

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

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Fe₃O₄-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.

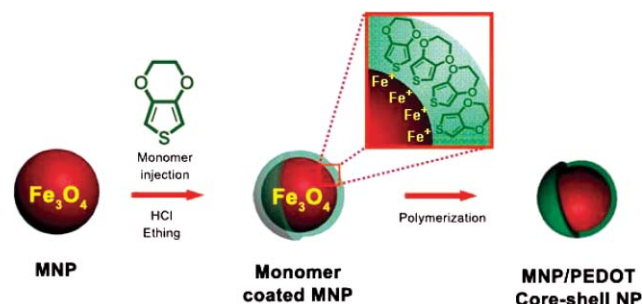
Heavy metal ion removal has attracted considerable attention for beneficial water usage due to their long-term environmental toxicity as well as short-term public health damage.¹ To date, there have been various techniques to remove heavy metal ions such as chemical precipitation, oxidation/reduction sedimentation, ion exchange, membrane filtration and carbon adsorption.² 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.³ 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.⁴ 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.⁵ 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. Fe₃O₄-PEDOT core-shell nanoparticles (Fe₃O₄-PEDOT NPs) were prepared by inducing ferric cations onto the magnetic nanoparticles (MNPs) with a partial etching process followed by seeded polymerization. The

prepared Fe₃O₄-PEDOT NPs were employed as reusable and recoverable adsorbents to extract heavy metal ions in aqueous solution. The adsorption capability of Fe₃O₄-PEDOT NPs was measured as a function of metal uptake time and type of heavy metal ions.

The synthetic procedure for Fe₃O₄-PEDOT NPs is illustrated in Scheme 1. Fe₃O₄ NPs were synthesized by a chemical precipitation method according to a previous report.⁶ Poly(vinyl alcohol) (PVA) was employed as a stabilizer of Fe₃O₄ NPs and dissolved in 1000 mL of distilled water (3 wt%). 12.43 g of iron(III) chloride hexahydrate (FeCl₃·6H₂O) and 4.57 g of iron(II) chloride tetrahydrate (FeCl₂·4H₂O) 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 Fe₃O₄ NPs were precipitated as a black sediment. The resultant MNPs were purified repeatedly by magnetic field separation with excess distilled water. The prepared Fe₃O₄ 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 Fe₃O₄ NPs by hydrophobic interaction between Fe₃O₄ NPs and EDOT monomer. To generate ferric cations on the Fe₃O₄ NP surface, 30 mL of HCl (0.5 M) solution was introduced into the mixture. Then the irregular shaped Fe₃O₄ NPs were partially etched to form spherical shapes. Newly generated ferric cations were used as oxidizing agent for polymerization of EDOT monomers.⁷ Consequently, Fe₃O₄ NPs were coated and functionalized with PEDOT. The uniform and thin PEDOT shell was produced by seeded polymerization mediated with acid treatment. The Fe₃O₄-PEDOT NPs were applied as highly efficient separable and reusable materials for heavy metal ion removal.



Scheme 1 The fabrication procedure of Fe₃O₄-PEDOT NPs by seeded polymerization mediated with acidic etching.

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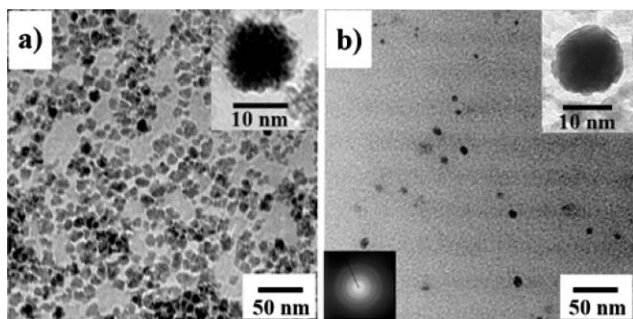


Fig. 1 TEM images of (a) Fe_3O_4 NPs, (b) Fe_3O_4 -PEDOT NPs. Inset images (a–b) are the magnified TEM images of Fe_3O_4 NP and Fe_3O_4 -PEDOT NP, and the electron diffraction pattern of Fe_3O_4 -PEDOT NP.

