Micelle-assisted synthesis of polyaniline/magnetite nanorods by in situ self-assembly process

Xuefeng Ding\textsuperscript{a,1}, Dongxue Han\textsuperscript{a}, Zhijuan Wang\textsuperscript{a}, Xiaoyu Xu\textsuperscript{a}, Li Niu\textsuperscript{a,\ast}, Qiang Zhang\textsuperscript{b,\ast}

\textsuperscript{a} State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China
\textsuperscript{b} Department of Chemistry, College of Science, Beijing Institute of Technology, Beijing 100081, PR China

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Abstract
Polyaniline/magnetite nanocomposites consisting of polyaniline (PANI) nanorods surrounded by magnetite nanoparticles were prepared via an in situ self-assembly process in the presence of PANI nanorods. The synthesis is based on the well-known chemical oxidative polymerization of aniline in an acidic environment, with ammonium persulfate (APS) as the oxidant. An organic acid (dodecylbenzenesulfonic acid, DBSA) was used to replace the conventional strong acidic (1 M HCl) environment. Here, dodecylbenzenesulfonic acid is used not only as dopant, but also as surfactant in our reaction system. So, DBSA can excellently control the morphology and size of PANI nanorods and magnetite particles. Magnetite particles were formed simultaneously during sedimentation, and the formed nanorods were also decorated by the particles. The resulting PANI/magnetite composites were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). It is found that PANI/magnetite nanorod composites have uniform size, superparamagnetism and a small mass fraction of magnetite, thermal stabilization even at a higher temperature.

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1. Introduction
Magnetic nanocomposite materials have attracted increasing attention because they offer the possibility of a new generation of nanostructure materials with diverse applications for immu

ity assay \cite{1}, separation and purification of biomolecules \cite{2,3}, extensive researches have been carried out to develop super-paramagnetic organic/inorganic hybrid spheres for biomedical applications, as carriers for targeted drug delivery \cite{4}, biomagnetic separations, and biosensors \cite{5–9}.

Polyaniline (PANI) is one of the most technologically important materials because of its environmental stability in a conducting form, unique redox properties, and high conductivity \cite{10}. PANI composite materials will possess the potential of a multitude of applications, such as in gas sensitivity, sensors, and inductors \cite{11–13}. In recent years, there has been increasing interest in the synthesis of conductive organic/inorganic nanocomposites. A few of works had been reported on the synthesis PANI/inorganic nanocomposites \cite{14–16}. Hopkins et al. chemically deposited polyaniline nanofibers directly onto a functionalized Au substrate \cite{17}. Yang’s group reported polyaniline nanofiber/gold nanoparticles device with a nonvolatile plastic digital memory \cite{18}. Kleinermanns et al. synthesized dispersed polyaniline (PANI)-Au composite particles with a core–shell structure by direct oxidation of aniline using AuCl\textsubscript{4} as the oxidant \cite{19}. Luca et al. described how to manipulate and build V\textsubscript{2}O\textsubscript{5}/polyaniline (PANI) nanocomposites at the molecular level via the layer-by-layer (LBL) technique \cite{20}. Recently, Ramirez and co-workers reported synthesis of a high magnetite fraction in superparamagnetic nanospheres by a three-step miniemulsion polymerization, but the as-synthesized nanospheres had a nonuniform magnetite fraction in each nanosphere \cite{21,22}. The fabrication of nanosized ferromagnetic magnetite/polyaniline nanoparticles (NCs) had been described

\textsuperscript{1} Also working in College of Chemistry, Jilin University, Changchun 130021, PR China.
by oxidatively polymerizing aniline using ammonium peroxodisulfate as oxidant \((\text{NH}_4)_2\text{S}_2\text{O}_8\) [23]. There, the obtained NCs with 20–30 nm average diameter were polydisperse, and show a core–shell structure. Aminabhavi et al. [24] reported novel high dielectric constant \(\text{Fe}_2\text{O}_3/\text{PANI}\) nanocomposites particles. Xu et al. [25] synthesized magnetite/poly(styrene-co-maleic anhydride) magnetic composite microspheres to immobilize amylase. Despite a few of papers concerning the preparation of magnetite nanocomposites and their applications in biomedicines, their practical application is still limited. Usually an external magnetic field was used to suspend paramagnetic particles in biomaterial applications, and the resulting materials were expected to do not agglomerate anymore after removal of the field. At present, the significant question is that magnetic particles can easily aggregate in the presence or even the absence of a magnetic field. Furthermore, the major difficulty lies in the interrelated effects in synthesis and assembly. Agglomeration of these particles originates from the strong interaction among the particles, which will diminish their magnetic properties. Therefore, it is of fundamental importance to develop a method to synthesize novel morphology composites with a high mass fraction of magnetite.

