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FERROMAGNETIC RESPONSE OF NANOCOMPOSITES BASED ON POLYANILINE AND TiO₂ NANOCRYSTALS OF DIFFERENT SHAPE

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ABSTRACT

Ferromagnetic polyaniline (PANI)/TiO₂ nanocomposites were synthesized by the oxidative polymerization of aniline with ammonium peroxydisulfate (APS), in the presence of colloidal TiO₂ nanoparticles and TiO₂ nanotubes, without added acid. The morphological, magnetic and structural properties of the PANI/TiO₂ nanocomposites were studied by SEM microscopy, SQUID magnetometer and FTIR spectroscopy. The electrical conductivity of synthesized nanocomposites was $\sim 10^{-3} \text{ Scm}^{-1}$. The room temperature ferromagnetic response significantly depends on shape of TiO₂ nanoparticles.

INTRODUCTION

Polyaniline (PANI) is one of the most important conducting polymers, due to its simple synthesis, unique doping/dedoping chemistry, low cost, high conductivity, and excellent environmental stability [1]. The crystallinity, solubility, thermal stability, electrical, magnetic and optical properties of PANI mainly depend on its oxidation state and protonation degree [2]. Depending on synthetic and isolation procedure, polyaniline contains various proportions of diamagnetic $[(-B-NH^+-Q-NH^+)_n(-B-NH-)_n](A^-)_{2n}$ and paramagnetic units $[(-B-NH^+-B-NH-)_n](A^-)_n$, where B, Q and A- denote a benzenoid ring, quinonoid ring and dopant anion, respectively. Magnetic properties of PANI and its derivatives have been extensively studied because they can provide important data on charge-carrying species and unpaired spins. It has been found that the magnetic susceptibility of doped PANI is strongly influenced by the manner of polymer preparation (e.g., doping level, dopant type), and measuring conditions (temperature, applied magnetic field) [3]. Although a numerous

studies on magnetic properties of PANI are published just a few of them reported on ferromagnetic behavior [4]. In this work, conducting PANI/TiO₂ nanocomposites have been prepared by the chemical oxidative polymerization of aniline in aqueous dispersions of TiO₂ nanoparticles and nanotubes, without added acid. Synthesized PANI/TiO₂ nanocomposites were studied by SEM analysis, FTIR spectroscopy and electrical conductivity measurements. In order to investigate the influence of the shape of TiO₂ nanoparticles on ferromagnetic response of PANI, magnetic susceptibility measurements were performed at room temperature.

EXPERIMENTAL

The colloidal dispersion of TiO₂ nanoparticles ($d \approx 4.5$ nm) was prepared by acid hydrolysis of TiCl₄ [5]. Titania nanotubes (outer and inner diameters 10 and 7 nm and length of few 100 nm) were synthesized by a hydrothermal process in alkaline medium [6]. PANI/TiO₂ nanocomposites were prepared by following procedures: the aqueous solution of APS (0.4 M, 25 ml) was poured into the aqueous solution of aniline (0.32 M, 25 ml). Thereupon dispersion of TiO₂ colloidal nanoparticles/nanotubes in water (50 ml) was added into the aniline/APS solutions. The reaction mixture was stirred for 3 h at room temperature. The precipitated PANI/TiO₂ nanocomposite was collected on a filter, rinsed with ethanol acidified with sulfuric acid (5×10^{-3} M), and dried in vacuum at 60 °C for 3 h. The mole ratios of aniline to TiO₂ nanoparticles and nanotubes were 80, (PT-80 and PT-NT-80). As a reference, the pure PANI sample was prepared by the same procedure.

RESULTS AND DISCUSSION

The changes in the morphology of the synthesized nanocomposites by varying a shape of TiO₂ nanoparticles are studied by SEM microscopy (Figure 1). The morphology of the nanocomposite samples (PT-80 and PT-NT-80) is significantly different compared to the morphology of pure PANI sample. Nanoribbons, as well as nanorods/tubes predominate in the non-uniform morphology of pure PANI sample. Incorporation of colloidal TiO₂ nanoparticles, as well as TiO₂ nanotubes caused predomination of nanotubular morphology in PANI/TiO₂ nanocomposite samples, while nanoribbons are not observed (Figure 1). PANI nanotubes have an outer diameter of 60–150 nm and a length up to few micrometers.

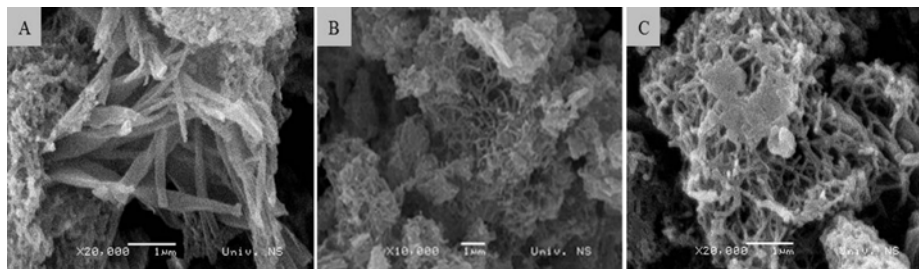


Figure 1. SEM images of the pure PANI (A) and PANI-TiO₂ nanocomposites PT-80 (B) and PT-NT-80 (C).

