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Processible nanomaterials with high conductivity and magnetizability. Preparation and properties of maghemite/polyaniline nanocomposite films*

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Abstract: A versatile process employing anionic surfactants has been developed for the preparation of processible nanocomposite films with electrical conductivity and magnetic susceptibility. Maghemite (γ-Fe_2O_3) nanoclusters (~10 nm in size) are coated with 4-dodecylbenzenesulfonic acid, and polyaniline (PAn) chains are doped with 10-camphorsulfonic acid. The coated nanoclusters and doped polymers are soluble in common solvents, and casting the solutions readily gives free-standing nanocomposite films with nanocluster contents as high as ~50 wt %. The γ-Fe_2O_3/PAn nanocomposites show high conductivity (82–237 S cm^{-1}) and magnetizability (up to ~35 emu/g γ-Fe_2O_3).

INTRODUCTION

The development of nanostructured materials is a topic of great current interest [1]. Quantum states in nanomaterials are size-dependent, leading to novel mesoscopic properties that are sometimes dramatically different from those of their atomic and bulk counterparts [2]. Nanomagnets, for example, show unusual phenomena such as superparamagnetism and quantum tunneling of magnetization. Magnetic nanoclusters are, however, inorganic entities and cannot be processible by macroscopic techniques. To realize the full potential of technological applications of magnetic nanomaterials, it is highly desirable to endow them with macroscopic processibility. Because of the excellent tractability of organic polymers, much effort has been directed toward the development of methodologies and processes for the incorporation of magnetic nanoclusters into polymeric matrices. We are interested in the integration of magnetic nanoclusters with conducting polymers because the resultant nanocomposites may possess unique magnetic and electrical properties. In this work, we developed a process for the fabrication of processible nanocomposites of γ-Fe_2O_3 nanoclusters and polyaniline (PAn). The γ-Fe_2O_3/PAn nanocomposite films have been found to be both electrically conductive and magnetically susceptible.

FABRICATION OF NANOCOMPOSITE FILMS

Because of the stronger preference of Fe^{2+} ions for octahedral interstices than Fe^{3+} ions, we used an iron salt mixture of $FeCl_3$ and $FeCl_2$ to facilitate the packing of the iron cations in the spinel structure of

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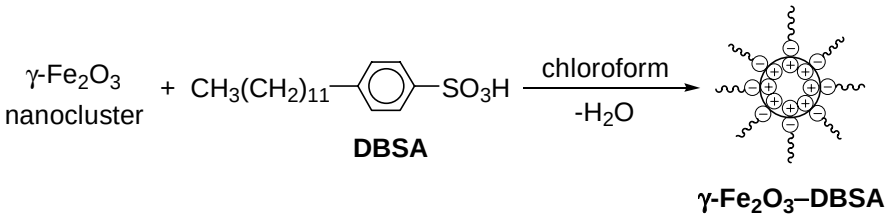

Fig. 1 Coating maghemite (γ-Fe_2O_3) nanoclusters with surfactant molecules of 4-dodecylbenzenesulfonic acid (DBSA).

γ-Fe_2O_3 [3]. The obtained γ-Fe_2O_3 nanoclusters are almost spherical in shape, whose average diameter are estimated by transmission electron microscopy to be ~10 nm.

Before being incorporated into a conducting polymer matrix, the nanoclusters are coated with surfactant molecules. The surfactant coating on the nanoclusters may increase their solubility in organic solvents, shield them from the attack of conducting polymer dopants, prevent them from aggregation during the film preparation process, improve their miscibility with organic polymers, and enhance the quality of the resultant nanocomposite films. The nanoclusters are prepared in the basic conditions (pH = 11–12), and their surfaces are negatively charged with the oxygen ions. When the nanoclusters are added into a dilute solution of DBSA, the protons of the acid combine with the oxygen ions on the surfaces of the nanoclusters, releasing water molecules (Fig. 1). The oxygen-deficient shells are positively charged, and the negatively charged sulfate ions are attracted by the positive ions on the cluster shells via ionic interaction, thus coating the nanoparticles in a micelle-like fashion.

