Thiol containing polymer encapsulated magnetic nanoparticles as reusable and efficiently separable adsorbent for heavy metal ions

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Fe$_3$O$_4$-PEDOT core–shell nanoparticles were fabricated by acid treatment mediated seeded polymerization and applied for highly efficient separation of heavy metal ions from contaminated waste water with an external magnetic field.

Heavy metal ion removal has attracted considerable attention for beneficial water usage due to their long-term environmental toxicity as well as short-term public health damage. To date, there have been various techniques to remove heavy metal ions such as chemical precipitation, oxidation/reduction sedimentation, ion exchange, membrane filtration and carbon adsorption. However, most of these processes require high capital investment and operation costs in order to maintain the separation and purification procedures for wastewater treatment. Recently, magnetic nanoparticle–polymer core–shell nanostructures have received attention in practical application fields including heavy metal ion removal from contaminated waste water. Polymer encapsulation provides the surface functionalization and protection of the magnetic core from environmental perturbation. Furthermore, the polymer shell also prevents the core part from particle–particle aggregation as well as improving the dispersion stability of the core–shell nanostructures in suspension medium.

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most promising conducting polymers because of its high conductivity, excellent environmental stability, and simple acid/base doping/dedoping chemistry. In addition, PEDOT contains sulfur which can endow two unpaired electrons. This thiol-functionalized polymer is readily conjugated with positively-charged heavy metal ions according to the coordination formation. Therefore, PEDOT-functionalized magnetic nanoparticles can be regarded as an excellent candidate for efficiently separable and reusable absorbance of heavy metal ions using an external magnetic field. However, there is limited information concerning a facile synthetic route to magnetic nanoparticle–PEDOT core–shell nanostructures. Thus, it is highly desirable to develop a simple and reliable method to fabricate magnetic–PEDOT core–shell nanoparticles with well-defined and uniform structure for heavy metal ion removal.

Herein we report the facile fabrication of thiol containing polymer encapsulated magnetic nanoparticles by seeded polymerization mediated with acidic etching. Fe$_3$O$_4$-PEDOT core–shell nanoparticles (Fe$_3$O$_4$-PEDOT NPs) were prepared by inducing ferric cations onto the magnetic nanoparticles (MNPs) with a partial etching process followed by seeded polymerization. The prepared Fe$_3$O$_4$-PEDOT NPs were employed as reusable and recoverable absorbents to extract heavy metal ions in aqueous solution. The adsorption capability of Fe$_3$O$_4$-PEDOT NPs was measured as a function of metal uptake time and type of heavy metal ions.

The synthetic procedure for Fe$_3$O$_4$-PEDOT NPs is illustrated in Scheme 1. Fe$_3$O$_4$ NPs were synthesized by a chemical precipitation method according to a previous report. Poly(vinyl alcohol) (PVA) was employed as a stabilizer of Fe$_3$O$_4$ NPs and dissolved in 1000 mL of distilled water (3 wt%). 12.43 g of iron(III) chloride hexahydrate (FeCl$_3$·6H$_2$O) and 4.57 g of iron(II) chloride tetrahydrate (FeCl$_2$·4H$_2$O) were added to a four-necked round-bottom reactor (2000 mL). The mixture was continuously stirred at 25 °C for 30 min followed by the addition of aqueous ammonia solution (1.5 M). The reaction proceeded for 2 h at room temperature. The Fe$_3$O$_4$ NPs were precipitated as a black sediment. The resultant MNPs were purified repeatedly by magnetic field separation with excess distilled water. The prepared Fe$_3$O$_4$ NPs were then dispersed in PVA aqueous solution (0.5 M). Subsequently, EDOT monomer was injected into the mixed solution with vigorous stirring at 25 °C. At this step, monomer was adsorbed and covered around Fe$_3$O$_4$ NPs by hydrophobic interaction between Fe$_3$O$_4$ NPs and EDOT monomer. To generate ferric cations on the Fe$_3$O$_4$ NP surface, 30 mL of HCl (0.5 M) solution was introduced into the mixture. Then the irregular shaped Fe$_3$O$_4$ NPs were partially etched to form spherical shapes. Newly generated ferric cations were used as oxidizing agent for polymerization of EDOT monomers. Consequently, Fe$_3$O$_4$ NPs were coated and functionalized with PEDOT. The uniform and thin PEDOT shell was produced by seeded polymerization mediated with acidic treatment. The Fe$_3$O$_4$-PEDOT NPs were applied as highly efficient separable and reusable materials for heavy metal ion removal.

