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# Synthesis and properties of magnetite/polypyrrole core-shell nanocomposites and polypyrrole hollow spheres

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### ARTICLE INFO

### ABSTRACT

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### 1. Introduction

Core-shell nanocomposites of inorganic and organic material are of special interest due to the combination of several very different properties. A core-shell system composed of a metal oxide core which is covered by a conducting polymer shell is an example of this type of material. The inorganic compound, in this case iron oxide, provides magnetic properties and the organic compound, the conducting polymer, provides tuneable electronic conductivity. Examples are the core-shell systems magnetite@polypyrrole [1] and maghemite@polypyrrole [2]. The diameters of the core-shell particles range between 10 nm [3] and 100 nm [7]. The powder conductivity of this type of core-shell particles can accomplish 11 S/cm [1]. The core-shell particles with iron oxide cores are ferromagnetic [4].

This type of core-shell system mostly is synthesized in a twostep procedure. In the first step the iron oxide core, e.g. magnetite or maghemite, is formed. In the next step this core is covered by a conducting polymer, e.g. polypyrrole (PPy) [5]. Hollow spheres of a conducting polymer can be produced by dissolving the iron oxide core with acid [6].

Possible applications of this type of nanocomposites are electromagnetic shielding, electro-chemical display devices and

In this work a new route for preparation of core-shell nanoparticles composed of an iron oxide core and a polypyrrole (PPy) shell is explored. During the preparation procedure the initially formed iron(0) core is converted to magnetite. It is demonstrated, that the magnetite cores can completely be dissolved by reaction with acid. Furthermore the dissolution of iron oxide cores by electrolysis also is possible. The resulting PPy hollow spheres as well as the core-shell nanocomposites are electrochemically active. © 2010 Elsevier Ltd. All rights reserved.

> microwave-absorbing material. Due to the magnetic properties and the possibility of drug release by the PPy shell a further interesting application for this type of material is a combined chemo and hyperthermia cancer therapy [7].

> In this work a new synthetic route for core-shell systems is presented. The core-shell system is based on iron(0) particles which were covered by polypyrrole. This approach enables the combination of a highly reactive iron(0) core with a conducting polymer shell. Furthermore hollow spheres of PPy are formed by dissolution of the iron or rather iron oxide cores by treatment with acid or by electrochemical methods.

### 2. Experimental

# 2.1. Preparation of $Fe_3O_4$ @PPy nanocomposites and PPy hollow nanocapsules

Iron(II) sulfate FeSO<sub>4</sub>·7H<sub>2</sub>O (Fluka), iron(III) sulfate Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·5H<sub>2</sub>O (Fluka) sodium borohydride NaBH<sub>4</sub> (Sigma–Aldrich), sodium hydroxide NaOH (Merck), sulfuric acid (Merck) and cetylpyridinium bromide monohydrate CPB (Sigma–Aldrich) were of analytical grade and were used as received. Pyrrole (Aldrich) was distilled before use. The preparation and purification were made in deionised water (18 MΩcm).

In the first step iron nano-particles are synthesized by the reduction of  $FeSO_4$  in alkaline solution. This preparation method is based on the reports of Wang and Zhang [8], Zhang [9] and Shin et al. [10]. Wang et al. described the formation of iron nano-particles

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by reduction of iron(II) salts with NaBH<sub>4</sub>. Zhang reported that an excess of borohydride is needed to accelerate the synthesis reaction and ensure uniform growth of iron particles. NaOH is added because of the higher stability of iron in alkaline solution. Shin et al. described the use of cetylpyridinium salt as cationic surfactant in the preparation of gold nano-particles covered with polypyrrole.

30 ml of an aqueous solution of 0.08 mol NaBH<sub>4</sub> and 0.0625 mol NaOH were added drop-wise to 400 ml of a stirred aqueous solution of 0.016 mol FeSO<sub>4</sub>. Because of the air-sensitivity of iron particles which easily form iron oxides the solution were kept in an inert gas atmosphere (N<sub>2</sub>) at room temperature. A black magnetic precipitate was formed. The precipitate was washed several times with deionised water and dried in desiccator.

In the second step the iron particles are covered by CPB. 0.2 g particles are dispersed in 90 ml deionised water and separated from the precipitate of aggregated particles. Then 0.5 m mol CPB was added. The suspension was shaken for 30 min and stored for 3 h.

