

FERROFLUID CONTAINING SOLUBLE CONDUCTIVE POLYANILINE AND ITS  
FREESTANDING FILMS\*

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**Abstract** Ferrofluid containing highly conductive polyaniline (PANI) was prepared, in which soluble PANI solutions doped with 10-camphorsulfonic acid (CSA) and dodecyl benzenesulfonic acid (DBSA) were used as the basic solution and  $\text{Fe}_3\text{O}_4$  nanoparticles ( $d = 10$  nm) as the magnetic material. Moreover, the freestanding films of the resulting ferrofluid can be obtained by an evaporation method. The electrical and magnetic properties of the ferrofluid or its films can be adjusted through changing the content of PANI and  $\text{Fe}_3\text{O}_4$ . High saturated magnetization ( $\approx 30$  emu/g) and high conductivity ( $\approx 250$  S/cm) of the composite films can be achieved when the composite film contains 26.6 wt% of  $\text{Fe}_3\text{O}_4$ . In particular, it was found that the composite films exhibit a super-paramagnetic behavior ( $H_c = 0$ ) attributed to the size of  $\text{Fe}_3\text{O}_4$  particles on the nanometer scale.

**Keywords** Ferrofluid, Polyaniline, Electrical and magnetic properties, Soluble conducting polymers

## INTRODUCTION

Composites of conducting polymers containing magnetic nanoclusters have attracted considerable attention because they have unique magnetic, electrical and optical properties, as well as potential applications in electromagnetic interference shielding<sup>[1]</sup>, electrochromic devices<sup>[2]</sup> and nonlinear optical systems<sup>[3]</sup>. Recently, conducting polymers containing nanomagnets have been reported in the literature<sup>[4–11]</sup>. Yoneyama *et al.*<sup>[4]</sup> and Partch *et al.*<sup>[5]</sup>, for example, reported the incorporation of metal oxide particles into polypyrrole (PPy) during electropolymerization. However, aggregation of oxide particles is difficult to avoid. In addition, Nguyen and Diaz<sup>[6]</sup> reported that sodium pyrrole-*N*-propylsulfonate (PyS) was polymerized in the presence of  $\text{FeCl}_3$  and the polymerization product was converted into  $\gamma\text{-Fe}_2\text{O}_3/\text{poly (PyS)}$  by an oxidation reaction. The resulting black powdery nanocomposites, however, were insoluble and insulating ( $\sigma = 3.4 \times 10^{-7}$  S/cm). In our laboratory, Wan *et al.*<sup>[7, 8]</sup> also reported composites of polyaniline (PANI) containing nanomagnets (*e.g.*  $\text{Fe}_3\text{O}_4$ ,  $d = 14$  nm) prepared by a chemical method. However, it was found that the magnetic and electrical properties of the resulting composites strongly depended on the pH values of the reaction solutions. For example, the composites prepared in a basic condition showed higher magnetic properties, but were almost insulating ( $10^{-4}$  S/cm). After further investigation, composites of PANI and PPy containing nanomagnets (*e.g.*  $\gamma\text{-Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$ ,  $d = 10\text{--}100$  nm) with high saturated magnetization (10–40 emu/g) and conductivity ( $\approx 10^0$  S/cm) were prepared by a chemical method<sup>[9–11]</sup>. However, the electro the magnetic composites mentioned above are insoluble. More recently, Tang *et al.*<sup>[12]</sup> have developed a versatile process to prepare processable PANI freestanding films with high electromagnetic properties. In particular, Biden *et al.*<sup>[13]</sup> reported a ferrofluid containing PPy, in which the magnetic core (*e.g.*  $\text{Fe}_2\text{O}_3$ ) was coated with surfactants to form an anionic complexed shell. However, the room-

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temperature conductivity of the resulting composite film was quite low, only about  $2.5 \times 10^{-6}$  S/cm. Thus, the development of macroscopically processable ferrofluid with soluble conducting polymers as a basic solution remains a challenge. In this article, ferrofluid containing highly conductive PANI was prepared by using soluble PANI doped with 10-camphorsulfonic acid (CSA) and dodecyl benzenesulfonic acid (DBSA) as the basic solution and nanomagnet ( $\text{Fe}_3\text{O}_4$ ,  $d = 10$  nm) as the magnetic material. The electrical and magnetic properties of the resulting ferrofluid and its freestanding films were investigated as a function of the content of PANI and  $\text{Fe}_3\text{O}_4$ .

