

Preparation and Characterization of Polymeric Films Embedded with Metal Oxides Nanoparticles via Ion-Exchange Technique

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Abstract: Fabrication of hybrid systems consisting of metal oxides nanoparticles and organic polymers is of considerable interest. These materials exhibit novel combinations of metal oxide particles and polymers that are attractive for application in sensor fabrication, catalysis, and magnetic materials etc. In this paper, several metal oxide nanoparticles, such as Co_3O_4 , embedded in polyimide thin films were achieved by potassium hydroxide hydroxylation of polyimide film surfaces and incorporation of metal ions through subsequent ion exchange. Thermal treatment in hot air not only recycloimidized the poly(amic acid) into polyimide, but also formed metal oxide clusters, which diffused and aggregated on the polymeric surface to give continuous metal oxide layers. The nanocomposite films were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and thermogravimetric analysis, as well as surface conductivity and hysteresis loop measurements. By this method, the double-sided metal oxide layers on the polyimide films could be easily fabricated. This ability provides an effective methodology for the preparation of metal-oxide/polymer nanocomposites with controllable microstructures and holds great promise toward the application in the area of anti-magnetic and electromagnetic coatings.

Keywords: Polyimide; film; metal oxide

1 Introduction

Fabrication of hybrid materials consisting of metal oxide nanoparticles and organic polymers is of considerable interest. These materials exhibit novel properties combining metal oxide particles and polymers, which are attractive for application in sensor fabrication, catalysis, optical materials, and magnetic materials. Of the many applications for metal oxide polymeric nanocomposites films, one of the most interesting aspects is in the field of magnetic materials. Among lots of polymeric matrixes, polyimide (PI) has been the focus of intensive studies because of its outstanding mechanical, thermal properties and chemical stability. It has been widely applied in electronic, aerospace and other fields. Therefore, PI is a promising candidate type for the matrix of these hybrids. Taking tricobalt tetraoxide (Co_3O_4) as instance, spinel type Co_3O_4 belongs to the family of transitional metal oxide and is an important magnetic *p*-type semiconductor that has great applications in anode materials in Li-ion rechargeable batteries^[1-5], solar energy absorbers, gas sensors^[2,6-7], ceramic pigments, magnetic materials^[8-11], heterogeneous catalysts^[12,13] and electrochromic devices. Polymeric composite materials with nanoparticles distributed in the matrix frequently display more versatile material properties than composites based on larger particles. Thus, polymeric magnetic nanocomposite materials can be expected by modifying PI films with Co_3O_4 particles in nanometer.

Conventional methods for fabricating PI/metal oxide nanocomposite films mainly focus on the in situ deposition process^[14-19]. This process involves the homogenous incorporation of an appropriate metal salt into PAA solution and subsequent thermal curing. During thermal treatment, PAA was imidized to final PI and the metal salt was decomposed to metal oxide. Taylor and co-workers have prepared a series of surface semiconductive^[16-18] and magnetic^[14,15] PI films via in situ deposition of metal salts. In this in situ deposition process, anions of the metal salts, which has great effect on the mechanical properties of PI composite films, are incorporated inside the PI matrix. When the content of the metal salt reach certain value, the nanocomposite films were often brittle^[15] because of the presence of these extra anions.

Akamastu group^[21-22] has developed a method for preparing PI/metal nanocomposite films, including PI/Cu, PI/Pt and PI/Ni nanocomposite films via ion exchange in inorganic metal salt

