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Formation and characterization of cobalt oxide layers on polyimide films via surface modification and ion-exchange technique

Shuxiang Mu, Zhanpeng Wu, Yue Wang, Shengli Qi, Xiaoping Yang, Dezhen Wu *

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

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ABSTRACT

Polyimide (PI) films with thin cobalt oxide (Co_3O_4) layers on both film sides have been prepared via a surface modification and ion-exchange technique. The method works by hydrolyzing the PI film surfaces in aqueous potassium hydroxide solution and incorporating Co^{2+} into the hydrolyzed layers of PI film via subsequent ion exchange, and followed by thermal treatment in ambient atmosphere. The PI composite films were characterized by Attenuated total reflection-Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, X-ray diffractions, scanning electron microscopy, transmission electron microscopy and thermogravimetric analyses, as well as surface resistance and mechanical measurements. By varying the absorbed cobalt ion content, a series of PI/Co_3O_4 composite films with insulative to semiconductive surfaces were obtained. The room temperature surface resistances of the semiconductive composite films reached to about 10^7 Ω. The Co_3O_4 particle formed on PI film surfaces was in the range of 10–40 nm. The final composite films maintained the essential mechanical properties and thermal stability of the pristine PI films. The adhesion between surface Co_3O_4 layers and PI matrix was acceptable.

1. Introduction

As a very famous engineering plastic, polyimide (PI) has been found very attractive in aerospace and microelectronic applications [1,2] due to its excellent mechanical properties, high thermal stability, low thermal expansion coefficient and low dielectric constant. Introducing certain inorganic nanoparticles in polyimide would broaden its use in some special applications where functional performances are required. Combining PI with transition metals oxide nanoparticles is one of the greatest choices in the past few years as this class of materials consist of the advantages of both PI and transition metal oxide moieties and have prospective application in catalysis, and electronic [3–9], magnetic [10–13] and optical devices [4,9,14–16]. Among various transition metal oxides, the magnetic p-type semiconductor Co_3O_4 is known as an important functional material that is involved in many advanced chemical and physical applications due to its unique properties such as high discharge capacity [17–20], electrochemical stability, gas-sensing [20–22], solar energy reflecting [23,24], catalysis [25,26] and magnetic [27–29] properties. Thus, incorporating Co_3O_4 nanoparticles into PI films could get a promising functional composite that has potential applications in catalysts, magnetic materials, anodes for lithium batteries, solid state gas sensor [4], electronic devices [4] and energy storage, etc.

Conventional methods for fabricating PI/metal oxide nanocomposites mainly focused on the in situ deposition process [3–9]. This method refers to developing PI/metal oxide hybrid materials from a single homogenous solution prepared by directly incorporating an appropriate metal salt into the PI precursor, poly(amic acid) (PAA) resin followed by subsequent thermal treatment. Thermal curing converts the PAA into its final PI form with concomitant decomposition or conversion of the metal salt generating the metal oxide nanoparticles in situ in the PI matrix. This process has been extensively studied since it can easily ensure the uniform distribution of the metal salts and the structural homogeneity of the PI precursors, which subsequently results in homogeneous dispersion of metal oxide particles in the final hybrid materials. With this method, many PI/metal oxide nanocomposites, including PI/Li_2O [3], PI/Fe_2O_3, PI/Fe_3O_4 [10–13], PI/Co_3O_4 [4–8] and PI/SnO_2 [4,9] have been prepared. However, PI composite films prepared by this method usually cannot make full use of the functional properties of metal oxide as most metal oxide particles remained in the matrix and only part of the metal oxides aggregates on the air side of PI film. For example, Boggess [7] and Rancourt [4,8] have prepared a series of PI/Co_3O_4 composite films via the in situ deposition process in order to improve the electrical conductivity of PI films. The room temperature resistances of the PI composite films only decreased to about 10^{12} Ω because many Co_3O_4 particles dispersed in the bulk of PI film and only limited amount of Co_3O_4 particles contribute to the air side surface semiconductive layer. Lower surface resistance could be obtained if high content of cobalt salt is added, but this will cause another problem. Due to the existence of the anions/ligands of the metal oxide precursor (typically acid radicals)

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* Corresponding author. Tel./fax: +86 10 64421693.
E-mail address: wdz@mail.buct.edu.cn (D. Wu).