## EXPERIMENTAL

Aniline monomer was distilled under reduced pressure. Other reagents, such as ammonium peroxydisulfate (APS) as the oxidant, HCl, DBSA and CSA as the dopants, as well as  $\text{NH}_4\text{OH}$  as the dedopant, were used as received. The ferrofluid and its freestanding films were prepared as follows.

### *Synthesis of Soluble and Highly Conductive PANI Doped with CSA and DBSA*

Soluble PANI with high conductivity was synthesized as follows: PANI doped with HCl was first synthesized by a common method reported by MacDiarmid<sup>[14]</sup>, then it was converted into its emeraldine base form (EB) after being doped with 3 wt%  $\text{NH}_4\text{OH}$  for about 6 h. The resulting EB was further redoped with CSA by a method reported by Cao *et al.*<sup>[15]</sup> to prepare the soluble and conductive PANI-CSA/*m*-cresol solution.

In addition, a soluble PANI-DBSA/ $\text{CHCl}_3$  solution was also prepared through one-step polymerization<sup>[16]</sup>. Then the PANI-DBSA/ $\text{CHCl}_3$  solution was mixed with PANI-CSA/*m*-cresol solution under supersonic agitation for 0.5 h to prepare a mixed conductive PANI solution. The conductivity of the mixed solution can be adjusted by changing the content of PANI-CSA/*m*-cresol solution. In this way, soluble and highly conductive PANI dissolved in  $\text{CHCl}_3$  can be obtained when only 8 vol% of PANI-CSA/*m*-cresol solution was used.

### *Synthesis of Nanomagnetic Particles*

The magnetic nanoparticles were prepared according to the following procedures: 1.99 g  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (10 mmol) and 3.25 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (12 mmol) were dissolved in 10 mL and 20 mL of de-ionized water, respectively. The above two iron-salt solutions were combined and added dropwise to 200 mL of aqueous ammonia solution (0.6 mol/L) in 20 min with vigorous stirring. The pH value of the reaction mixture was kept within the range of 11 to 12 by the addition of a concentrated ammonium hydroxide solution. The resulting nanoparticles were separated and washed with distilled water three times and then further washed with THF three times and dried in air.

The resulting nanoparticles were confirmed to be  $\text{Fe}_3\text{O}_4$  by X-ray diffraction and their size was about 10 nm measured from transmission electron microscope (TEM) images.

### *Preparation of Ferrofluid and its Freestanding Films*

The nanomagnets ( $\text{Fe}_3\text{O}_4$ ) obtained were blended with a solution of DBSA (1.5 g) in 25 mL of chloroform with supersonic agitation at room temperature. After the larger particles were removed by centrifugation at 2900 rpm for about 20 min, a stable and homogeneous solution with 2.85 wt% of  $\text{Fe}_3\text{O}_4$  (presented as  $\text{Fe}_3\text{O}_4/\text{DBSA}/\text{CHCl}_3$ ) was obtained. Finally, quantitative amounts of PANI solutions and  $\text{Fe}_3\text{O}_4/\text{DBSA}/\text{CHCl}_3$  solutions were combined with stirring at room temperature. The resulting solutions then were cast onto glass plates to prepare the freestanding films by an evaporation method<sup>[17]</sup>.

### *Structural Characterization and Measurements of Electrical and Magnetic Properties*

UV-Vis, FTIR spectra and X-ray diffraction were used to characterize the molecular structures of the resulting composite films. UV-Vis spectra and FTIR spectra were recorded on an UV-3100 spectrometer and a Bruker Equinox 55 spectrometer, respectively, while X-ray diffraction was obtained on a RINT 2000 Wilder-angle goniometer. The morphology of the materials was examined through TEM (Hitachi-9000) and scanning electron microscopy (SEM, Hitachi-530). Magnetization at different applied magnetic fields was measured at room temperature by an extracting sample magnetometer (Neel Laboratory CF-1). The conductivity at room

temperature was measured by a standard four-probe method with a Keithley 196 System DM digital multimeter and an Advantest R6142 programmable DC voltage/current source.

## RESULTS AND DISCUSSION

### *Synthesis of Ferrofluid and its Freestanding Films*

It is well known that ferrofluid is a stable micellar solution, which consists of magnetic nanoparticles, a basic solution and a surfactant. It has been demonstrated that the surfactant is a key constituent for a stable ferrofluid. In general, the surfactant should function<sup>[18]</sup>: (1) to prevent the oxidation of nanomagnets; (2) to improve their miscibility with the basic solution; (3) to prevent the aggregation of the nanomagnets caused by Van der Waals forces, and (4) to decrease the static magnet force of the internanomagnets.

