation), surface functionalization via ligand addition and silica encapsulation can be performed.

• Silica encapsulation via a modified Stöber method provides a facile surface functionalization and particle stabilization avenue, opening a wide range of end-use applications due to well-studied silane functionalization methods.

Procedure

Si Encapsulation of Neat MNPs
• MNPs were produced using a facile coprecipitation method.[14]
• A modified Stöber method was implemented using NH₄OH as base to create a core-shell MNP.

Si Encapsulation of Child-capped MNPs
• Neat MNPs were surface modified via ligand addition prior to the encapsulation.

• Neat MNPs were capped with citric acid.

• A modified Stöber method was applied to effectively encapsulate the ligand-capped MNPs.

Results

• Bare MNPs and citric acid surface-modified MNPs where encapsulated via a modified Stöber method, which follows the same mechanism as the production of silica nanoparticles (Figure 3).

• Attenuated total reflectance Fourier transform infrared (ATR-FTIR) measurements (Figure 4) showed signature peaks at ca. 1000 cm⁻¹ representative of Si encapsulation associated with a siloxane network.

• The two types of encapsulation gave different ζ-potentials, which can be attributed to possible citric acid ligands remaining at the particle surface and the variability in particle size (Figure 5).

• The polydispersity was also reduced when the MNP were initially capped with citric acid (Table 1).

• The neat MNP possessed particle sizes ca. 232.6 nm. Upon ligand addition with citric acid, the diameter was found to be ca. 258.77 nm. The encapsulation resulted in particles with a considerably larger particle size (Table 1). The neat MNPs that were encapsulated gave a mean effective diameter of ca. 1170.33 nm; whereas, the citric acid-capped MNPs gave an effective mean diameter of ca. 1053.37 nm after the silica encapsulation process.

• The polydispersity index was also reduced when the MNP were initially capped with citric acid (Table 1).

Conclusions
• ATR-FTIR confirmed the encapsulation of MNPs with silica.

• Solubility of bare MNPs was extremely low in water and ethanol, which lead to a significant waste of solvent and potential issues with process scale-up.

• Larger particle sizes and a broader particle size distribution was observed using dynamic light scattering (DLS).

• Citric acid functionalized MNPs showed a lower polydispersity in comparison to the neat MNPs after the encapsulation reaction. This could be a direct result of the increased particle stability provided by the capping ligand, which prevents the particles’ tendency to aggregate due to the increased steric repulsion and surface charge.[3]

• FTIR peaks associated with Si-OH bending along with ζ-potential measurements confirmed the surface modification of MNPs through the modified Stöber method.

Future Work
• Further silica encapsulation efforts will be carried out using (3-aminopropyl)triethoxysilane (APTES) as the silica precursor.

• The use of a co-catalyst system such as LiOH and NaOH will be explored in hopes of improving the control over particle size and polydispersity during the encapsulation process[17].

• Further surface modifications will be performed utilizing the well-studied silane chemistries to effectively graft polymer to the surface of the core-shell MNPs.

• Additional manners to maintain proper MNP dispersion during the encapsulation reaction will be explored.

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Literature Cited