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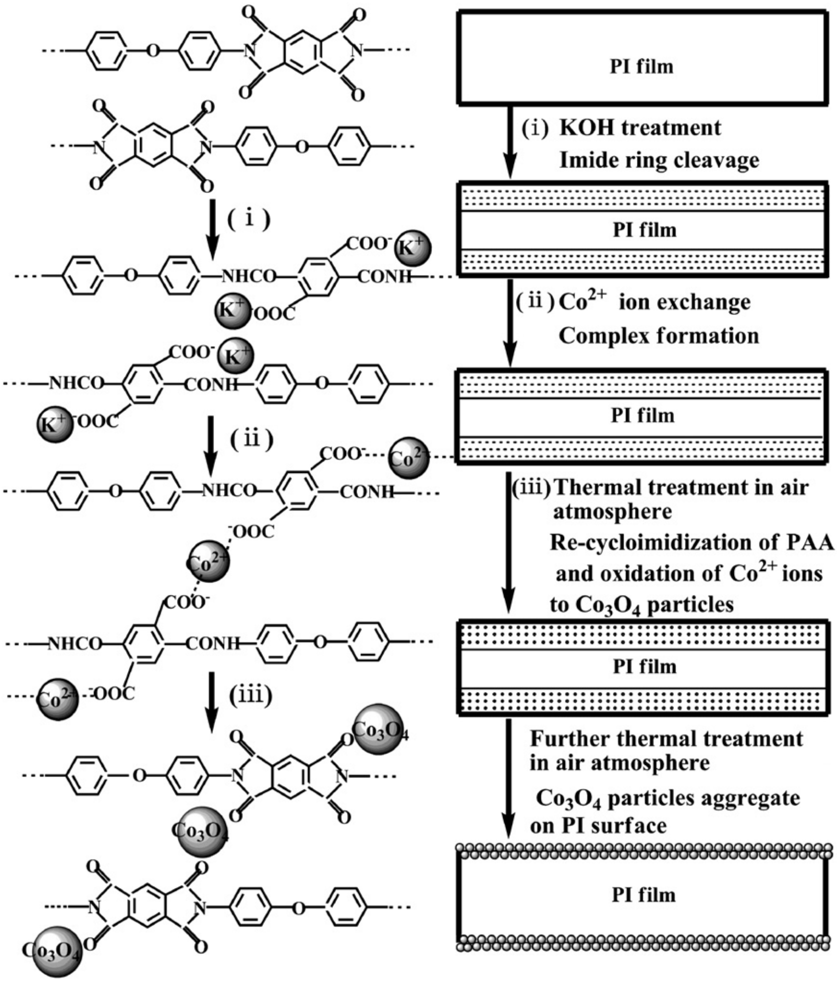

Fig. 1. Ideal illustrative scheme for the preparation of PI/Co_3O_4 nanocomposite films via a surface modification and ion-exchange technique.

in the hybrid system, degradation was usually occurring on the PI matrix. If the content of the metal salt is too high, the final PI composite film would be very brittle and visually degraded without mechanical usefulness [4,10]. Thus, metal salts with strong acid radicals such as SO_4^{2-}, CO_3^{2-} and NO_3^- should not and could not be chosen as the precursor of metal oxide.

It is very important and meaningful to prepare a kind of PI/metal oxide nanocomposites which would make full use of the functional properties of the metal oxide nanoparticles while maintaining the excellent mechanical and thermal properties of PI. The surface modification and ion-exchange technique is a desirable route to this kind of composites, which has been mainly used to prepare surface metallized polyimide films [1,2,30,31]. This method comprises the surface hydrolysis of commercial PI film in alkali solution resulting in the cleavage of the imide rings and the formation of carboxylic acid

Table 1
Sample codes for the PI composite films prepared at different conditions.

Sample code	KOH treatment conditions			Ion-exchange conditions in $Co(NO_3)_2$ solution[a]		Thermal treatment time at 350 °C/h
	Concentration /mol/l	Temperature /°C	Time /min	Concentration /mol/l	Time /min	
A-350-0	2.0	25	570	0.4	120	0
A-350-1	2.0	25	570	0.4	120	1
A-350-3	2.0	25	570	0.4	120	3
A-350-5	2.0	25	570	0.4	120	5
A-350-7	2.0	25	570	0.4	120	7
B-0.01 M	5.0	50	5	0.01	5	2
B-0.05 M	5.0	50	5	0.05	5	2
B-0.20 M	5.0	50	5	0.20	5	2
B-0.40 M	5.0	50	5	0.40	5	2

[a] The ion-exchange processes were all performed at room temperature.

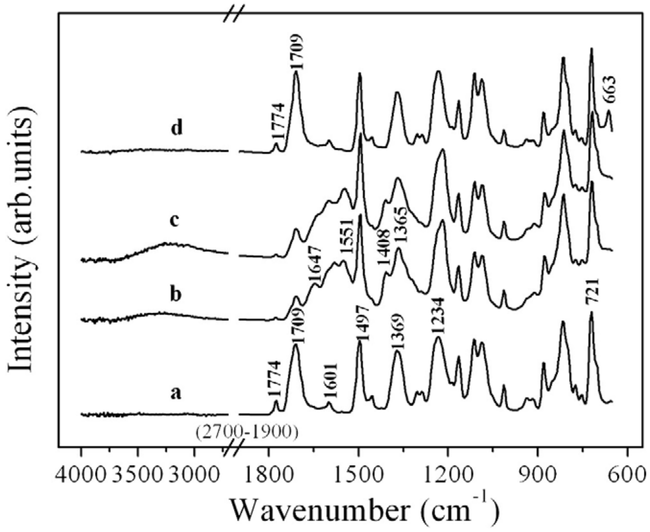

Fig. 2. ATR-FTIR spectra of the PMDA-ODA polyimide film: (a) pristine, (b) after KOH treatment (5 M, 50 °C, 5 min), (c) after Co^{2+} exchange (0.4 M, room temperature, 5 min), and (d) after thermal treatment at 350 °C for 2 h.