



Feasibility of Electrostatic-Mediated *Post*-Functionalization to Induce Long Term Colloidal Stability and Stability After Freeze Drying of Amphoteric Nanoparticles

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ABSTRACT

A commercialized iron oxide nanoparticles (of amphoteric nature) were surface modified with poly(sodium 4-styrenesulfonate) (PSS) via a simple electrostatic-mediated *post*-functionalization technique. The modification is successful if the iron oxide nanoparticles experience a complete alteration in surface properties. Such observation was obtained when the functionalization was conducted at pH 3.5, in which the iron oxide nanoparticles and the PSS molecules were of opposite charge. Here, the PSS can be attached onto the iron oxide via electrostatic attraction. In contrast, poor surface modification was resulted when the functionalization was conducted at pH > 9, in which iron oxide and PSS repulse each other upon having similar surface charge. Later on, the ability of the electrostatic-mediated *post*-functionalization to continually impose good colloidal stability on the iron oxide nanoparticles for a long period (6 months) and its ability to sustain from lyophilization process were evaluated by tracking the evolution of particle hydrodynamic size.

1. Introduction

Modification of nanoparticles with polymer is a well-known approach to suppress the tendency of particle agglomeration. The idea implemented here is to impose steric effect which functions as repelling force when the adsorbed polymer on two neighboring particles overlap [1,2]. While in the case where the polymer possesses net positive or net negative charge, electrostatic repulsion further enhances the particle-particle repulsion [1,3,4]. Besides reducing the extent of particle agglomeration, modifying the particle surface with polymer also provides specific functionality to the nanoparticles, which further enhance their application efficiency [5–7].

The surface modification can be done at the time when the particles are being synthesized [8,9]. This type of modification procedure is regarded as *pre*-functionalization. In another word, growth of nanoparticles from their precursors happens concurrently with functionalization of polymers onto the particle surface. On the other hand, *post*-functionalization refers to the procedure in which the already made nanoparticles are mixed with a polymer solution in order to allow the adsorption of the polymer molecules on the particle surface [3]. Even though the *pre*-functionalization method seems rather simple as it omit the need to dry and to re-disperse the as-made nanoparticles [10], one

of the biggest challenges associated to this technique is the potential change in particle shape, surface morphology, and the intrinsic properties [11]. The added polymer solution during particle growth could change the pH of the synthesizing medium and leads to change in particle morphology [12]. Meanwhile, the *post*-functionalization method seems to be more promising and versatile as the core structure of the particles is unaffected [11] since the particle synthesizing step is separated from the subsequent polymer modification step. *Post*-functionalization can be done by either growing the polymer from the nanoparticle surface, or by directly adsorbing polymer molecules onto the particle surface. It was reported that the latter strategy is technically less time- and material-consuming [13].

The mechanism that promotes polymer adsorption onto the particle surface plays the main role in determining successfulness of the functionalization. For instance, polymer molecules with carboxylate groups (COO[−]) such as carboxymethylcellulose and polyacrylate may form complexation with the iron via monodentate chelating, bidentate chelating and/or bidentate bridging [3,14,15]. The adsorption mechanism could be pH-dependent. For instance, in the study by McGuire et al. [16], it was found that at pH above or below pH 8.5 (isoelectric point of iron oxide nanoparticles), the adsorption of anionic polyacrylamide on the particle surface was promoted by both bidentate chelation and

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hydrogen bonding. Meanwhile, at pH 8.5, monodentate chelation and hydrogen bonding play the role in the adsorption. On the other hand, for the adsorption of non-ionic polyacrylamide on the iron oxide nanoparticles, it was found that hydrogen bonding is the dominant adsorption mechanism, at all pHs. Besides carboxylate groups, molecules with silane, thiol and amine [17] functional groups also can directly anchor to the iron oxide surfaces.

Nevertheless, not all polymers possess the aforementioned surface ligands that can directly bind to oxide surfaces. To solve this issue, researchers have allocated extra effort to pre-modify these polymers with the desired ligand groups. For instance, Kohler and coworkers modified polyethylene glycol (PEG) with silane group; this PEG silane capable of ligand immobilization on iron oxide [18]. Besides that, modification of PEG with phosphoric [19] or catechol [20–22] anchoring groups also can enhance the direct binding of PEG onto iron oxide surfaces via Fe-O-Phosphoric and Fe-O-Catechol coordination bonds, correspondingly. However, it should be noted that such pre-modification of polymer requires extra step of synthesis that can be rather time consuming. Thus, an alternative route of functionalizing the polymer onto nanoparticle surfaces worth to be developed.

Considering the nature of amphoteric nanoparticles, in which their surface charge can be manipulated to positive or negative by making the medium pH below or above the isoelectric point, respectively, it is possible to adsorb a polymer of opposite charge on the particle surface via electrostatic attraction. In this regard, it is the aim of the present study to systematically evaluate the feasibility of electrostatic attraction to induce the attachment of charged polymer onto the surface of amphoteric nanoparticles. More importantly, whether or not this electrostatic-mediated functionalization can impose long term colloidal stability on the nanoparticles, as well as its ability to remain stabilizing the nanoparticles after being subjected to freeze drying are investigated.