PAn has often been referred to as one of the most promising conducting polymers for commercialization [4]. PAn is easy to prepare and is inexpensive. Most importantly, especially to this project, the doped PAn is readily soluble, chemically stable, and electrically conductive [5]. In this work, we chose PAn as a conducting polymer matrix and doped it with CSA (Fig. 2). The doping is realized by the protonation of the imine nitrogen of the PAn emeraldine base.

Both the coated γ-Fe_2O_3 nanoclusters and the doped PAn chains are soluble in common organic solvents, which enables ready fabrication of nanocomposite films by simple static casting of the

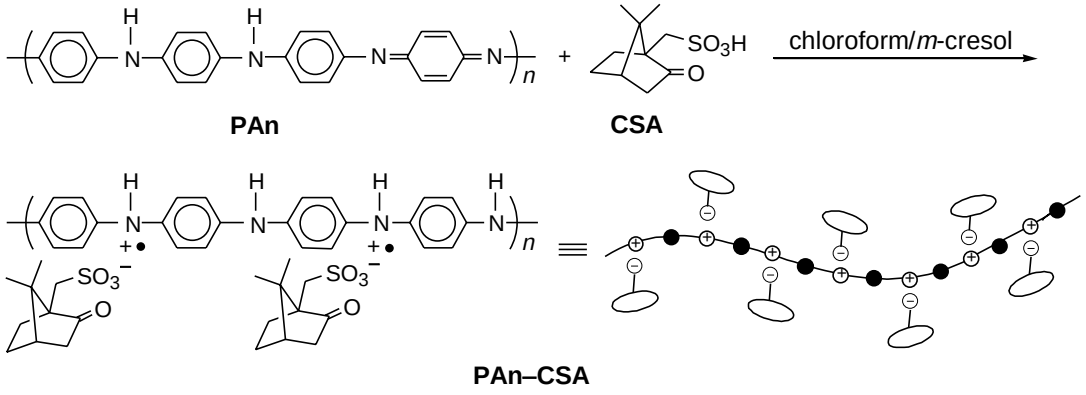

Fig. 2 Doping polyaniline (PAn) chains with surfactant molecules of 10-camphorsulfonic acid (CSA).

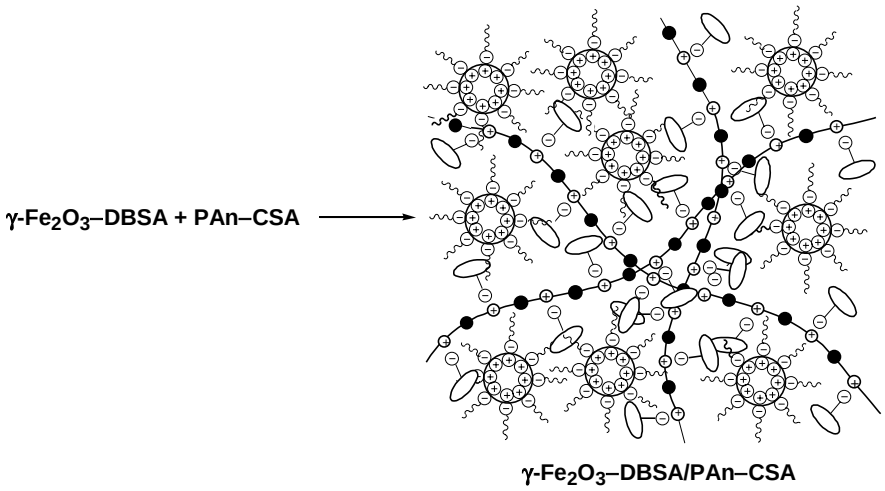

Fig. 3 Fabrication of maghemite/polyaniline nanocomposite films by static casting of homogeneous solutions of DBSA-coated γ-Fe_2O_3 nanoclusters and CSA-wrapped PAn chains.