In this study, DBSA was used as a surfactant.  $\text{Fe}_3\text{O}_4$  particles were coated with DBSA before being incorporated into the polymer matrix of PANI doped with CSA and DBSA. At the same time, DBSA as a proton acid can be combined with oxygen ions on the surface of the magnetic nanoparticles to release water molecules, leading to the coating of magnetic nanoparticles in a micelle-like fashion. Usually, water or organic solvent is used as a basic solution for a ferrofluid, so the common ferrofluids are insulating. In our study, however, soluble and highly conductive PANI doped with CSA and DBSA was used as a basic solution, thus the ferrofluid was conductive. In other words, the resulting ferrofluid has both electrical and magnetic properties.

In general, PANI-CSA shows high conductivity ( $\approx 400 \text{ S/cm}$ )<sup>[15]</sup> in the presence of *m*-cresol. *m*-Cresol is a solvent with high boiling point, so it is difficult to expell from the film. Although the conductivity of PANI-DBSA films cast from  $\text{CHCl}_3$  is lower than that of PANI-CSA ( $\approx 10^0 \text{ S/cm}$ )<sup>[16]</sup>,  $\text{CHCl}_3$  is a low boiling point solvent. In this study, a soluble PANI doped with a mixed dopant (CSA and DBSA) was prepared, which can be soluble in  $\text{CHCl}_3$ . Moreover, it was found that the conductivity of PANI film doped with CSA and DBSA is as high as that of PANI-CSA film when only 10 vol% of PANI-CSA/*m*-cresol solution was used. So it is expected that the soluble PANI-CSA molecules bestow the high conductivity on the mixed PANI solution. Moreover, the freestanding films of the resulting ferrofluid can be prepared easily by an evaporation method. In particular, the electrical and magnetic properties of the ferrofluid and its composite films can be adjusted by changing the content of PANI-CSA/*m*-cresol solution and  $\text{Fe}_3\text{O}_4$  nanoparticles.

## ELECTRICAL AND MAGNETIC PROPERTIES

The influence of CSA content on the conductivity of freestanding PANI films is shown in Fig. 1. The conductivity of PANI-CSA films cast from *m*-cresol increases with increasing CSA content up to a CSA/PANI (EB) ratio of 2.0 and then decreases. The maximum conductivity at room temperature is about 300 S/cm, which is consistent with the conductivity reported by MacDiarmid<sup>[19]</sup>. The conductivity is much higher than that of PANI doped with  $\text{HCl}$ <sup>[14]</sup> due to the fact that the conformation changes from "compact coil" to "expanded coil" because of the secondary doping of *m*-cresol<sup>[19]</sup>. The secondary doping effect was also verified by UV-Vis absorption spectra as shown in Fig. 2. As one can see, all samples have a polaron band at 900 nm with a free carrier tail, which is consistent with MacDiarmid's suggestion<sup>[19]</sup>. Moreover, The "compact coil" to "expanded coil" conformation transition has been further confirmed by the interaction of PANI chains in clay particles upon secondary doping<sup>[20]</sup>.

Figure 3 shows the effect of the content of PANI-CSA/*m*-cresol solution on the conductivity of the PANI-DBSA/PANI-CSA films. It is noted that the conductivity was as high as 202 S/cm when the content of PANI-CSA was higher than 8 vol%. It was much higher than that of PANI doped with DBSA<sup>[16]</sup>. Based on the discussion above, it is expected that the "compact coil" to "expanded coil" transition caused by the secondary doping may be responsible for the high conductivity of PANI-DBSA/PANI-CSA films.

The influence of the content of  $\text{Fe}_3\text{O}_4$  nanomagnets on the conductivity of the composite films is depicted in Fig. 4. It was found that the conductivity decreased with increasing content of  $\text{Fe}_3\text{O}_4$ . It decreased to 170 S/cm when the content of  $\text{Fe}_3\text{O}_4$  was 47.5 wt%. The decrease in conductivity may be due to partial blockage of the

conductive path by the  $\text{Fe}_3\text{O}_4$  nanoparticles embedded in the PANI matrix. Nevertheless, composite films with relatively high saturated magnetization and room-temperature conductivity were obtained.

