Research Paper

Highly reactive and stable nanoscale zero-valent iron prepared within vesicles and its high-performance removal of water pollutants

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A B S T R A C T

Nanoscale zero-valent iron particles have large specific surface area and high reaction activity, and have been increasingly used for the degradation of environmental contaminants. However, rapid aggregation and deactivation hinder their wide applications. In this work, nanoscale zero-valent iron (NZVI) particles were prepared in vesicles, which were formed by self-assembly of amphiphilic block copolymer poly(1-vinylpyrrolidone-co-vinylacetate) (PVV) in aqueous tetrahydrofuran medium, and characterized with the aid of XRD, FTIR, SEM-EDX, TEM, XPS and DLS techniques. It was found that the NZVI particles were well encapsulated in the vesicles, and they could be stored directly in the air as solids, but the dried NZVI particles could be easily released from the vesicles once they were put in water. These NZVI particles showed some unique features, such as uniform nanometer size distribution (from 70 to 100 nm), vesicle-like morphology, and good dispersion. Activity and stability of the NZVI in vesicles were examined by using Cr(VI) and nitrobenzene as the model pollutants, and compared with the bare NZVI particles synthesized with the same procedures but without PVV. A dramatic difference in activity and stability was observed for the two different NZVI particles. The NZVI in vesicles showed a good chemical stability in the air, and still maintained its high reactivity in water. Such excellent performance might be attributed to the encapsulation of the NZVI by vesicles, which could impede well the strong agglomeration of metal particles in water and prevent metal particles from being oxidized in the air.

1. Introduction

Over the past years, nanoscale zero-valent iron (NZVI) particles have attracted much attention in the control of environmental pollutants because of their large specific surface area, high reaction activity, and strong reductive power [1]. Indeed, NZVI particles are very effective for the removal of various wastewater contaminants, such as nitrite [2], selenate [3], organic dyes [4], aromatic halides [5], and heavy metals contaminants [6,7]. However, due to the strong van der Waals and magnetic attraction forces as well as strong reductive power, bare NZVI particles not only tend to agglomerate into larger particles in the micro- to milli-meter scale, but also can be oxidized easily in the air with sharp deterioration of activity, durability and efficiency, which greatly impedes their large-scale application in real-life conditions [8].

To solve these problems, some techniques have been developed to prepare stable and well-dispersed NZVI particles, such as surface coating of NZVI with surfactant, polyelectrolyte or nature biopolymer [9–11], and immobilization of NZVI on inorganic or organic supports [12–15]. However, it is still a challenge to simultaneously strike a

trade-off between chemical reactivity in water and stability in the air [16]. Most strategies for the NZVI coating and supporting cannot be used to control dispersion, nanometer distribution, structure and morphology of the particles, which will significantly affect their reactivity in practical application. In addition, owing to the high reaction activity of NZVI, the surface modified NZVI particles have to be protected by inert gas in the preparation and storage processes. This has to increase the complexity of preparation and the cost of operation in real applications.

In recent years, polymeric vesicles or micelles, prepared by self-assembly of amphiphilic block copolymers in selective solvents, have attracted particular interest because of their unique properties and potential application in the fields of pharmaceutical, medical and catalysis. In this context, a very promising strategy is the preparation of stable and active noble metal nanoparticles, such as Au or Pd nanoparticles, by the in situ reduction in the vesicles or micelles of amphiphilic block copolymers. Li et al. [17] reported a thermally responsive vesicle system that could be easily decorated with gold nanoparticles by simply mixing the polymer solution with a NaAuCl4 solution at 50 °C.