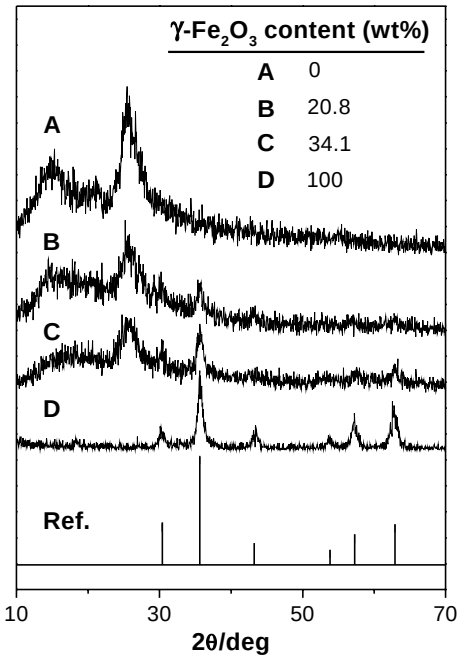

Fig. 4 X-ray diffraction patterns of (A) polyaniline powder, (B, C) γ-Fe_2O_3/PAn nanocomposite films, and (D) γ-Fe_2O_3 nanocluster powder. The vertical lines are the reference data for the γ-Fe_2O_3 standard.

nanoclusters/polymer solutions (Fig. 3). Free-standing films can be obtained when the nanocluster contents are below 50 wt %, above which, the films become too fragile to be of any practical value.

Figure 4 shows X-ray diffraction patterns of the γ-Fe_2O_3/PAn nanocomposite films, as well as those of the parent PAn powders and the γ-Fe_2O_3 nanoclusters. The pure PAn powders exhibit a few broad peaks at 2θ angles around 15°, 21°, and 26°. When the nanoclusters are embedded in the polymer

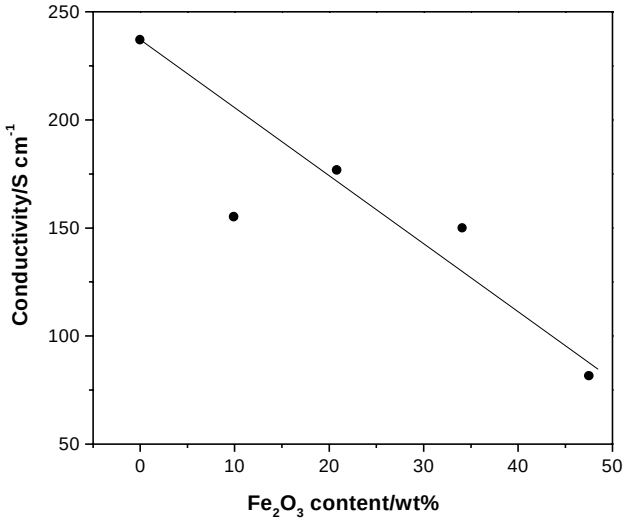

Fig. 5 Effect of γ-Fe_2O_3 content on conductivity of γ-Fe_2O_3/PAn nanocomposite films.