In the FTIR spectrum of PANI/TiO₂ nanocomposite, characteristic bands of PANI were observed at wavenumbers 1569, 1497, 1305, 1246, 1146 and 825 cm⁻¹ indicating the presence of emeraldine salt form of PANI chains in PANI and PANI/TiO₂ nanocomposites. Weak bands at 1635 and 1400 cm⁻¹ observed in the FTIR spectra of pure PANI and all nanocomposites can be attributed to the substituted phenazine-like units which are responsible for formation of polyaniline nanostructures.

The conductivity of both PANI-TiO₂ nanocomposites was $\sim 2.0 \times 10^{-3}$ S cm⁻¹, which is twice the conductivity of a pure PANI (9.1×10^{-4} S cm⁻¹) synthesized under the same conditions, without added TiO₂.

The field dependence magnetization after diamagnetic correction is shown in Figure 2. At room temperature, the weak ferromagnetic behavior can be observed in all samples. Pure PANI and PT-80 samples showed hysteresis loop with the coercive field of $H_c=300$ Oe, remanent magnetization of $M_r=4.35 \times 10^{-4}$ emu g⁻¹ and the saturation magnetization of

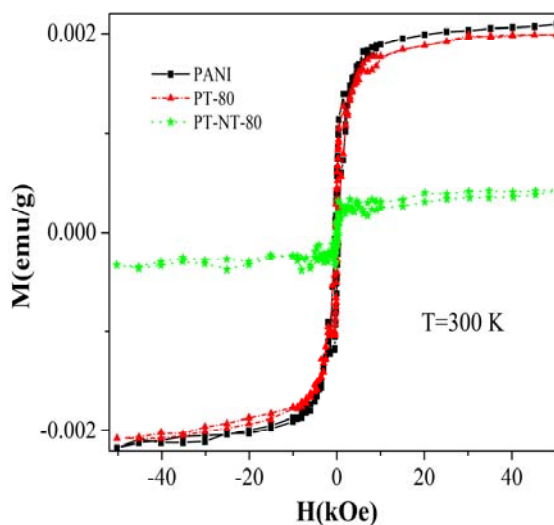


Figure 2. The magnetic field dependence of magnetization after diamagnetic correction at 300 K for the pure PANI and PANI/TiO₂ nanocomposite samples (PT-80 and PT-NT-80).

about $M_s=2\times 10^{-3}$ emu g^{-1} . In comparison to pure PANI and PT-80 samples, PT-NT-80 nanocomposite sample exhibit much weaker ferromagnetic ordering. Saturation magnetization was approximately $M_s=2.5\times 10^{-4}$ emu g^{-1} . The presence of TiO_2 nanotubes in PANI-based nanocomposite reduced several times the saturation magnetization value. Such behavior could be the consequence of the increased spin disordering as well as the reduction of the total number of magnetic moments. The reason for decrease of ferromagnetism in PT-NT-80 nanocomposite sample is conversion of single-charged polarons into double-charged bipolarons ($S=0$) induced by the presence of TiO_2 nanotubes.

CONCLUSION

PANI/ TiO_2 nanocomposites were successfully synthesized through the oxidative polymerization of aniline with ammonium peroxydisulfate in aqueous dispersions of TiO_2 nanoparticles and TiO_2 nanotubes, without added acid. FTIR measurements confirmed presence of conductive emeraldine salt form of PANI in all synthesized samples. Incorporation of TiO_2 nanoparticles and nanotubes caused significant changes in morphology and conductivity of nanocomposites compared to pure PANI. Much weaker ferromagnetic ordering in PANI/ TiO_2 nanocomposites which contains TiO_2 nanotubes is due to the presence of higher amount of double-charged bipolarons ($S=0$).

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REFERENCES

- [1] K. Lee, S. Cho, S.H. Park, A.J. Heeger, C.-W. Lee, S.-H. Lee, *Nature*, 2006, 44, 65.
- [2] J. Stejskal, P. Kratochvíl, A.D. Jenkins, *Polymer*, 1996, 37, 367
- [3] Y. Long, Z. Chen, J. Shen, Z. Zhang, L. Zhang, H. Xiao, M. Wan, and J.L. Duvail, *J. Phys. Chem. B*, 2006, 110, 23228.
- [4] Y. Zhang, C. Zhu, and J. Kan, *J. Appl. Polym. Sci.*, 2008, 109, 3024.
- [5] T. Rajh, D. Tiede, M. Thurnauer, *J. Non-Cryst. Solids*, 1996, 207, 815.
- [6] Z.Šaponjić, N. Dimitrijević, D. Tiede, A. Goshe, X. Zuo, L.X. Chen, A.S. Barnard, P. Zapol, L. Curtiss L, T. Rajh, *Adv. Mater.*, 2005, 17, 965.