aqueous solution and subsequent thermal treatment in hydrogen atmosphere. During the ion exchange process, metal cations are exchanged with no risk of anionic group, such as Cl^- , SO_4^{2-} and NO_3^- , being incorporated into the films. During thermal treatment in hydrogen atmosphere, PAA at the surface modified layer of PI films converts to PI and simultaneously hydrogen reduces the metal ions to metal atoms which aggregate at both surfaces of PI films. Recently, our group has tried to cure the PI films modified by potassium hydroxide and subsequent ion exchange in silver nitrate solution in ambient atmosphere and got a series of PI/silver nanocomposite films with high reflective and conductive surfaces^[20]. Thermal treatment under tension converts the poly(amic acid) into PI and simultaneously reduces the silver(I) to silver(0) without the addition of reducing agents, yielding silver layers with excellent reflectivity and conductivity on both surfaces of the PI films. Significant progress has been achieved with ion exchange method. The aim of this work is to fabricate Co_3O_4 magnetic nanocomposite films via the ion exchange technique. The procedure is outlined in Figure 1. In the first step, the surfaces of PI films are chemically etched in potassium hydroxide (KOH) aqueous solution into potassium polyamate. Secondly, the cobalt polyamate could be formed by immersing the surface etched PI films into cobalt nitrate aqueous solution and exchanging K^+ with Co^{2+} . Thermal curing in hot ambient atmosphere re-cycloimidizes the PAA to the final PI. At the same time, cobalt oxide particles formed and aggregated at the surfaces of PI films. The procedure for fabricating the PI/ Co_3O_4 nanocomposite films resembles the ion exchange in situ self metallization for fabricating PI/metal nanocomposite films, but the chemistry involved in the thermal treatment process is different, that is, the cobalt ions are not reduced to cobalt atoms in hot ambient atmosphere but oxidized to Co_3O_4 particles, which can diffuse and aggregate to give semiconductive surfaces. We studied the structure and morphology of the Co_3O_4 particles on the surfaces of PI films and the magnetic properties of the nanocomposite films. The mechanical and thermal properties of the nanocomposite films were also investigated.

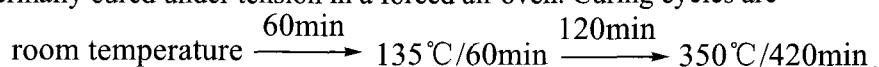
2. Experimental section

2.1 Materials

Pyromellitic dianhydride oxydianiline (PMDA-ODA) polyimide films with thickness of 80 μm used in this study were purchased from Shengyang Huajing Ltd., Jiangsu province, China. The films were cleaned prior to use in distill water at room temperature for 10 min under ultrasonication. Cobalt nitrate ($\text{Co}(\text{NO}_3)_2$) (> 99.0%) with analytical quality was purchased from Tianjin Wenda rare reagent Chemical Company and used as received. KOH with analytical quality was obtained from Beijing Chemicals Reagent Factory and used without further purification.

2.2 Preparation of PI/ Co_3O_4 nanocomposite films

PI films were initially treated by 2 M KOH aqueous solution at 25 °C for 9.5 hours and washed with copious amount of distill water. Then the surface modified polyimide films were immersed into a 0.4 M $\text{Co}(\text{NO}_3)_2$ aqueous solution at room temperature for 120 min to perform the ion exchange. After being rinsed with distill water, the films were dried in atmosphere. Subsequently the cobalt ion-doped films were thermally cured under tension in a forced air oven. Curing cycles are



2.3 Characterization

ATR-FTIR spectra of the films between 4000 and 650 cm^{-1} were recorded on the Nicolet Nexus670 IR spectrometer. XRD of the hybrid films were performed using an X-ray diffractometer (D/Max2500VB2+/PC, Rigaku, Japan). The X-ray beam was generated by a Cu Ka target ($\lambda=0.154056$ nm), using a tube voltage of 40 kV and a current of 200 mA. All the samples had the scanning angle between 5° to 90°. The surface morphology of the nanocomposite films was characterized with SEM (SEM-4700, Hitachi, Japan) at accelerating voltage of 20 kV after samples were coated with ca. 5 nm of palladium-gold alloy.

3. Results and Discussion

The formation of Co_3O_4 layers on the PI surfaces attributes to the diffusion of newly born Co_3O_4 particles. XRD patterns of the nanocomposite films prepared by hydrolyzing PI films in KOH solution (2 M, 25 °C, 9.5 h), ion exchange in $\text{Co}(\text{NO}_3)_2$ aqueous solution (0.4 M, room temperature, 2 h) and followed

by curing in different thermal treatment stages are showed in Figure 1. For the curing temperature below 350 °C, the XRD pattern also shows no reflection for Co₃O₄ and the films have the yellow appearance, which is very similar to the color of the pristine films. When extending thermal treatment time at 350 °C to 1 h, reflections (220, 311, 400, 511, and 440) corresponding to the major characteristic peaks of cubic Co₃O₄ can be clearly observed from the XRD pattern of the nanocomposite film. The film presents metallic luster, which is the color of Co₃O₄. Further thermal treatment of the films at 350 °C, the above diffraction peaks become slightly sharp and the reflections (111, 222, 422) associated with Co₃O₄ are also became evident. No obvious peaks corresponding to other cobalt oxides have been detected throughout the whole curing procedure, indicating that the nanocomposite films are mainly consisted of the cubic Co₃O₄ particles. The average sizes of Co₃O₄ crystallites estimated by the Scherrer equation using the full width at half-maximum (FWHM) of the strongest reflection (311) are less than 15 nm at 350 °C/1 h and 20 nm at 350 °C/7 h, respectively.

