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Research paper

8-Hydroxyquinoline aluminum-polypyrrole and 8-hydroxyquinoline aluminum-polyaniline composites: A comparative study on the preparation and property

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ABSTRACT

Polypyrrole (PPy) and polyaniline (PANI)-organometallic complexes were obtained by chemical oxidation of pyrrole and aniline with 8-hydroxyquinoline aluminum (Alq_3) using ammonium persulfate as an oxidant. The mechanism of Alq_3-PPy and Alq_3-PANI composites based on π–π interaction and H-bonding interaction was proposed and proved by the changes in Fourier transform infrared spectroscopy (FTIR) diffraction peaks. The electric conductivity property of conducting composites was measured by means of the four-probe method. FTIR and X-ray diffraction (XRD) results showed that composites with different chemical structures, presented different crystallinity, which resulted in a different electric conductivities. The morphology of composites was observed by scanning electron microscopy (SEM). X-ray photoelectron spectrometer (XPS) and energy dispersive X-ray spectroscopy (EDS) were used for elemental analysis of composites. The optimal reaction condition of the Alq_3-PPy and Alq_3-PANI composites by in an situ polymerization method was established. It was the first time that the effect of Alq_3-PPy and Alq_3-PANI composites polymerization conditions on the morphology, structure and properties are comparative studied.

1. Introduction

Attention has been given to the research of conducting polymers (CPs) in optoelectronic devices, electrochemical displays, and sensors owing to their excellent optical, electronic, and magnetic properties related to their unique π-conjugated polymeric chains [1]. In terms of CPs, polypyrrole (PPy) and polyaniline (PANI) have been intensively studied because of their environmental stability, good electric conductivity, fast oxidation-reduction reaction, high energy density, low cost [2,3], biocompatibility, outstanding mechanical property [4,5], adjustable redox states by doping or dedoping [6], and potential applications such as actuators, light emitting diodes [7], batteries, sensors, supercapacitors, and corrosion protection [2]. Composites with conducting polymer have attracted much interest because of their special properties for specific interactions and applications [8]. Therefore, these composites particles have various applications in antistatic coatings, electrodes materials, separation membranes, electrochromic devices, electrochemomechanical actuators, clutches, dampers, and sensors [9].

Owing to the advantages of PPy and PANI, a variety of PPy-based particles and PANI-based composites have been reported to date in the pioneering literature. For instance, in order to improve the poor rate capability and rapid capacity fading during cycling, Liang Zhan et al. [10] have used a hydrothermal method to successfully synthesize coaxial Co_3O_4@PPy nanowire arrays (NWAs). When directly used the composites as an anode material for lithium-ion batteries, the Co_3O_4@PPy NWAs electrode exhibited good rate capability, improved reversible capacity, and high cycling stability. Zhiyuan Yu et al. [11] have reported the synthesis of the $NiCo_2O_4$@PANI nanocomposites via the assistance of a facile hydrothermal treatment method, and followed by a post-PANI coating process. The obtained composites showed higher electrocatalytic activity toward the oxidation of glucose. Apart from the above two composites materials, most papers have fabricated conducting polymer hybrids, such as Fe_3O_4@PPy composites [12], Pd-doped TiO_2@polypyrrole composites [13], Fe_3O_4@PANI nanocomposites [14], gold decorated SiO_2@PANI microspheres [15], and so on.

We all know that PPy and PANI are polymers consisting of conjugated double bonds in the backbone, which allows similar properties of them [16]. There are many research reports on the preparation of PPy and PANI composites with excellent structure and properties. However, the results reported for these conducting composites are difficult to compare because of the different conditions of preparation

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and characterization by various research groups. Our group has already fabricated an 8-hydroxyquinoline aluminum@PPy (Alq_3@PPy) and an Alq_3@PANI composite in order to improve the electric conductivity and thermal stability of Alq_3 [17,18]. To our best knowledge no comparative study on the synthesis and performance of such materials has been presented so far. Therefore, the purpose of this study is to revisit the effect of the oxidant-monomer molar ratio and the dopant-monomer molar ratio on the synthesis of Alq_3-PPy and Alq_3-PANI composites.

The main objectives of the present investigation were the following: (i) PPy and PANI powder and Alq_3-PPy and Alq_3-PANI composites were obtained in aqueous solution and using ammonium persulfate as an initiator; (ii) The influence of the oxidant-monomer molar ratio and the dopant-monomer molar ratio on the performance of the Alq_3-PPy and Alq_3-PANI were discussed; (iii) A comparative discussion of the synthesis, structure, and conductivity property on the Alq_3-PPy and Alq_3-PANI composites.