Mai et al. [18] described a general method for the incorporation of Au particles into the central portion of the vesicles to allow the particles to be preferentially localized in the central portion of the walls, and the nanoparticles were radially distributed in the vesicles. KlingelhÖfer et al. [19] prepared palladium hybrid colloids consisting of palladium colloids in the core of amphiphilic block copolymer micelles, which showed a strong catalytic activity and stability in the Heck reaction. Jaramillo et al. [20] synthesized highly dispersed Au nanoparticles by block copolymer micelle encapsulation and observed their catalytic activity to electro-oxidation of CO. More recently, Lin et al. [21] prepared photosensitizer-loaded gold vesicles for integrated photodynamic cancer therapy by a novel theranostic platform based on photosensitizer-loaded plasmonic vesicular assemblies. However, to the best of our knowledge, there are no studies on the preparation and application of more active NZVI in vesicles or micelles.

In this study, poly(1-vinylpyrrolidone-co-vinylacetate) (PVV) was selected to form vesicles in aqueous tetrahydrofuran (THF) solution by self-assembly due to its amphipathy, low toxicity and biodegradability. Then for the first time, NZVI particles were prepared in the vesicular nanoreactors and used to degrade environmental pollutants. Thus, the objective of this study is three-fold: (i) To synthesize NZVI particles in PVV vesicles and the possible mechanism was also studied with the aid of various characterization techniques; (ii) To investigate the reactivity in water and the stability in the air of NZVI in vesicles using Cr(VI) as a model; and (iii) To use the synthesized NZVI in vesicles as reductant in the application of nitrobenzene degradation in simulated wastewater, where the reaction kinetics was studied by using the pseudo-second-order decay model and the time evolution, and the intermediate and final products were analyzed.

2. Experimental

2.1. Chemicals

Amphiphilic block copolymer poly(1-vinylpyrrolidone-co-vinylacetate) (PVV) (copolymer $(C_6H_9NO)_n.(C_4H_6O_2)_m$, 7:3 or 3:7; 50% in ethanol; molecular weight = 591.69) was purchased from Aldrich Chem. Co. Inc. Sodium borohydride ($NaBH_4$), tetrahydrofuran (THF, C_4H_8O), ferric chloride hexahydrate ($FeCl_3·6H_2O$), nitrobenzene, and commercial micro-scale Fe powder were purchased from Tianjin Kemiou Chemical Reagent Co. All the chemicals used in this work were analytical grade reagents and all the solutions were prepared using deionized water.

2.2. Synthesis of the NZVI in vesicles

Aqueous THF is a well-known solvent for the preparation of various block copolymer vesicles. In the present study, this mixed solvent was also used in the preparation of PVV assembly. To prepare the vesicles, 0.5 g of PVV (PVP-co-PVA) block copolymer (7:3) and 50 mL of deionized water were mixed in a 250 mL three-necked flask at room temperature, and the solution was kept sealed with stoppers. Then the mixture was titrated by 100 mL of THF with a rate of 0.03 mL min^{-1} under stirring. When the system became cloudy, the formation of vesicles was suggested. The stirring was continued for another 60 min after completion of the titration. For comparison, 0.5 g of PVV block copolymer (3:7) was mixed with 50 mL of THF within 250 mL three-necked flask at room temperature, and 75 mL of deionized water was then added into the flask through titration with the same rate of 0.03 mL min^{-1}.

As depicted in Scheme 1, the resulting solutions were mixed with $FeCl_3·6H_2O$ powder at different Fe^{3+} concentrations, and the mixtures were stirred for 30 min to allow Fe^{3+} was bound to ester groups of vinylacetate by coordination. To each vesicle/Fe^{3+} solution, $NaBH_4$ powder was added immediately with a molar ratio of $NaBH_4$ to Fe^{3+} at 5:1. As expected, the solution became black quickly with spilling of a lot

of bubbles and a quicksand-like mixture was formed. The black paste was separated from the mixture by a magnet and washed with aqueous THF (H_2O: THF = 1:2 (v/v)) three times, then dried in a vacuum oven at 60 °C overnight. In this way, PVV/NZVI particles with different Fe^0 contents were synthesized, which were denoted by PVV/NZVI (8:1), PVV/NZVI (4:1), PVV/NZVI (2:1), PVV/NZVI (1:2) and PVV/NZVI (1:4) respectively, according to the increased concentration of Fe^{3+}. As a control experiment, bare NZVI particles were also synthesized by the identical procedures, but no copolymer was added in this case.

