Polyelectrolyte multilayer film-assisted formation of zero-valent iron nanoparticles onto polymer nanofibrous mats

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Abstract. A facile approach that combines the electrospinning technique and layer-by-layer (LbL) assembly method has been developed to synthesize and immobilize zero-valent iron nanoparticles (ZVI NPs) onto the surface of nanofibers for potential environmental applications. In this approach, negatively charged cellulose acetate (CA) nanofibers fabricated by electrospinning CA solution were modified with bilayers composed of positively charged poly(diallyl-dimethyl-ammonium chloride) (PDADMAC) and negatively charged poly(acrylic acid) (PAA) through electrostatic LbL assembly approach to form composite nanofibrous mats. The composite nanofibrous mats were immersed into the ferrous iron solution to allow Fe(II) ions to complex with the free carboxyl groups of PAA, and then ZVI NPs were immobilized onto the composite nanofibrous mats instantly by reducing the ferrous cations. Combined scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and thermogravimetry analysis demonstrated that the ZVI NPs are successfully synthesized and uniformly distributed into the polyelectrolyte (PE) multilayer films assembled onto the CA nanofibers. The present approach to synthesis ZVI NPs opens a new avenue to fabricating various materials with high surface area for environmental, catalytic, and sensing applications.

1. Introduction

LbL self-assembly technique has drawn much attention as a powerful and highly versatile approach to prepare nanostructured materials with tailored properties.\cite{1, 2} In a typical process, the oppositely charged polyelectrolyte solutions sequentially deposited onto a substrate, through controlling the dipping cycles and composition of polyelectrolyte (PE), the obtained composites with desired thickness, morphology and composition can be easily realized. The versatility of LbL assembly technique makes a broad range of materials including polymers, nanoparticles, and biomolecules etc. be able to be assembled onto various substrates (e.g. planar, solid spheres) to form functional nanomaterials.\cite{3-7} In our previous work,\cite{8} we immobilized ZVI NPs into the PE multilayer films assembled onto microsized glass beads via LbL assembly approach to mitigate their aggregation.\cite{9} The ZVI NPs thus obtained had a narrowly size distribution from 1 to 4 nm and displayed an excellent
reactivity for the dechlorination of trichloroethylene, a kind of typical organic contaminants.

In this study, we attempted to extend our previous work to the synthesis and immobilization of ZVI NPs onto a continuous, porous medium with high surface-to-volume ratio by combining electrospinning and LbL assembly techniques, and thereby developing a functional filtration material for environmental applications. To our best knowledge, immobilization of ZVI NPs onto surface of electrospun nanofibers using LbL assembly approach is not reported in literature.

2. Materials and methods

Poly(acrylic acid) (PAA, Mw = 240,000, 25 wt% in water) and poly(diallyl-dimethyl-ammoniumchloride) (PDADMAC, Mw = 100,000-200,000, 20 wt% in water) were obtained from Aldrich. Sodium borohydride was from J&K Chemical ®. FeCl₂·4H₂O (ACS reagent grade), cellulose acetate (powder, viscosity = 300.0 – 500.0 mPa.s), acetone, and N,N-dimethylformanide (DMF) were all in reagent grade and used as received. Water used in all experiments was purified using a Milli-Q Plus 185 water purification system (Millipore, Bedford, MA) with resistivity higher than 18 MΩ cm.

CA nanofibers were fabricated by electrospinning a 12 mg/mL CA solution with an applied voltage of 20 kV and a collection distance of 20 cm. The homogenous CA solution was prepared by dissolving a measured amount of CA powder into a mixed solvent of acetone and DMF (v/v = 2:1). The negatively charged electrospun CA nanofibrous mats were then assembled with PDADMAC and PAA alternatively using the LbL assembly approach to form six bilayers of PAA/PDADMAC (a polymer pair of PAA/PDADMAC was considered as a bilayer). Subsequently, the nanofibrous mats were immersed into ferrous iron solution to form a Fe(II)-nanofiber complex, and then ZVI NPs were simultaneously synthesized and immobilized into the PE multilayer-modified CA nanofibers by in situ reducing the Fe(II) ions.

Morphologies of the prepared samples were observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-ray energy dispersive spectroscopy (EDS) was used to confirm the presence of ZVI NPs. Thermogravimetry analysis (TGA) was used to determine the iron loading capacity on the nanofibrous mats.