In the third step pyrrole was concentrated in the CPB shell at the surface of the iron particles. 7 m mol pyrrole was added to the suspension. The dispersion was shaken for 30 min and stored for 7 h.

In the fourth step the chemical polymerization of pyrrole was performed. 2 m mol of the oxidant  $Fe_2(SO_4)_3$  was added to the suspension. The suspension was shaken for 2 h and stored over night. The suspension slowly turned black.

The dissolution of the iron oxide core was achieved by treatment of the core–shell particles in 0.25 M sulfuric acid at room temperature for one day.

### 2.2. Characterization of the particles

The crystal structure of the nanoparticles was measured by X-ray diffraction analysis (XRD) of samples in powder form (Siemens Kristalloflex; Cu K<sub> $\alpha$ </sub>).

Iron ions in solution were detected by atomic absorption spectroscopy AAS (Perkin-Elmer 1100B).

TEM images are made with a Philips EM420 transmission electron microscope.

Electrochemical measurements were made by cyclic voltammetry (CV) with a three-electrode electrochemical cell (potentiostat: EG&G 263A). The working electrode was either a carbon fleece (SGL Carbon; volume 1 cm<sup>3</sup>; connected with a platinum wire) soaked with particles or a carbon paste electrode (BAS; MF-2010; cylindrical volume of 0.03 cm<sup>3</sup>). The carbon fleece was consecutively washed with ethanol and water in an ultrasonic bath. Then the dried fleece was soaked by a suspension of particles. The carbon paste electrode was prepared by mixing a particle suspension with an oil based carbon paste (BAS). The counter electrode was a platinum foil. Reference electrode was a Ag/AgCl/saturated KCl electrode. The measurements were made in a 0.25 mol  $l^{-1}$  Na<sub>2</sub>SO<sub>4</sub> solution in an inert gas atmosphere (N<sub>2</sub>) at room temperature.

### 3. Results and discussion

### 3.1. Preparation of nanocomposites and hollow spheres

The preparation steps of the core-shell nanocomposites and of the PPy hollow spheres are shown in Scheme 1. The preparation start with die reduction of iron(II) salt to get iron(0) nanoparticles ((a) in Scheme 1). In order to prevent immediate dissolution of the iron(0) particles the reaction is accomplished in alkaline solution. This favors the formation of a protective iron hydroxide and/or oxide layer at the surface of the iron particles. The iron nanoparticles show no peaks in XRD measurements. Also no peaks of iron oxides are observed in XRD. This result is in contrast to the XRD



Scheme 1. Synthesis of Fe<sub>3</sub>O<sub>4</sub>@PPy core-shell particles and PPy hollow spheres.

measurements reported by Nurmi et al., who described a broad reflex at  $2\theta = 44.7^{\circ}$  for iron(0) particles smaller than 1.5 nm [11].

CPB is added ((b) in Scheme 1) in order to minimize aggregation of the particles and also as a layer which concentrates pyrrole which is added in the next step ((c) in Scheme 1).

The oxidation of pyrrole to form PPy is accomplished by the addition of iron(III) salt as an oxidant ((d) in Scheme 1). The generated core–shell particles showed in XRD peaks at  $2\theta = 30.1^{\circ}$ ,  $35.4^{\circ}$ ,  $43.1^{\circ}$ ,  $53.5^{\circ}$ ,  $57.1^{\circ}$ ,  $62.7^{\circ}$  which correspond to the Bragg reflections of magnetite Fe<sub>3</sub>O<sub>4</sub> [3] 220, 311, 400, 422, 511 and 440, respectively. Magnetite was also identified by Mössbauer spectroscopy (results not shown here). It is not clear which reaction step leads to the conversion of iron(0) to crystalline magnetite. There are two possibilities: an oxidation due to contamination with oxygen during the addition of CPB and the following washing procedure or a parallel reaction to the oxidation of pyrrole favored by hydroxide groups at the surface of the iron particles in combination with the addition of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. Further studies to explain this conversion are in progress.