2. Materials and Methods

2.1. Post-Functionalization of PSS on Iron Oxide Nanoparticles under Various Medium pH

A bath sonicator was used to disperse 2.5 g/L of bare iron oxide nanoparticles (Iron (II,III) oxide, 98% purity, Nanostructured & Amorphous Materials, USA) in deionized water. This process would help to disperse the nanoparticles, which are agglomerated initially. On the other hand, 0.005 g/mL of poly (sodium 4-styrenesulfonate) (hereafter denoted as PSS) was prepared at stirring speed of 700 rpm last for 1 h. Both the bare iron oxide nanoparticles and the PSS solution were adjusted to pH of interest. Then, 7 mL of the bare iron oxide nanoparticles was added into 20 mL of the PSS solution. The mixture was capped tightly and placed on an end-over-end rotating mixer. The mixer was adjusted to 40 rpm and the rotating process would require at least 12 h in order to ensure adsorption process complete [23]. The resultant entity, i.e. PSS/iron oxide nanoparticles, was then separated by a

permanent magnet. The isolated nanoparticles were then re-suspended into deionized water after decanting the supernatant.

2.2. Characterization of Nanoparticles

2.2.1. Particle Sizing by Transmission Electron Micrograph (TEM) and Dynamic Light Scattering (DLS)

The morphology and core size of iron oxide nanoparticles were determined by TEM analysis. The nanoparticle suspension was ultra-sonicated before a droplet of the suspension was deposited onto a TEM grid. The sample was then subjected to air drying for few minutes before being observed under various magnifications by TEM analyser (Phillips/Fei CM12).

The hydrodynamic size of the iron oxide nanoparticles was determined via DLS technique (Malvern Instruments Zetasizer nanoZS, U.K.) with 173° Non-Invasive Back Scatter. The concentration of the nanoparticles was set at 5–10 mg/L in order to reduce particle-particle interaction. Three measurement runs were conducted to obtain the average data. The hydrodynamic size of the selected nanoparticles was traced over a period of time in order to reveal their long term colloidal stability [24,25].

2.2.2. Zeta Potential Measurement

Zeta potential profile of both iron oxide nanoparticles and PSS molecules was determined in order to know their surface charge at various medium pHs. It can be done via Laser Doppler Velocimetry (LDV) incorporated in the Malvern instruments Zetasizer NanoZS. Samples were dispersed in 10^{-3} M NaCl solution before pH adjustment. 1 M HCl and 1 M NaOH were prepared for the pH adjustment; further dilution was done when necessary.

2.2.3. X-Ray Photoelectron Spectroscopy (XPS) Analysis

XPS measurements were done via XPS Axis Ultra (Kratos Analytical Shimadzu). The powder samples were illuminated with a monochromatic Al K α -X-ray source. Analysis and data extraction was then conducted using Vision Instrument Manager (Vision 2.2.10). Note that the binding energies in the XPS spectra were calibrated using carbon C 1s peak (285 eV) as reference value.

2.3. Converting Nanoparticle Suspension to Nanopowder via Freeze Drying

The freeze drying (lyophilization) method was used to turn the iron oxide suspension into nanopowder. Briefly, a concentrated suspension of PSS/iron oxide nanoparticles was filled into a round bottom flask. The sample was then kept in the ice maker compartment of the fridge for overnight until the sample frozen into ice crystals. Then, the frozen sample was subjected to freeze drying process using freeze dryer (TELSTAR Cryodos, Spain) which coupled with a vacuum pump (PFE-IFFER, Germany). The freeze drying process was conducted at low temperature around -50°C and vacuum pressure 1.2×10^{-3} mbar.

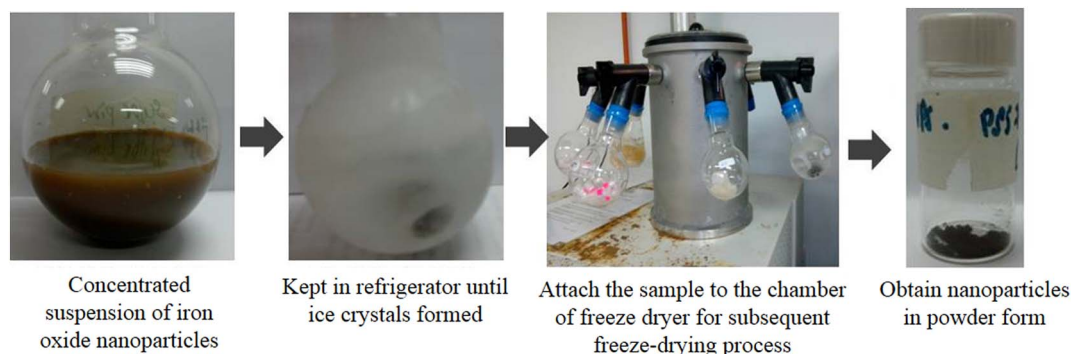


Fig. 1. Overall procedure for preparing of PSS/iron oxide nanopowders from its suspension through freeze drying process.

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