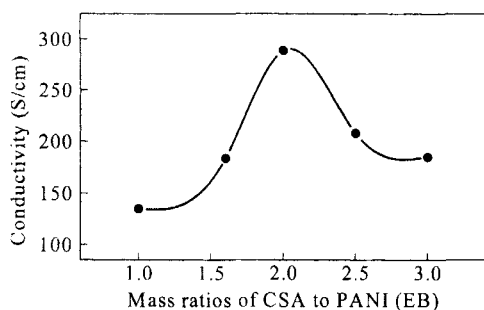


**Fig. 1** Room-temperature conductivity of PANI-CSA films with different mass ratios of CSA to PANI (EB)

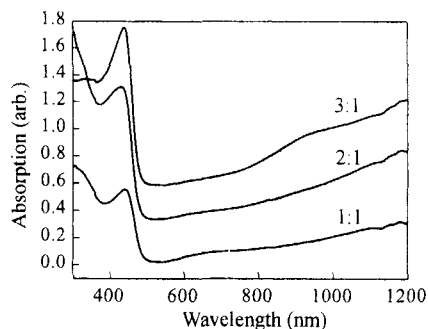


**Fig. 2** UV-Vis spectra of PANI-CSA films with different mass ratios of CSA to PANI (EB)

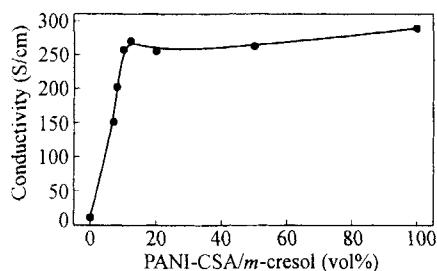


**Fig. 3** Influence of the volume content of PANI-CSA/m-cresol solution on the room-temperature conductivity of the PANI mixture films

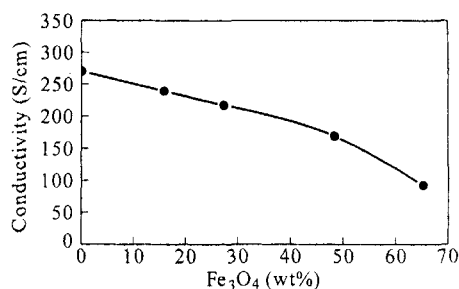


**Fig. 4** Influence of the weight content of  $\text{Fe}_3\text{O}_4$  on the room-temperature conductivity of the PANI composite films

For the composite film with 26.6 wt% of  $\text{Fe}_3\text{O}_4$ , the magnetization at different magnetic fields was measured at room temperature (Fig. 5). Its saturated magnetization ( $M_s$ ), remnant magnetization ( $M_r$ ) and coercive force ( $H_c$ ) were estimated to be  $M_s = 30 \text{ emu/g}$ ,  $M_r = 0$  and  $H_c = 0$ , respectively. No hysteresis loop (*i.e.*  $M_r = 0$  and  $H_c = 0$ ) was observed, indicating a superparamagnetic behavior due to nanomagnets. This is a typical characteristic for a ferrofluid.

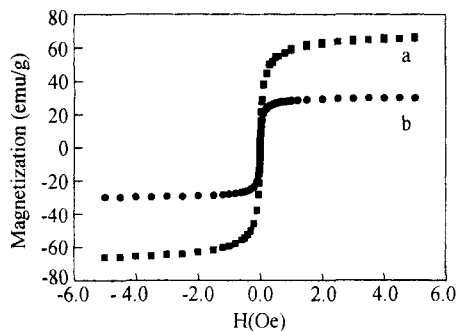


**Fig. 5** Dependence of the magnetization with the applied magnetic field at room temperature (a)  $\text{Fe}_3\text{O}_4$  nanoparticles, (b) the composite film (26.6 wt%  $\text{Fe}_3\text{O}_4$ )

### Structural Characterization of the Composite Films

The SEM and TEM images of  $\text{Fe}_3\text{O}_4$  nanomagnets and the composite films are shown in Fig. 6. Figure 6(a) shows that  $\text{Fe}_3\text{O}_4$  particles are granular in shape and their diameters are about 100–150 nm. TEM measurements

prove that these granules are solid and consist of some smaller granules with an average diameter of  $\approx 10$  nm. It is expected that the intermolecular interactions make the  $\text{Fe}_3\text{O}_4$  nanoparticles cluster into some larger granules. The crystallinity of  $\text{Fe}_3\text{O}_4$  is confirmed by its electron diffraction pattern as shown in Fig. 6(b). The SEM images of the composite films are also ball-like (Fig. 6c), indicating that  $\text{Fe}_3\text{O}_4$  particles were covered with PANI-CSA and PANI-DBSA.