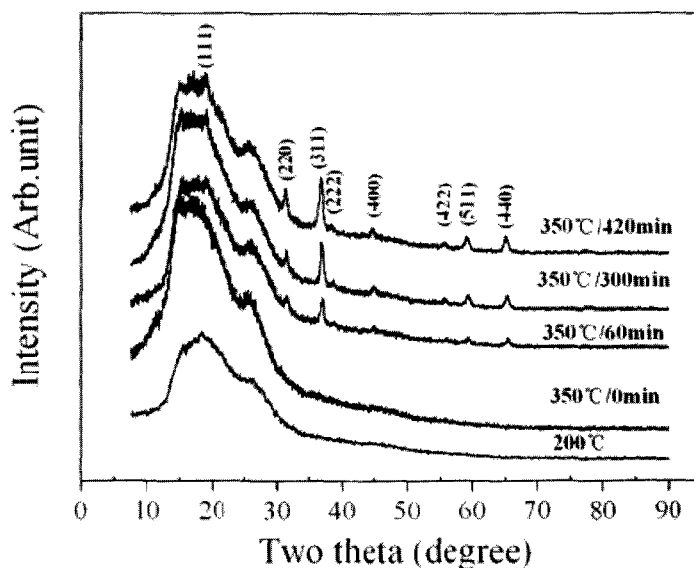


Figure 1 XRD patterns for the PI/Co₃O₄ nanocomposite films obtained in different thermal treatment stages. The precursor of the nanocomposite films was prepared by hydrolyzing PI film in KOH solution (2 M, 25 °C, 9.5 h) and ion exchange in Co(NO₃)₂ aqueous solution (0.4 M, room temperature, 2 h)

The micromorphologies of the PI/Co₃O₄ nanocomposite films are essentially dependent on the content of cobalt ion loading. In the present investigation, alkali treatment-promoted reaction allows precise control of the modified thickness of the PI film and then the amount of the doped ions. Figure 2 shows the SEM micrographs of the PI/Co₃O₄ nanocomposite films prepared by hydrolyzing PI films in KOH solution (2 M, 25 °C, 9.5 h), ion exchange in Co(NO₃)₂ aqueous solution (0.4 M, room temperature, 2 h) and thermal treatment at 350 °C / 1 h and 350 °C / 7 h, respectively. It can be seen in Figure 2(A) that Co₃O₄ particles aggregate at the surface of the PI films and form continuous layers. The average Co₃O₄ particle size, ranging from 15 to 30 nm, is larger than the estimated value by XRD results. Longer annealing at 350 °C does not change the size of Co₃O₄ particles by comparing Figure 2(A) and (B). As insulator, the room temperature surface electrical resistance of the pristine PI films is more than 10¹⁵Ω, while electrical resistance measurement indicate that room temperature surface electrical resistances of all the PI/Co₃O₄ nanocomposite films obtained at 350 °C for 1 h to 7 h are in the range of 1.26×10⁷ ~ 2.76×10⁷ Ω, categorizing them as semiconductors. We suggest that two main reasons contribute to the formation of surface continuous Co₃O₄ layer.

4. Conclusion

This present work demonstrated that the ion-exchange technique is a powerful methodology for fabricating PI/Co₃O₄ nanocomposite films. The precursor of the PI/Co₃O₄ nanocomposite films were prepared by hydrolyzing commercial PI films in KOH solution and exchanging K⁺ with Co²⁺ in Co(NO₃)₂ aqueous solution. Subsequent thermal treatment in air atmosphere results in re-cyclimidization of the matrix of precursor and simultaneous oxidation of Co²⁺ to Co₃O₄. Different thickness of surface modified layer and ion loadings provide control over the microstructure of the PI/Co₃O₄ nanocomposite films. The thickness of the surface Co₃O₄ layer decreased with extending calcining time at higher temperature. The nanocomposite films basically maintained the thermal and

mechanical properties of the pristine PI. Furthermore, this method is of general importance for fabrication of nanocomposite films with controlled micromorphology and other PI-based nanocomposite films containing a wide variety of semiconducting or magnetic metal oxide, such as CuO, NiO and Fe₂O₃.

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