Fabrication and biocompatible characterization of magnetic hollow capsules

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Abstract

Monodispersed Fe_3O_4/polypyrrole (PPy) hollow particles were synthesized via controllable in-situ deposition and polymerization techniques using poly(styrene-co-acrylic) (PSA) latex as template. Field-dependent magnetization plot illustrates that the capsules are superparamagnetic at 300 K. FTIR spectrum confirms that the myoglobin (Mb) molecule adsorbed on the surface of Fe_3O_4/PPy hollow particle essentially retains its native structure. Furthermore, direct electrochemistry of Mb can be realized on Fe_3O_4/PPy capsules modified pyrolytic graphite disk electrode, which indicates that the magnetic conductive polymer capsules can promote the electron transfer of protein.
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Functional microcapsules are of considerable interests for the current and potential applications as sub-micro-to-micrometer carrier for drugs, enzymes, DNA owing to their small size, large surface/inner volume, and tunable property [1]. To realize the controlled transfer of objects at the right moment, in the right place by exterior magnetic field, there is a trend to combine magnetic property with hollow structure [2]. In addition, conductive polymer, with its electrical conductivity and ion exchange capacity [3], has been intensively focused on due to the novel affinity with many organic and biological species [4]. Accordingly, protein-electroactive polymer surface interaction has been intensively studied [5]. Polypyrrole was confirmed to be a good binder in the planar electrochemical biosensors [6]. Chen and co-workers have characterized bovine serum albumin adsorption on the poly(ethylene glycol)-modified polyaniline [7].

Recently, conductive and ferromagnetic hollow microcapsules with polypyrrole (PPy) shell and Fe_3O_4 inner-wall were successfully accomplished via sequential processes of electrostatic attraction between negatively charged polystyrene (PS) latex and Fe_3O_4 nanoparticles, the polymerization of pyrrole and the dissolution of PS core [8]. While polyelectrolyte hollow capsules with 8 nm size magnetite nanoparticles as a shell constituent were prepared via similar route [9]. In this study, monodispersed Fe_3O_4/PPy hollow capsules (FPHCs) were fabricated via controllable in-situ

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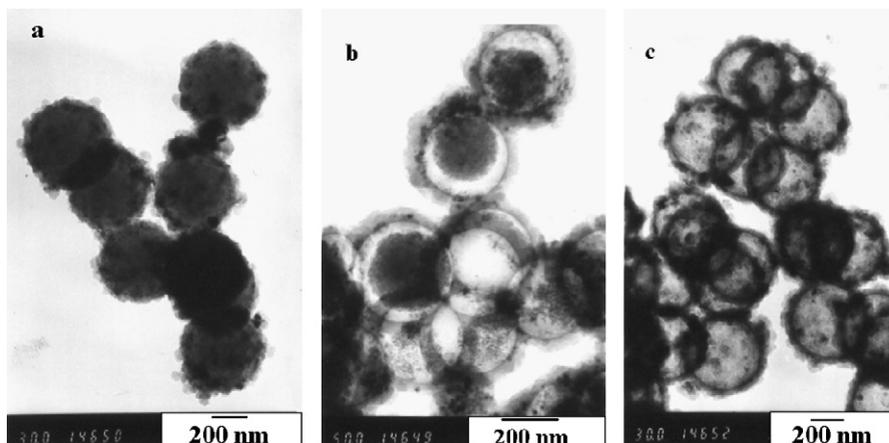*E-mail address:* haolingyun66@hotmail.com (L.Y. Hao).

Fig. 1. TEM images of PSA@Fe$_3$O$_4$/PPy spheres (a), PSA@air@ Fe$_3$O$_4$/PPy (b) and Fe$_3$O$_4$/PPy (c) capsules.

deposition and polymerization techniques by poly(styrene-co-acrylic) latex template. It was found that the horse heart myoglobin (Mb) molecules, adsorbed on the capsules, could retain naturally. Furthermore, directly electrochemical response of Mb could realize on the FPHCs modified electrode, indicating that the capsules could promote the electron transfer of the absorbed protein.