Scheme 1 The fabrication procedure of Fe$_3$O$_4$-PEDOT NPs by seeded polymerization mediated with acidic etching.
NPs in the aqueous solution can be attracted and arranged vertically by a magnetic bar. Hysteresis loop of Fe₃O₄ NPs and Fe₃O₄–PEDOT NPs at 300 K with the expanded hysteresis loop (inset). The photograph indicates that Fe₃O₄–PEDOT was added to the Fe₃O₄ NP solution without acid treatment, and the pristine MNPs revealed an irregular shape and significant agglomeration after drying. The average diameter of the pristine Fe₃O₄ NPs was measured directly from TEM images and calculated as ca. 11 nm. Fig. 1(b) demonstrates the uniform and well-dispersed Fe₃O₄–PEDOT NPs. The Fe₃O₄–PEDOT NPs displayed improved stability and dispersibility in aqueous solution. This is because the PEDOT shell has a low surface energy compared to the core magnetic nanoparticles. A control experiment was performed without HCl addition and exhibited no core–shell formation. This means that seeded polymerization could occur at the surface of the magnetic nanoparticles with newly generated ferric cations by acidic etching. From the inset magnified image in Fig. 1(b), Fe₃O₄ NP is clearly encapsulated with a PEDOT shell. Fe₃O₄–PEDOT NP has a spherical shape with a core diameter of ca. 9 nm and shell thickness of ca. 2 nm. In addition, an electron diffraction pattern demonstrates that Fe₃O₄ NPs have high crystallinity and polycrystallinity.

Fig. 2(a) represents diffuse-reflectance infrared Fourier transform (DRIFT) spectra of Fe₃O₄ NPs, Fe₃O₄–EDOT NPs and Fe₃O₄–PEDOT NPs. The DRIFT technique is an effective and powerful surface sensitive analysis. The characteristic peak of Fe₃O₄ NPs appeared at 587 cm⁻¹. This band was shifted to high wavenumber compared to the Fe–O bond peak of bulk magnetite at 570 cm⁻¹ due to nanoparticle size. In order to confirm the adsorption of EDOT onto the Fe₃O₄ surface, the EDOT monomer was added to the Fe₃O₄ NP solution without acid treatment, and the Fe₃O₄–PEDOT NP was obtained after a washing process. The peaks at 1186 and 890 cm⁻¹ were attributed to the –C–H in-plane and out-of-plane deformation of EDOT monomer. These peaks disappeared after polymerization. The FT-IR spectrum of Fe₃O₄–PEDOT NPs showed characteristic PEDOT bands at 1384, 942 and 1083 cm⁻¹, which are due to C–C stretching of thiophene ring, C–S stretching and C–O stretching, respectively. Judging from these data, it can be concluded that the EDOT monomer on the Fe₃O₄ surface is successfully polymerized with acid treatment. In addition, the band at 1640 cm⁻¹ is ascribed to C–C stretching vibration, which is strongly related with the doping level of polymer. High intensity of this peak indicated that the PEDOT was highly doped. Fig. 2(b) exhibits the X-ray diffraction (XRD) pattern of Fe₃O₄ NPs and Fe₃O₄–PEDOT NPs. In the case of both the pristine Fe₃O₄ NPs and Fe₃O₄–PEDOT NPs, characteristic peaks of Fe₃O₄ were observed at 2θ = 30, 35 and 43°. However, the XRD pattern of Fe₃O₄–PEDOT NP was broader than that of the pristine Fe₃O₄ NP according to the size reduction of Fe₃O₄ NP with acid treatment. Based on the peak at 2θ = 35.68°, the mean size of Fe₃O₄ crystallites was calculated using the Scherrer equation. The value of ca. 11 nm of pristine Fe₃O₄ NP decreased to 9 nm after polymerization. These values are in good agreement with the average diameters of Fe₃O₄ NPs and Fe₃O₄–PEDOT NPs in the TEM image. The magnetic properties of Fe₃O₄–PEDOT NPs were investigated using a SQUID magnetometer. Fig. 2(c) demonstrates the hysteresis loop of Fe₃O₄–PEDOT core–shell NPs at 300 K. The magnetization was measured at external magnetic fields ranging between ±10 kOe and the magnetization was saturated at 24 emu g⁻¹. In particular, the coercivity (Hc) from the expanded hysteresis loop between −15 and +15 Oe was found to be 7 Oe. This Hc value is considerably higher than that of bulk iron (Hc ≈1 Oe). The inset photograph indicates that Fe₃O₄–PEDOT core–shell NPs in aqueous solution can be readily attracted and separated by an external magnetic field.