3. Results and discussion

The SEM images and diameter distribution histograms of CA nanofibers and ZVI NP-immobilized CA nanofibrous mats are shown in Figure 1. The morphology of CA nanofibers does not significantly change after the immobilization of ZVI NPs. Some membrane-like structures are observed between the adjacent nanofibers for ZVI NP-immobilized CA nanofibers, which could be caused by the assembly of multilayer films in the limited space in between the adjacent fibers.[10] The average diameter of pure CA nanofibers (Figure 1b) was estimated to be 295 ±145 nm. However, after the immobilization of ZVI NPs, the fiber diameter was increased to 461±157 nm (Figure 1c).

In order to observe the distribution of ZVI NPs in the composite nanofibrous mats, the ZVI NP-immobilized composite nanofibrous mats were embedded in epoxy resin and cut into ultrathin sections with ultramicrotome equipped with a diamond knife. The cross-sectional images of the sample were observed by TEM, which was shown in Figure 2. It was clear that the PE multilayers were successfully coated onto the surface of CA nanofibers (Figure 2a). But, it was difficult to identify the layered structure of PE multilayers due to the fuzzy characteristics of the LbL structure associated with the interpenetration between the layers.[2] And, it seems that the thickness of ZVI NPs/PE multilayer films is irregular and cannot be estimated, which might be closely related to the deposition conditions (e.g. pH value, deposition time and the number of bilayers) and the overlapping of samples during the sample preparation. Figure 2b displays the magnified cross-sectional TEM image of ZVI NPs immobilized composite nanofibrous mats. ZVI NPs were dispersed into the PE multilayers with dense and uniform distribution. The iron particle size was narrowly ranged from 0.8 to 2.2 nm, and the average size of ZVI NPs was measured to be 1.4 ±0.29 nm.
Figure 1. SEM images and diameter distribution histograms of pure CA nanofibers (a and b) and ZVI NP-immobilized CA nanofibers (c and d).

Figure 2. A typical TEM image (a) and a magnified TEM image (b) of cross-sectional ZVI NP-immobilized composite nanofibers embedded in epoxy resin.

Figure 3 shows the EDS spectrum of ZVI NP-immobilized composite nanofibrous mats. The presence of iron signals from EDS spectrum suggests that ZVI NPs are successfully synthesized and immobilized in the PE multilayer films assembled on CA nanofibers. The presence of oxygen signal may stem from the iron/iron oxide core-shell structure, which is consistent with literature.[8] And, the oxygen is also partly from the carboxyl groups of the PAA polymer layers and the CA nanofiber templates. The element carbon was from the polymer components and the carbon thin film coating.
during the sample preparation. Element sodium was likely from sodium borohydride residues used for ferrous reduction.

![Figure 3. EDS spectrum of ZVI NP-immobilized composite nanofibrous mats.](image)

Iron loading of six PE bilayers assembled onto the CA nanofibrous mats with 2 cycles of binding/reduction process was measured using thermogravimetric analysis (TGA) at a heating rate of 10 °C/min under air (Figure 4). It is clear that at 600 °C, all the polymer component was nearly burned out and only the iron oxide was left (Fe2O3). Thus, we could calculate that the iron loading of composite nanofibrous mats was 19.7 %.

![Figure 4. TGA results of composite nanofibrous mats before (b) and after (a) immobilization of ZVI NPs.](image)

4. Conclusion
In summary, ZVI NP-immobilized composite nanofibrous mats were successfully fabricated by a unique combination of electrospinning technology and electrostatic layer-by-layer self-assembly techniques. The synthesis of ZVI NPs in the composite nanofibrous mats were confirmed by TEM and EDS. We show that ZVI NPs are uniformly dispersed into the PE multilayer films with a dense and
even distribution. The average particle size of ZVI NPs was 1.4 nm. Such ZVI NP-immobilized fibrous mats with high surface-area-to-volume ratio and porous structure should have great potential for environmental applications. Furthermore, the developed approach to immobilizing ZVI NPs onto electrospun polymer nanofibers with LbL approach may open a new avenue in the fabrication of 3-dimensional porous nanostructured materials with tunable size, composition, and surface properties for various applications.

5. References
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