1. Experimental

PSA latex has been synthesized by emulsion co-polymerization in our group [10]. 0.01 mol/L Na$_2$SO$_3$ and 0.06 mol/L FeCl$_3$·6H$_2$O solutions were slowly dropped into the PSA emulsion. The reaction was carried out at 333 K for 4 h. After collected by a magnet, the product was washed then re-dispersed in ethanol containing poly(N-vinylpyrrolidone) (PVP) macromolecules by ultrasound. Pyrrole monomer (reagent grade, Fluka) was purified by vacuum distillation and stored below 277 K. Pyrrole monomer was injected into the emulsion then polymerized at 298 K for 12 h using FeCl$_3$·6H$_2$O as initiator. PSA@ Fe$_3$O$_4$/PPy composite particles were converted to Fe$_3$O$_4$/PPy hollow structures soaked in tetrahydrofuran (THF).

The pyrolytic graphite (PG, Advanced Ceramics, geometric area 0.16 cm^2) disk electrode, adsorbed by positively charged PDDA on the surface as precursor, was alternately immersed for 20 min in negatively FPHCs capsule water dispersion and positively Mb molecule solution (1 mg mL^{-1} at pH 5.0) with intermediate water washing and nitrogen stream drying.
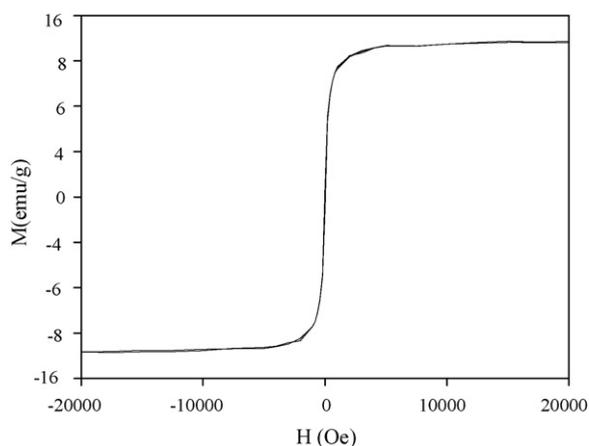

Fig. 2. Magnetic hysteresis loops of Fe$_3$O$_4$/PPy capsules at room temperature.
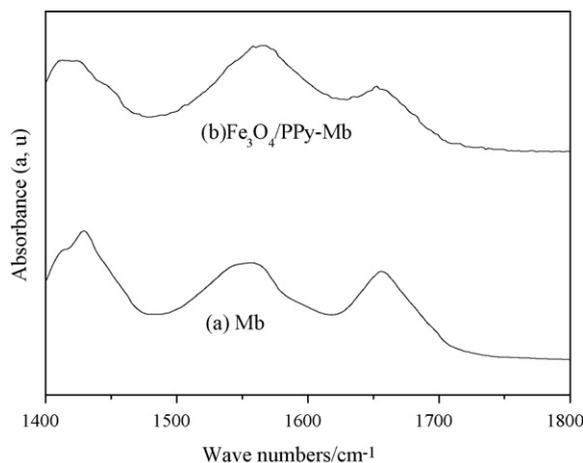
Fig. 3. FTIR spectra of pure Mb (a) and {Fe$_3$O$_4$/PPy–Mb} films (b).

2. Results and discussion

A reduction-co-precipitation approach was taken to deposit Fe$_3$O$_4$ nanoparticles directly on the surface of PSA latex.

$$6Fe^{3+} + Na_2SO_3 + 18NH_3 \cdot H_2O \rightarrow 2Fe_3O_4 \downarrow + SO_4^{2-} + 18NH_4^+ + 9H_2O$$

The as-prepared PSA–Fe$_3$O$_4$ particles saved as second templates to form PSA@Fe$_3$O$_4$/PPy composite core–shell structure. The chemical polymerization of pyrrole monomer were performed using Fe^{3+} ions as oxidant. It was important to pre-modify the surface of PSA–Fe$_3$O$_4$ particles by PVP macromolecules which could provide active sites to induce the polycationic PPy chains coating [11]. When the PSA cores were eroded by THF, PSA@Fe$_3$O$_4$/PPy composite particles were transformed to FPHCs. Clearly etching process of PSA cores was registered by TEM measurements (Fig. 1).

The coercivity of as-synthesized magnetites approaches to be 0 Oe, indicating that the obtained magnetite nanoparticles are superparamagnetic. Magnetization curves of the magnetic hollow spheres recorded with SQUID are illustrated in Fig. 2. Neither remanence nor coercivity was observed, indicating these magnetic particles produced are superparamagnetic and the single-domain magnetite nanoparticles remained in the polymer capsules.