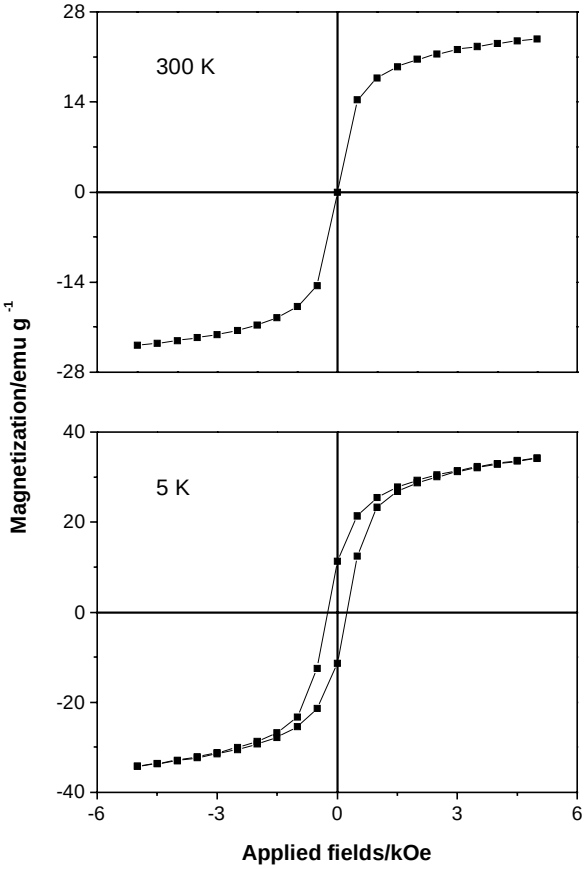

Fig. 6 Magnetization versus applied field plots at 300 and 5 K for a γ-Fe_2O_3/PAn nanocomposite film containing 20.8 wt % of γ-Fe_2O_3 nanoclusters.

matrix, a few new reflection peaks appear in the high-angle region. The average diameters of the nanoclusters associated with the strongest (311) reflection of γ-Fe_2O_3 at 2θ = 35.6° (Fig. 3, curve D) is estimated from Scherrer's equation to be ~12.0 nm, in good agreement with the average size (~10 nm) obtained from the transmission electron microscopy measurements.

CONDUCTIVITY AND SUPERPARAMAGNETISM

As shown in Fig. 5, the conductivity of the nanocomposite films decreases with increasing γ-Fe_2O_3 content. While the parent PAn–CSA film (containing no nanoclusters) cast from the chloroform/*m*-cresol solution is very conductive (237 S cm^{-1}), the conductivity of the nanocomposite film with a γ-Fe_2O_3 content of 20.8 wt % decreases to ~180 S cm^{-1}. Although the γ-Fe_2O_3 content of a γ-Fe_2O_3/PAn nanocomposite film is as high as 47.5 wt %, its conductivity is still 82 S cm^{-1}. This is much higher than that (~10^{-4} S cm^{-1}) of the Fe_3O_4/PAn nanocomposite prepared by Wan and Li [6] and also higher than that (1.9 S cm^{-1}) of the γ-Fe_2O_3/poly(pyrrole) nanocomposite prepared by Bidan et al. [7].

At 300 K, the plots of magnetization versus applied field of the nanocomposite film with a γ-Fe_2O_3 content of 20.8 wt % are perfectly superimposable as the field is cycled between ±5 kOe (Fig. 6). There is no hysteresis at room temperature. Both remanence and coercivity are zero, consistent with the superparamagnetism and the nanodimension of the clusters. As the temperature is lowered to 5 K, the magnetization increases and a hysteresis loop appears; the system is now left with a net remanence magnetization that decays very slowly compared to the time scale of the measurement.

CONCLUSION

In summary, in this study, we have developed a simple process for the fabrication of processible nanocomposite materials. Utilizing the anionic surfactants, the γ-Fe_2O_3/PAn films are readily prepared by a simple macroscopic processing technique of static casting. The nanocomposite films show electrical conductivities of 82–237 S cm^{-1}, much higher than those of the iron oxide/ conducting polymer nanocomposites reported in the literature (3.4×10^{-7}–1.9 S cm^{-1}) [8,9]. The γ-Fe_2O_3/PAn films are superparamagnetic, exhibiting no hysteresis loop at room temperature. The nanocomposites thus have the following noteworthy features: they are macroscopically processible, electrically conductive, and magnetically susceptible.

ACKNOWLEDGMENTS

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