Fig. 1 shows transmission electron microscope (TEM) images of the pristine Fe_3O_4 NPs and Fe_3O_4 -PEDOT NPs. In Fig. 1(a), the pristine MNPs revealed an irregular shape and significant agglomeration after drying. The average diameter of the pristine Fe_3O_4 NPs was measured directly from TEM images and calculated as *ca.* 11 nm.⁸ Fig. 1(b) demonstrates the uniform and well-dispersed Fe_3O_4 -PEDOT NPs. The Fe_3O_4 -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), Fe_3O_4 NP is clearly encapsulated with a PEDOT shell. Fe_3O_4 -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 Fe_3O_4 NPs have high crystallinity and polycrystallinity.⁹

Fig. 2(a) represents diffuse-reflectance infrared Fourier transform (DRIFT) spectra of Fe_3O_4 NPs, Fe_3O_4 -EDOT NPs and Fe_3O_4 -PEDOT NPs. The DRIFT technique is an effective and powerful surface sensitive analysis.¹⁰ The characteristic peak of Fe_3O_4 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.¹¹ In order to confirm the adsorption of EDOT onto the Fe_3O_4 surface, the EDOT monomer was added to the Fe_3O_4 NP solution without acid treatment, and the Fe_3O_4 -EDOT 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.¹² The FT-IR spectrum of Fe_3O_4 -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 Fe_3O_4 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.¹² High intensity of this peak indicated that the PEDOT was highly doped. Fig. 2(b) exhibits the X-ray diffraction (XRD) pattern of Fe_3O_4 NPs and Fe_3O_4 -PEDOT NPs. In the case of both the pristine Fe_3O_4 NPs and Fe_3O_4 -PEDOT NPs, characteristic peaks of Fe_3O_4 were observed at $2\theta = 30$, 35 and 43° .¹³ However, the XRD pattern of Fe_3O_4 -PEDOT NP was broader than that of the pristine Fe_3O_4 NP according to the size reduction of Fe_3O_4 NP with acid treatment.¹⁴ Based on the peak at $2\theta = 35.68^\circ$, the mean size of Fe_3O_4 crystallites was calculated using the Scherrer equation. The value of *ca.* 11 nm of pristine Fe_3O_4 NP decreased to 9 nm after polymerization. These values are in good agreement with the average diameters of Fe_3O_4 NPs and Fe_3O_4 -PEDOT NPs in the TEM image. The magnetic properties of Fe_3O_4 -PEDOT NPs were investigated using a SQUID magnetometer. Fig. 2(c) demonstrates the hysteresis loop of Fe_3O_4 -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 (H_C) from the expanded hysteresis loop between -15 and $+15$ Oe was found to be 7 Oe. This H_C value is considerably higher than that of bulk iron ($H_C \approx 1$ Oe).¹⁵ The inset photograph indicates that Fe_3O_4 -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 adsorbents. The adsorption capacities for target heavy metal ions were measured in aqueous solution to examine the surface reactivity of Fe_3O_4 -PEDOT NPs. Ag^+ , Hg^{2+} and Pb^{2+} 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.¹⁶ Heavy metal ion uptake of Fe_3O_4 -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