2. Materials and methods

2.1. Materials

Pyrrole (Py) was purchased from Guoyao Group Chemical Reagent Co., Ltd; sodium dodecyl benzene sulfonate (SDBS) was supplied by Guangfu Institute of Fine Chemicals, Tianjing; aniline (ANI) and hydrochloric acid (HCl, 36.5%) were obtain from Kelon Chemical Reagent Factory, Chengdu; ammonium persulfate (APS) was provided by Kemiou Chemical Reagent Co., Ltd; ethanol (95%) was get from Laiyang Economic & Technological development zones Fine Chemicals Factory. All these chemicals were of analytical reagent grade and used as received without further purification. All solutions were prepared using distilled water.

2.2. Preparation of Alq_3

The preparation of Alq_3 is consistent with our previous work [17].

2.3. Polymerization of Alq_3-PPy composites

For preparation of Alq_3-PPy composites, Alq_3 (0.2 mmol) and ethanol were added to deionized water at room temperature and sonicated for 30 min. Then, Py (0.01 mol) was added into previous solution and sonicated for additional 30 min. After this step, the SDBS solution (0.01 mol of SDBS was dissolved in 30 mL of HCl) was added into above solution, and ultrasonic dispersion for 30 min to obtain a homogeneous dispersion mixed solution. Finally, the APS solution (0.01 mol) was slowly dropwised while stirring the solution for 6 h in order for Py to get oxidized to PPy. The resulting composite was filtered and rinsed with water and ethanol for several times, and dried at 60 °C for 24 h under vacuum. For comparison, Alq_3-PPy composites with different oxidant-Py and dopant-Py molar ratios were also prepared by changing the amount of oxidant and dopant as above steps.

2.4. Polymerization of Alq_3-PANI composites

Alq_3-PANI composites was prepared and named in accordance with the above method apart form the PPy was replaced by PANI. The experiment parameters of preparation on Alq_3-PPy and Alq_3-PANI products are summarized on Tables 1 and 2.

2.5. Instrumentation

The chemical composition of the products was characterized by a Nicolet 380 Fourier transform infrared spectra (FT-IR, Thermo Fisher Scientific Company) in the region of 4000–450 cm^{-1} using resolution of 4·cm^{-1}. The result samples and KBr powder were mixed and pressed into thin discs under a pressure of 10 MPa, then subjected to the FT-IR spectrometry.

Table 1
The experiment parameters of Alq_3-PPy composites designed by single factor analysis method.

composites	Experiment number	SDBS-pyrrole molar ratio	oxidant–pyrrole molar ratio
Alq_3-PPy	X1	1	0.5
	X2	1	1
	X3	1	1.5
	X4	1	2
	X5	0.5	1
	X6	1.5	1
	X7	2	1

Table 2
The experiment parameters of Alq_3-PANI composites designed by single factor analysis method.

composites	Experiment number	SDBS-aniline molar ratio	oxidant–aniline molar ratio
Alq_3-PANI	Y1	1	0.5
	Y2	1	1
	Y3	1	1.5
	Y4	1	2
	Y5	0.5	1
	Y6	1.5	1
	Y7	2	1

The X-ray diffraction (XRD) study was carried out to obtain crystallinity of composites at room temperature (ca. 298 K) on Rigaku Dmax 2500 X-ray diffractometer (Japan Science Analysis Instrument Factory) with CuKα radiation (λ = 0.15418 nm) at 30 kV and 15 mA using a scanning rate of 4° s^{-1} in the range of 2θ = 4 − 70°.

The X-ray photoelectron spectrometer (XPS) was performed on a Thermo ESCALAB 250Xi system (USA) with an Al K a X-ray source (1486.6 eV). Shirley background subtraction and properly curve-fitted peaks were applied in the XPS spectra peak fitting procedure.

The structure and morphology of the samples were observed by scanning electron microscopy and the elemental analysis was characterized by energy dispersive X-ray spectroscopy (SEM and EDS, Nova Nano SEM450, FEI) working at a voltage of 20 kV. The surface of the samples were coated with gold before SEM analysis.

The electric conductivity of various products was recorded with ST2263 double testing digital four-probe tester (Suzhou Jingge Electronic Co., Ltd.). The samples were pressed into disks with diameters of 13 mm under a pressure of 15 MPa for 5 min using a powder pressing machine at room temperature before testing. The calculation method of the electric conductivity was as follows:

$$\sigma = \frac{1}{\rho} \quad (1)$$

where σ is the electric conductivity (S cm^{-1}), ρ is the resistivity of the samples (Ω cm).

3. Results and discussion

3.1. Preparation the Alq_3-PPy and Alq_3-PANI composites

The formation process of Alq_3-PPy and Alq_3-PANI composites is as follows: in the initiation step, Alq_3 was homogeneously dispersed in the aqueous solution with ethanol as a dispersing aid; in the propagation step, Py or ANI was added to form a homogeneous emulsion; after the APS was dropped, Py or ANI was oxidized with Alq_3 to form a composite because of π–π conjugate interaction and hydrogen bond between oxygen atom of Alq_3 and hydrogen atom of N—H in aniline or pyrrole using SDBS as a dopant. The possible H-bonding and π–π