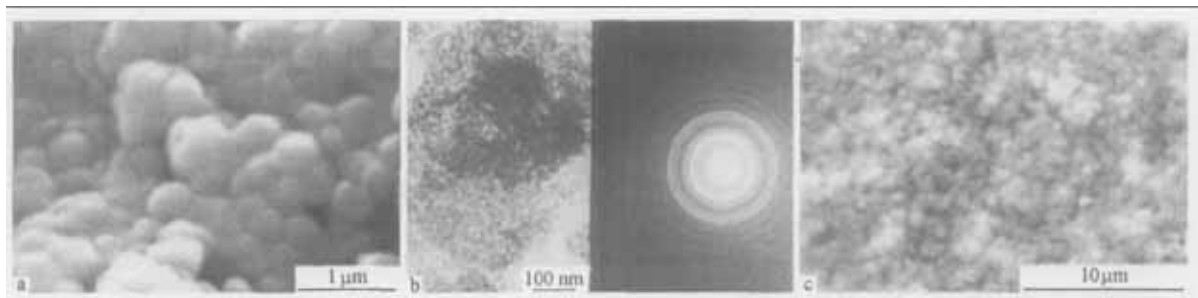


**Fig. 6** SEM and TEM images of  $\text{Fe}_3\text{O}_4$  nanoparticles and the composite films (a)  $\text{Fe}_3\text{O}_4$  SEM, (b)  $\text{Fe}_3\text{O}_4$  TEM and (c) SEM of the composite films

Except for the characteristic peaks of PANI doped with CSA and DBSA, the FTIR spectra of the composite films also show an obvious band at  $550\text{ cm}^{-1}$ , which belongs to iron oxide<sup>[18]</sup>. This proves that  $\text{Fe}_3\text{O}_4$  particles have been incorporated into the composite films.

The influence of the content of  $\text{Fe}_3\text{O}_4$  on the X-ray scattering patterns of the composite films is shown in Fig. 7. The diffraction peaks of the magnetic nanoparticle synthesized in this study were measured to be  $2\theta = 30.10^\circ$  ( $d = 0.297\text{ nm}$ ),  $35.42^\circ$  ( $d = 0.253\text{ nm}$ ),  $43.20^\circ$  ( $d = 0.209\text{ nm}$ ),  $53.48^\circ$  ( $d = 0.171\text{ nm}$ ),  $56.94^\circ$  ( $d = 0.162\text{ nm}$ ), and  $62.54^\circ$  ( $d = 0.148\text{ nm}$ ), which are in very good agreement with these of  $\text{Fe}_3\text{O}_4$ <sup>[21]</sup>. For the PANI mixture films, two broad peaks centered at  $2\theta = 15^\circ$  and  $26^\circ$  were observed, which are consistent with those of PANI-DBSA and PANI-CSA<sup>[19]</sup>. For the composite films, however, both the broad and sharp peaks corresponding to those of PANI and  $\text{Fe}_3\text{O}_4$ , respectively, were observed. And the intensity of those sharp peaks increases with increasing content of  $\text{Fe}_3\text{O}_4$  in the composite films.

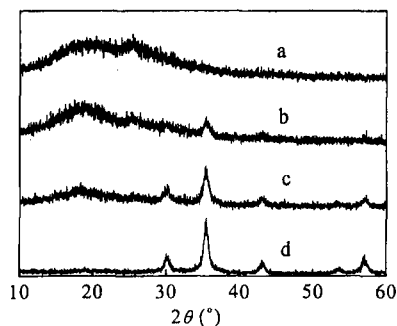


**Fig. 7** X-ray diffraction patterns of  $\text{Fe}_3\text{O}_4$  nanoparticles and PANI composite films

(a) PANI mixture film (12.2 vol% PANI-CSA), (b) PANI/ $\text{Fe}_3\text{O}_4$  composite film (26.6 wt%  $\text{Fe}_3\text{O}_4$ ), (c) PANI/ $\text{Fe}_3\text{O}_4$  composite film (64.4 wt%  $\text{Fe}_3\text{O}_4$ ), (d)  $\text{Fe}_3\text{O}_4$

## CONCLUSIONS

Ferrofluid and its freestanding films with electro-magnetic function were successfully prepared. The ferrofluid was composed of soluble conductive PANI doped with CSA and DBSA as the basic solution, with  $\text{Fe}_3\text{O}_4$  as a nanomagnet and DBSA as a surfactant. The results of SEM, TEM, UV-Vis, FTIR and X-ray diffraction studies

indicate that PANI in the composites, resulting in the electrical conductivity of the ferrofluid, is identical to the emeraldine salt form of PANI. The electrical and magnetic properties of the ferrofluid and its films can be adjusted by changing the content of PANI and nanomagnetic particles. However, all samples show a superparamagnetic behavior ( $H_c = 0$ ) due to the magnetic particles in nanometer scale.

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