2.3. Characterization of the NZVI in vesicles

X-ray diffraction (XRD) spectra of NZVI in vesicles were recorded with a Bruker D8 Advance instrument (Germany) using K radiation over the 10–70° scan range. The elemental distribution analysis of the NZVI in vesicles was performed using an energy-dispersive X-ray (EDX) spectroscopy (Supra-40, Zeiss, Germany). Fourier transform infrared (FT-IR) spectra were recorded using a FTIR Analyzer (Perkin-Elmer, Spectrum 400, American) in the wavelength range of 4000–500 cm^{-1}, and the KBr was served as a reference. X-ray photoelectron spectroscopy (XPS) analysis was carried out using a EscaLab 250Xi (UK) with a Al k X-ray (1486.7 eV). Surface charging effects were corrected with C 1s peak at 285 eV as a reference. Shirley baseline and a Gaussian-Lorentzian peak shape were used for fitting the data.

The microstructure and morphology of NZVI in vesicles were identified by transmission electron microscope (TEM, JEM-2100, Japan) with selected area electron diffraction (SAED) operated at 200 kV. The size distribution of NZVI in vesicles was calculated by visual particle counting with more than 100 particles. Dynamic light scattering (DLS) measurements were performed at 298.2 K by using a laser light scattering photometer (Nano-ZS90, Malvern, UK). Light of λ = 633 nm from a solid-state He-Ne laser (4.0 mW) was used as the incident beam. All measurements were made at 90° scattering angle and the intensity-average hydrodynamic diameter and particle dispersion index of the vesicles were calculated. All sample solutions were filtered through a 0.22 μm membrane filter.

2.4. Estimation of reactivity and stability

For the sake of convenience, the reactivity of PVV/NZVI particles was estimated by their ability to remove Cr(VI) from simulated wastewater. Typically, each of the seven iron sources including commercial micro-scale Fe powder (0.0022 g), bare NZVI (0.0026 g), PVV/NZVI (8:1, 0.045 g), PVV/NZVI (4:1, 0.030 g), PVV/NZVI (2:1, 0.020 g), PVV/NZVI (1:2, 0.005 g), PVV/NZVI (1:4, 0.003 g) were, respectively, added into a 50 mL conical flask containing 40 mL of aqueous Cr(VI) solution (initial pH = 5.6, and initial concentration C_0 = 5 mg L^{-1}). In these procedures, the iron sources were used at the same iron content of 0.050 g L^{-1}. Besides, in the control experiment, pure block copolymer (0.045 g) was also used alone in a separate experiment. The Cr(VI) stock solution was deoxygenated by N_2 stream for 10 min before addition of iron sources and kept sealed with a stopper during the reaction. The removal experiment was carried out by putting the flask in a thermostatic shaker bath at 25 ± 0.5 °C for 100 min, with a rotation speed of 180 rpm. At the given time interval, 1 mL of solution was sampled and filtered through a 0.22 μm membrane. The Cr(VI) concentration was analyzed using the diphenylcarbohydrazide method [22]. The loading amount of NZVI was determined by the 1,10-phenanthroline colorimetric method [23]. The Cr(VI) concentration at time t (C_t, mg L^{-1}) was determined, and the removal percent of Cr(VI) was calculated according to the equation: removal (%) = $(C_0 - C_t)/C_0 \times 100\%$. The experimental data of batch experiments were obtained in triplicate.

After the reduction of Cr(VI) by PVV/NZVI and bare NZVI, the solid samples were washed by deaerated ethanol twice with inert gas protection and were analyzed by XPS to test the composition of final