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Fabrication of magnetic core PEI-silica shell particles

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ABSTRACT

Magnetic core-silica shell particles combine the physico-chemical properties of the silica shell with the magnetic properties of the core. Seven possible particle coating methods utilizing the biomimetic polyamine polyethyleneimine (PEI) as the silication catalyst, have been identified and the objective of this study was to link the properties of the final PEI-silica coating with the methodology. The PEI-silica coated carbonyl iron particles were characterized via scanning electron microscopy, energy dispersive X-ray spectroscopy and Fourier transfer infrared spectroscopy. Varying the fabrication method and silane concentration successfully tuned the shell characteristics. Methods using sonication produced smooth more evenly distributed coatings with a tendency towards multicore particles. In contrast, raspberry-like coatings were produced via the slow addition, one- and two-pot methods. The magnetic separation process after synthesis achieved a degree of purification that makes these core–shell particles useful for potential applications that require specific surface interactions and the ease of magnetic separation.

1. Introduction

Core–shell particles seamlessly combine the advantageous properties of the core and shell materials into a single entity. Magnetic core-silica shell particles in particular have garnered much recent research attention [1–7] with their ability to combine the magnetism afforded by their magnetic core with the advantageous properties of their silica shell, including ease of functionalization, physical/chemical stability and biocompatibility [6–9]. These combined properties allow magnetic core-silica shell particles to be utilized in catalysis, environmental clean-up, magnetorheology, adsorption and biomedical applications [1,4,6,10–13,7].

To develop core–shell particles for these applications, a number of studies have been dedicated to silica shell fabrication techniques, with a special focus on those that allowed the introduction of enhanced or tunable surface properties, such as thiol or amine functionalization, control over shell thickness or control over morphological features [2,6,14–21]. For example, Wang et al. [20] silica coated magnetite microspheres through the ammonia catalyzed silication of tetraethylorthosilicate (TEOS) in an ethanol medium (a modified Stöber process [22]). An amine functionalization was added to the silica surface through a separate reaction where dropwise additions of NH_4F and TEOS were made at 40 °C followed by a 20 h reaction [20].

Roto et al. [6] developed a thiol-functionalized silica surface on magnetite nanoparticles. First, a silica shell was fabricated from the silication of sodium silicate in a slightly acidic solution at 80 °C, and next a layer of 3-mercaptopropyltrimethoxysilane (3-MPTMOS) was polymerized onto the surface using a zeolite catalyst, resulting in a thiol functionalization [6]. In addition, Vogt et al. [21] utilized an optimized inverse microemulsion method to produce silica shells of tunable thickness designed for biomedical applications. However, these methods of silica shell fabrication often require an unideal combination of a complex procedure, long reactions times, high temperatures and harsh conditions [6,20,21].

A bioinspired silica particle synthesis technique, referred to as "PEI-silica" particle synthesis, employs the biomimetic polyamine, polyethyleneimine (PEI), to induce silication in mild conditions and an aqueous reaction medium within a relatively short reaction period [23]. Previous studies have shown the advantage of morphological control over particle size and size distribution that can be exercised through variations in the reactant concentrations and mixing conditions of the PEI-silica method [24,25]. Furthermore, PEI-silica includes an inbuilt amine functionalization

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Abbreviations: ATR-FTIR, attenuated total reflectance – Fourier transform infrared spectroscopy; PB, phosphate buffer; EDX, energy dispersive X-ray spectroscopy; 3-MPTMOS, 3-mercaptopropyltrimethoxysilane; PEI, polyethyleneimine; SEM, scanning electron microscopy; TEOS, tetraethylorthosilicate; TMOMS, trimethoxymethylsilane.

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resulting from the entrapped PEI (polyamine) template molecule [8,23]. Amine functionalized magnetic core-silica shell particles display an excellent adsorptive capacity for heavy metal ions and carbon dioxide [20,26,27]. PEI-silica has been shown to possess hydrophobic surface properties [24] and an ability to be functionalized via a one-pot method [8].

In this paper, we investigate seven different PEI-silica coating processes for carbonyl iron cores with the aim of tuning the properties of the silica shell fabricated. We have compared the morphologies obtained by the different methods for four concentrations of the silica precursor, trimethoxymethylsilane (TMOMS). In addition, we have contrasted the effects of double silica coats versus a single coat. The PEI-silica shell was extensively characterized via scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and attenuated total reflectance – Fourier transfer infrared (ATR-FTIR) spectroscopy. Through these characterization techniques the PEI-silica methodology and reactant concentration utilized could be related to shell coverage, morphology and thickness.

2. Materials and methods

2.1. Materials

Hydrochloric acid, polyethyleneimine (PEI) (molecular weight 25 kDa), sodium dihydrogen phosphate, disodium hydrogen phosphate, methanol and trimethoxymethylsilane (TMOMS) were purchased from Sigma–Aldrich. All reagent-grade chemicals were used as received and deionised water (18.2 Ω cm) was used in the preparation of all aqueous solutions, unless otherwise noted. A stock solution of 500 mM phosphate buffer (PB) was prepared by adding a combination of 500 mM $Na_2HPO_4.2H_2O$ and NaH_2PO_4 solutions until the pH was pH 7.4.