The PEDOT coated MNPs were applied as heavy metal ion absorbents. The adsorption capacities for target heavy metal ions were measured in aqueous solution to examine the surface reactivity of Fe₃O₄–PEDOT NPs. Ag⁺, Hg²⁺ and Pb²⁺ ions were selected as representative heavy metal ions. The adsorption of heavy metal ions progressed by means of surface complex formation between PEDOT shells and heavy metal ions. Heavy metal ion uptake of Fe₃O₄–PEDOT NPs was monitored as a function of contact time (Fig. 3(a)). Under this experimental condition, uptake saturation occurred within 2 h, when the initial

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**Fig. 1** TEM images of (a) Fe₃O₄ NPs, (b) Fe₃O₄–PEDOT NPs. Inset images (a–b) are the magnified TEM images of Fe₃O₄ NP and Fe₃O₄–PEDOT NP, and the electron diffraction pattern of Fe₃O₄–PEDOT NP.

**Fig. 2** (a) DRIFT spectra of Fe₃O₄ NPs, Fe₃O₄–EDOT NPs and Fe₃O₄–PEDOT NPs. (b) XRD pattern of Fe₃O₄ NPs and Fe₃O₄–PEDOT NPs. (c) Hysteresis loop of Fe₃O₄ NPs and Fe₃O₄–PEDOT NPs at 300 K with the expanded hysteresis loop (inset). The photograph indicates that Fe₃O₄–PEDOT NPs in the aqueous solution can be attracted and arranged vertically by a magnetic bar.
concentration of heavy metal ion was ca. 15 ppm. Based on the weight of PEDOT, the amount of Ag⁺, Hg²⁺ and Pb²⁺ ion uptake were ca. 27.96, 16.02 and 14.99 mmol g⁻¹, respectively. The maximum adsorption capacity (437 mg g⁻¹) of PEDOT-coated Fe₃O₄ NPs was approximately 7 times higher than that of chitosan-coated Fe₃O₄ NPs. In addition, this value was also high compared with that for thiol-functionalized particles (below 200 mg g⁻¹) due to the high surface area of Fe₃O₄–PEDOT NPs and abundant unpaired electrons of PEDOT shells. Fig. 3(b) displays the uptake of heavy metal ions after 0.5 and 24 h contact time with an excess amount of Fe₃O₄–PEDOT NPs. Heavy metal ions were removed up to 95% after 24 h, whereas the adsorption rate was observed in the order of Ag⁺ > Hg²⁺ > Pb²⁺, in accord with cation radius, and interaction enthalpy values. Importantly, Fe₃O₄–PEDOT NPs provide the convenient recovery of absorbents in aqueous phase by use of a magnetic field. There was no loss of adsorption capacity and morphological change of Fe₃O₄–PEDOT NPs in recycling tests (10 repeats). TEM analysis indicated that morphological change of Fe₃O₄–PEDOT NPs does not occur after the acid treatment (1 h, 25 °C). In addition, the acid-treated Fe₃O₄ NPs were also attracted by the external magnetic field. Therefore, it can be concluded that the PEDOT shell strongly protects the magnetic core under acidic conditions. Fe₃O₄–PEDOT NPs could be considered as a potential candidate as an excellent reusable and recoverable adsorbent of heavy metal ions.

In conclusion, Fe₃O₄–PEDOT NPs were fabricated using an acid-mediated seeded polymerization. Fe₃O₄ NPs encapsulated with PEDOT were used as an efficiently separable and reusable adsorbent of heavy metal ions under an external magnetic field and had high uptake capacities for different heavy metal ions (Ag⁺, Pb²⁺ and Hg²⁺). In addition, this synthetic methodology could be expanded for diverse magnetic core/polymer shell applications such as MRI contrast agents, ferrofluids, specific target drug delivery systems and data storage devices.

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Notes and references
18 Y. Chang and D. Chen, J. Colloid Interface Sci., 2005, 283, 446.