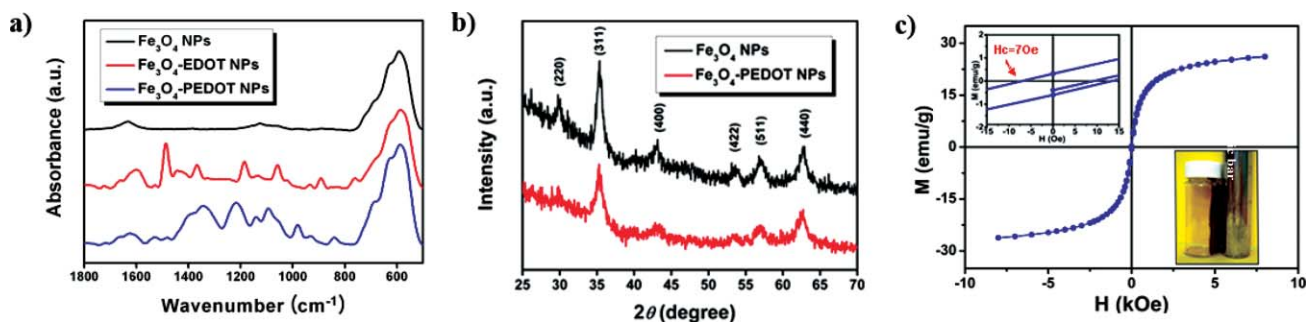


Fig. 2 (a) DRIFT spectra of Fe_3O_4 NPs, Fe_3O_4 -EDOT NPs and Fe_3O_4 -PEDOT NPs. (b) XRD pattern of Fe_3O_4 NPs and Fe_3O_4 -PEDOT NPs. (c) Hysteresis loop of Fe_3O_4 NPs and Fe_3O_4 -PEDOT NPs at 300 K with the expanded hysteresis loop (inset). The photograph indicates that Fe_3O_4 -PEDOT NPs in the aqueous solution can be attracted and arranged vertically by a magnetic bar.

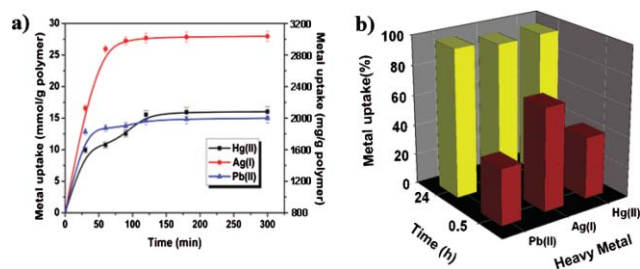


Fig. 3 Heavy metal ion uptakes of (a) Fe_3O_4 -PEDOT NPs as a function of different contact times and (b) fixed contact time: 0.5 and 24 h.

concentration of heavy metal ion was *ca.* 15 ppm. Based on the weight of PEDOT, the amount of Ag^+ , Hg^{2+} and Pb^{2+} 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 Fe_3O_4 NPs was approximately 7 times higher than that of chitosan-coated Fe_3O_4 NPs.¹⁷ 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 Fe_3O_4 -PEDOT NPs and abundant unpaired electrons of PEDOT shells.¹⁸ Fig. 3(b) displays the uptake of heavy metal ions after 0.5 and 24 h contact time with an excess amount of Fe_3O_4 -PEDOT NPs. Heavy metal ions were removed up to 95% after 24 h, whereas the adsorption rate was observed in the order of $\text{Ag}^+ > \text{Hg}^{2+} > \text{Pb}^{2+}$, in accord with cation radius, and interaction enthalpy values.¹⁹ Importantly, Fe_3O_4 -PEDOT NPs provide the convenient recovery of adsorbents in aqueous phase by use of a magnetic field. There was no loss of adsorption capacity and morphological change of Fe_3O_4 -PEDOT NPs in recycling tests (10 repeats). TEM analysis indicated that morphological change of Fe_3O_4 -PEDOT NPs does not occur after the acid treatment (1 h, 25°C). In addition, the acid-treated Fe_3O_4 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. Fe_3O_4 -PEDOT NPs could be considered as a potential candidate as an excellent reusable and recoverable adsorbent of heavy metal ions.

In conclusion, Fe_3O_4 -PEDOT NPs were fabricated using an acid-mediated seeded polymerization. Fe_3O_4 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^+ , Pb^{2+} and Hg^{2+}). 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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