In this paper, we report a facile one-pot synthesis of PANI/magnetite nanorod composites through DBSA micelle-assisted synthesis by in situ self-assembly method. The presence of a high concentration of DBSA can effectively prevent the formation of larger particles, thereby producing nanometer-sized particles only. PANI nanorods and magnetite nanoparticles can form stable nanocomposites. PANI/magnetite nanorod composites have uniform size, superparamagnetism, thermal stabilization even at a higher temperature.

2. Materials and methods
2.1. Materials

Aniline was obtained from Beijing Xingjin Chemical Factory, and was distilled at a reduced pressure before use. DBSA (Anyang Xingya Chem. Ltd.) was used as the surfactant and dopant. Ammonium persulfate [APS, \((\text{NH}_4)_2\text{S}_2\text{O}_8\), Beijing Chemical Factory], Ferric chloride hexahydrate \((\text{FeCl}_3\cdot6\text{H}_2\text{O}, \text{Tianjin Bodi Chem. Factory})\), and Iron (II) sulfate heptahydrate \((\text{FeSO}_4\cdot7\text{H}_2\text{O}, \text{Tianjin Bodi Chem. Ltd.})\) were used as received. Water was distilled before use. And all other reagents were analytical grade and used without further purification.

2.2. Synthesis of DBSA-Doped PANI

The doped PANI was synthesized using the HCl as dopant. The DBSA-doped PANI with nanorods structure was synthesized as follow. In a typical experiment, 5 ml of DBSA and 0.093 g of purified aniline were dissolved in 50 ml of distilled water in a three-necked round-bottom flask at room temperature. DBSA were used as the surfactant and dopant. This solution was purged with nitrogen for 30 min and was quickly cooled to 0–4°C using the ice-water bath. Then, 1 ml of 1 mol/L aqueous solution of ammonium persulfate (used as the oxidant) was added under vigorous stirring. After a few minutes, a green precipitate formed. During the polymerization process, it was observed that the color of the solution changed to dark green. The whole polymerization reaction was carried out at 0–4°C for 5 h. Finally, the DBSA-doped PANI was obtained.

2.3. Synthesis of PANI/magnetite nanorods

The 10 ml of 1 mol/L \(\text{FeCl}_3\cdot6\text{H}_2\text{O}\) and 10 ml of 0.5 mol/L \(\text{FeSO}_4\cdot7\text{H}_2\text{O}\) aqueous solution were then rapidly added into the above polymerization reaction, respectively. This solution was purged with nitrogen to remove all traces of oxygen and was slowly heated up to 60°C under magnetic stirring. Then, 5 ml of 25% \(\text{NH}_3\cdot\text{H}_2\text{O}\) were rapidly added. The entire reaction system became black. After 5 h, the emulsion of PANI/magnetite nanorods were obtained. The resulting precipitate was centrifugated to separate the byproducts (inorganic salts, oligomers, etc.), washed/centrifugated with deionized water and methanol for several times. Finally, the pure dark precipitate was dried at 50°C under vacuum for 12 h.

2.4. Characterizations

The morphology of the nanocomposite particles was investigated by scanning electron microscopy (SEM) (JEOS JSM-5600). Thermogravimetric analysis (TGA) of the nanocomposites particles was performed on TGA/SDTA851\textsuperscript{\textregistered} analyzer at a heating rate of 10°C min\textsuperscript{-1} from 50–800°C under an atmosphere flow. X-ray diffraction analysis of the samples was carried out using an X-ray diffractometer (XRD, Model D/MAX2500, Rigaka) with Cu KR radiation.

3. Results and discussion

Fig. 1 illustrates the synthesis process of PANI/magnetite nanorods. The synthesis is based on the well-known chemical oxidative polymerization of aniline in an acidic environment, with ammonium persulfate as the oxidant. Here we use an organic acid (DBSA) instead of conventional strong acids (such as HCl). DBSA is used not only as the dopant, and also as the surfactant, which can control the morphology of PANI nanorods and magnetite particles. A scheme of the possible synthesis mechanism of the composite particles is shown in Fig. 1. By taking advantage of the micelle reaction system, we firstly obtained colloidal PANI doped with DBSA by the one-step chemical oxidative polymerization of aniline in the presence of micelles of DBSA. Micelle-assisted synthesis had previously been used widely to prepare polymer particles in which the particle sizes were controlled by the micelle “reactor” sizes [26]. The presence of a high concentration of DBSA can prevent the formation of larger particles, thereby only producing nanometer-sized particles. The PANI nanorods have nearly uniform diameters and lengths by using DBSA. Second, magnetite particles were easily formed inside micelle “reactor” during sedimentation process and decorated the nanorods through...
such reverse micelles. And PANI/magnetite nanocomposite materials could be readily obtained by such a self-assembly process in the presence of PANI nanorods. Moreover, it is worth noticing that the resulting PANI/magnetite nanocomposites can form stable nanorods with uniform size and high yields, and also show good superparamagnetism.