Infrared absorption spectroscopy can provide information on the secondary structure of Mb immobilized on FPHCSs. The amide I and II bands of Mb in {Fe$_3$O$_4$/PPy–Mb} film are located at 1655 and 1562 cm^{-1}, respectively
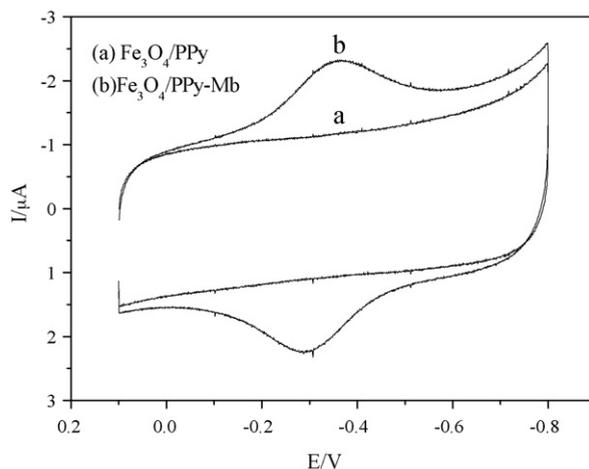
Fig. 4. CV curves of Fe$_3$O$_4$/PPy film (a) and Fe$_3$O$_4$/PPy–Mb film (b) in pH 7.0 buffers at scan rate is 0.2 V s^{-1}.

(Fig. 3b), which are almost same as that in the pure Mb films, indicating that Mb absorbed on the surface of magnetic core–shell particles essentially retains its natively secondary structure.

It is hard for Mb to realize direct electron transfer at the surface of bare PG electrode [12]. But when {Fe_3O_4/PPy–Mb} film was absorbed on the surface of electrode, a pair of well-defined nearly reversible peaks was observed at about −0.340 V, characteristic of Mb heme Fe^{III}/Fe^{II} redox couples (Fig. 4b) [13]. It indicates that the existence of Fe_3O_4/PPy can promote the electron transfer between Mb and electrode. The good biocompatibility of PPy with protein [14] may provide the possibility for FPHCSs as a potential candidate labeling probes in biological detection [15]. Actually, the application of FPHCSs in drug carriers has be found and will be reported elsewhere.

Acknowledgments

References

[1] C.Y. Gao, S. Leporatti, S. Moya, E. Donath, H. Mőwald, Chem. Eur. J. 9 (2003) 915.
[2] W.Q. Jiang, H.C. Yang, S.Y. Yang, et al. J. Magn. Magn. Mater. 283 (2004) 210.
[3] S. Cosnier, Biosens. Bioelectron. 14 (1999) 443.
[4] B. Saoudi, N. Jammul, M.M. Chehimi, et al. J. Colloid Interface Sci. 192 (1997) 269.
[5] Y.L. Li, K.G. Neoh, E.T. Kang, J. Colloid Interface Sci. 275 (2004) 488.
[6] S. Bousalem, S. Benabderrahmane, Y.Y.C. Sang, et al. J. Mater. Chem. 15 (2005) 3109.
[7] F. Zhang, E.T. Kang, K.G. Neoh, et al. Biomaterials 23 (2002) 787.
[8] H. Yang, W. Jiang, Y. Lu, Mater. Lett. 61 (2007) 2789.
[9] D.V. Andreeva, D.A. Gorin, D.G. Shchukin, G.B. Sukhorukov, Macromol. Rapid Commun. 27 (2006) 931.
[10] L.Y. Hao, Y. Zhou, W.Q. Jiang, et al. Chem. J. Chin. Univ. 22 (2001) 1945.
[11] I. Seo, M. Pyo, G. Cho, Langmuir 18 (2002) 7253.
[12] K. Chattopadhyay, S. Mazumdar, Bioelectrochemistry 53 (2001) 17.
[13] J.F. Rusling, Z. Zhang, in: R.W. Nalwa (Ed.), Handbook of Surfaces and Interfaces of Materials, vol. 5, Biomolecules, Biointerfaces and Applications, Academic Press, San Diego, 2001, pp. 33–71.
[14] H. Mattoussi, J.M. Mauro, E.R. Goldman, et al. J. Am. Chem. Soc. 122 (2000) 12142.
[15] W.C. Chan, S. Nie, Science 281 (1998) 2016.