The iron carbonyl $\geq$95% Fe basis (product C3518) was also purchased from Sigma–Aldrich and used as the magnetic core material. The production of carbonyl iron is through the purification of liquid iron. First the iron is converted into iron pentacarbonyl which is subsequently purified through distillation and finally decomposed into a carbonyl iron powder. The relative purity and sphericity of the carbonyl iron particles has made them an attractive material for research studies as well as other powder metallurgy applications in the food industry and in electronics [28].

As specifications were not provided by the manufacturer, our own SEM analysis of the iron carbonyl powder (via Zen 2 blue edition software, Zeiss) has shown the iron carbonyl particles were highly polydispersed with an average diameter of 2100 ± 1000 nm and with an approximate diameter range of 500 nm and 5000 nm (Supplementary Fig. 1). Most particles appeared spherical in shape. However, some particles were observed to be elongated or conjoined. It is unclear whether the observed conjoined particles were artefacts of the drying process for SEM sample preparation or resulted from the production process.

2.2. Methods

The magnetic separation process was trialed first to determine whether the non-coating PEI-silica by-product of the coating fabrication reactions could be successfully removed (Section 2.2.1). Seven different coating fabrication methods and four different reactant concentrations were used for coating; these methods and concentrations are outlined in Section 2.2.2. In Section 2.2.3, the techniques to characterize the success of the magnetic separation process and the shell features of the core–shell particles are detailed.

2.2.1. Preliminary tests. Use of magnetic separation

We first tested the magnetic separation of the magnetic core/core–shell particles from the core-free silica. To do so, PEI-silica particles were synthesized in accordance with previously specified methods [20]. The PEI-silica particle synthesis method was analogous to the Method E coating technique outlined in Section 2.2.2.3 (without carbonyl iron cores).

After synthesis, the PEI-silica particles were washed with water twice and suspended with carbonyl iron (5 mg mL^{-1}) in a 9:1 water:methanol medium. After thorough mixing a permanent neodymium magnet was used to trial the separation of the magnetic particles from the PEI-silica particles. The magnetically separated particles were subsequently washed thrice through resuspension in 1 mL water and analyzed with SEM (Section 2.2.3.2) and EDX (Section 2.2.3.3) to assess if magnetic separation had been attained (see Section 3.1).

2.2.2. Coating methods

In this study seven coating methods were trialed. The procedures for each method are detailed in the sections below.

For all coating methods, the final concentration of reactants were approximately 5 mg mL^{-1} carbonyl iron particles, 1:9 methanol:H_2O, 50 mM phosphate buffer (PB), 2.5 mg mL^{-1} PEI and a TMOMS concentration of 0.05, 0.1, 0.2 or 0.3 M. In the methods requiring pre-hydrolyzed TMOMS, the hydrolysis reaction was conducted by incubating 1 M TMOMS in 1 mM HCl for 15 min prior to being added to the synthesis reaction.

Also for all methods, after reactants were added, synthesis was conducted at room temperature for 30 min. During the synthesis reaction time, tubes were upended at 5 min intervals to prevent settling of the carbonyl iron particles. The methods investigated are detailed below.

2.2.2.1. Two pot methods (A and B). In Method A, carbonyl iron suspended in methanol was combined with hydrolyzed TMOMS and half the amount of PB by vortex mixing. In a separate vessel PEI was combined with the other half of the PB. Both tubes were incubated separately for 15 min, then combined (through vortex mixing) for a 30 min reaction. Method B followed the same sequence as Method A, however the positions of TMOMS and PEI in the method were exchanged, *i.e.* instead of carbonyl iron being combined with TMOMS and half the PB, the carbonyl iron was combined with the PEI and half the PB, and in the other tube the TMOMS was combined with the other half of the PB.

2.2.2.2. Sonication methods (C and D). In Method C, neat (non-hydrolyzed) TMOMS was combined with dry carbonyl iron, the mixture was then sonicated for 5 min. Immediately after sonication PEI was added to the mixture, followed by another 5 min of sonication. Then PB and methanol were added with a final 5 min of sonication and a 30 min reaction period. Method D follows Method C, but with the TMOMS and PEI additions swapped.

2.2.2.3. All in one method (E). Method E involved all reactants being added in a quick succession (Fe in methanol, PB, PEI, hydrolyzed TMOMS) and combined through a few seconds of vortex mixing followed by a 30 min reaction.

2.2.2.4. Slow addition methods (F and G). In Method F, carbonyl iron suspended in methanol was combined with PEI and PB. Then hydrolyzed TMOMS was added in even fractions at 1 min intervals over a 10 min period. After each fraction was added, the reaction tube was upended to incite mixing. After the 10 min period, reactants were thoroughly combined through vortex mixing and the reaction left to proceed for 30 min. Method G used the same

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