Fig. 1A shows TEM images of core-shell  $Fe_3O_4@PPy$  particles and Fig. 1B of PPy hollow spheres. The black dots are iron oxide cores and the grey spheres are polypyrrole shells. The diameters of the spherical core-shell particles are between 10 and 30 nm. The diameters of the spherical hollow spheres are less than 50 nm with broad size distribution due to aggregation.

The dissolving of the iron oxide core ((e) in Scheme 1) is achieved by sulfuric acid. AAS analysis showed an increasing concentration of iron ions after treatment of the core-shell particles with sulfuric acid. The comparison of TEM images (Fig. 1) of core-shell and hollow spheres shows that all iron oxide cores are dissolved. In contrast to the core-shell particles the hollow spheres exhibit no magnetic properties and XRD measurements of the hollow spheres showed no peaks. These results indicate a complete dissolving of the iron oxide cores.

## 3.2. Electrochemical characterization of nanocomposites and hollow spheres

Electrochemical switchable  $Fe_3O_4$ @PPy core-shell particles and PPy hollow spheres are of interest for technical applications, e.g. switchable ion exchangers or catalyst support. The electrochemi-



Fig. 1. TEM images of  $Fe_3O_4$ @PPy core-shell particles (A) and PPy hollow spheres (B).

cal properties of these particles are measured by CV. In Fig. 2, the CV of Fe<sub>3</sub>O<sub>4</sub>@PPy core-shell particles adsorbed on a carbon fleece electrode for different scan rates are shown. White et al. [12] assigned the anodic peak of magnetite at 0.69 V vs. Ag/AgCl/KCl<sub>sat</sub> to the oxidation of Fe(II) to Fe(III) leading to a conversion of magnetite to maghemite (Fe<sub>2</sub>O<sub>3</sub>) and to dissolved Fe<sup>2+</sup> ions (Eq. (1)).

$$3[Fe^{II}Fe_2^{III}]O_4 \rightarrow 4[Fe_2^{III}]O_3 + Fe^{2+} + 2e^{-}$$
(1)

The cathodic peak at 0.18 V vs. Ag/AgCl/KCl<sub>sat</sub> is due to the reduction of Fe(III) followed by a dissolution of magnetite (Eq. (2)).

$$[Fe^{II}Fe_2^{III}]O_4 + 8H^+ + 2e^- \rightarrow 3Fe^{2+} + 4H_2O$$
(2)

The dissolution of magnetite cores as a result of polarization is proofed by the loss of magnetic properties and decreasing peak



**Fig. 2.** Cyclic voltammogram of Fe<sub>3</sub>O<sub>4</sub>@PPy core-shell particles fixed in a carbon fleece electrode at different scan rates: (a) 10 mV/s, (b) 25 mV/s, (c) 50 mV/s, (d) 100 mV/s (measured in 0.25 moll<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> solution).



**Fig. 3.** (a) Cyclic voltammogram of PPy hollow spheres embedded in carbon paste electrode and (b) background current of the carbon paste (scan rate 50 mV/s; measured in 0.25 mol  $l^{-1}$  Na<sub>2</sub>SO<sub>4</sub> solution).

currents in multi sweep CV. This opens a new route to synthesize PPy hollow spheres by electrolysis.

Fig. 3 exhibits a CV of PPy hollow spheres in a carbon paste electrode. The hollow spheres show a capacitive like current curve. The current values are about 100 times higher compared to the background current. In the core–shell system the current caused by PPy is very low compared to the current caused by the redox reactions described by Eqs. (1) and (2). Therefore currents caused by redox reactions of PPy are not observable in Fig. 2.

The electrochemical experiments demonstrated that the core-shell and also the PPy hollow spheres are electrochemical active.

#### 4. Conclusions

In this work a new route for preparation of core-shell nanoparticles composed of an iron(0) core and a PPy shell is explored. However, during the preparation procedure the initial formed iron(0) is converted to magnetite. In case this oxidation could be avoided, highly reactive iron cores enclosed by a PPy shell can be realized. Corresponding studies are in progress.

The iron oxide cores can be completely dissolved by treatment with acid which is demonstrated by different analytical methods.

Electrochemical measurements demonstrated that core-shell particles and also the PPy hollow spheres are electrochemically active. Furthermore it is demonstrated, that the electrolytic dissolution of magnetite cores to produce PPy hollow spheres is possible.

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