Fig. 2 gives typical SEM images of the resulting PANI/magnetite nanorods prepared by in situ self-assembly method. As shown in Fig. 2A, PANI/magnetite nanorods has an unique nanorods structure in shape, ca. 80 nm in diameter and ca. 600 nm in length. It is clear that a great number of nanoparticles adsorbed on the surface of the PANI nanorods. The small particles are magnetite nanoparticles derived from sedimentation. Furthermore, we further magnify the micrograph of Fig. 2A. The morphology of PANI/magnetite nanorods can be distinctly observed. As shown in Fig. 2B, there are several PANI/magnetite nanorods in this micrograph, but it includes all features of its regular forms. PANI/magnetite nanorods have nonslippery surface, which are surrounded by magnetite particles on the surface. The magnetite nanoparticles are spherical shape with 20 nm diameter.

X-ray diffraction (XRD) patterns of magnetite (curve a), PANI/magnetite (curve b), and PANI (curve c) nanoparticles were shown in Fig. 3. Scan range is ranging from 2θ = 20.00° to 80.00°. Curve a showed diffraction peaks at 2θ = 30.1°, 35.5°, 43.2°, 57.1°, 62.7°, which can be indexed to (220), (311), (400), (511), and (440) planes of magnetite, respectively. According to the reflection peaks in this figure, the main phases can be indexed as magnetite, which are in good agreement with the magnetite standard (Card No. PDF#01-1111). Curve c showed that PANI nanorods had amorphous structure. The XRD pattern of PANI/magnetite was shown as curve b. Clearly, the diffraction peaks of PANI/magnetite nanoparticles are similar to that for magnetite nanoparticles (as shown in curve a). But, the intensity of diffraction peaks from PANI/magnetite is quite different from that from pure magnetite nanoparticles. The results
confirmed that the PANI/magnetite nanorods had been obtained successfully.

Fig. 4 shows the magnetic hysteresis loop of PANI/magnetite nanorod sample. Magnetic property of the sample was measured at room temperature. The hysteresis loop of the PANI/magnetite nanorods shown in Fig. 4 revealed a ferromagnetic behavior with saturation magnetization (\(M_s\)) and coercivity (\(H_c\)) values of ca. 17.73 emu/g and 63.8 Oe, respectively. The \(M_s\) value of PANI/magnetite nanocomposites is much lower than those of the pure magnetite nanoparticles. As seen in Fig. 2A, the small particles were magnetite nanoparticles, which adsorbed on the surface of the PANI nanorods. PANI nanorods in such composite structure restricted the random movement and interactions of the magnetite particles. Therefore, we considered that the remarkable decrease of \(M_s\) values should be attributed to the formation of many magnetite particles absorbed on the surface of PANI nanorods. As shown in Fig. 4, the magnetic hysteresis loops of PANI/magnetite nanocomposites sample are S type curve through coordinate origin, no such typical hysteresis loop can be observed at this moment. The results indicate PANI/magnetite nanocomposites particles have the property of superparamagnetism. Moreover, it is revealed that the diameter of magnetite particles is very small and has spinelle structure. It is also consistent with our observation in TEM micrograph.

Fig. 5 shows the TGA curves of the pure PANI and PANI/magnetite nanocomposites under atmosphere flow at a heating rate of 10 °C min\(^{-1}\) from 50 to 800 °C. Three main inflection regions can be observed. The first region at lower temperatures (<200 °C) is originated from loss of absorption water and methanol. The second region at higher temperature (200–499 °C) is associated with the decomposition of PANI. As seen from the TGA curves, the rate of weight loss of PANI (curve a) is much fast, the residue of PANI is 44.06%; while the rate of weight loss of PANI/magnetite nanocomposites (curve b) is slower, the residue of PANI/magnetite nanocomposites is 64.23%. In the third region (499–682 °C), the rate of weight loss of PANI (curve a) is similar with that of PANI/magnetite nanocomposites. The final residue of PANI is 0.53%, while the final residue of PANI/magnetite nanocomposites is 9.30%. The results reveal that the inlaid magnetite nanoparticles retard the thermal decomposition of the polymer chain of PANI at higher temperature (<499 °C). The mass fraction of magnetite in PANI/magnetite nanocomposites is ca. 9%. And the mass fraction of magnetite can be further increased by increasing the thickness of magnetite coating.

4. Summary

In summary, PANI/magnetite nanorod composites were synthesized through DBSA micelle-assisted self-assembly method. PANI nanorods and magnetite nanoparticles can form stable nanocomposites. SEM images clearly show that the magnetite particles absorbed on the surface of each PANI nanorods are uniformly dispersed. The resulting PANI/magnetite nanorods show very good property of superparamagnetism due to its small mass fraction of magnetite.

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