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Development of novel hybrid materials based on poly(2-aminophenyl disulfide)/silica gel: Preparation, characterization and electrochemical studies

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ABSTRACT

Hydrochloric acid functionalized silica gel (SiO_2) has been successfully used for the grafting of poly(2-Aminophenyl disulfide) (poly(2APhS)) moieties through in-situ polymerization in the presence of ammonium peroxodisulfate (APS) as oxidant. The organic-inorganic hybrid (poly(2APhS)/SiO_2 with different amounts of SiO_2: 0.5 g, 1.5 g and 2 g) were thoroughly characterized through powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and ultraviolet spectroscopy (UV) measurements. The results confirm the successful formation of the poly(2APhS)/SiO_2 composite. The surface morphology of the samples was characterized by transmission electron microscopy (TEM). The obtained images show the formation of poly(2APhS) on surface of silica gel. Although the incorporation of SiO_2 nanoparticles reduces the electric conductivity of the poly(2-APhS), the resulting samples still keep high conductivities, ranging between 8.2×10^{-4} to 1.1×10^{-6} S cm^{-1}. The electrochemical properties of the composite were characterized by the cyclic voltammetry. The comparison between the different samples shows that the electrochemical activity is significantly depending on the amount of added SiO_2. There is a clear and good electroactivity for poly(2APhS)/SiO_2 with amounts of SiO_2: 0.5 g and 1.5 g, respectively, compared to that observed in materials nanocomposite with amounts of SiO_2: 2.0 g. However, that effect may be explained by a decrease of polymer in surface area with increase amount of SiO_2 nanoparticle.

1. Introduction

Polyaniline (PANI) and PANI-derived have a wide range of useful applications due to unusual electronic properties such as good electrical conductivity, low ionization potential and high electron affinity [1,2]. Composites consisting of organic conducting polymers and one or more components, which can be metals, metalloids, nonmetals, inorganic and organic/bioorganic compounds, as well as biological materials and natural products, were prepared and characterized by numerous research groups [3].

In recent years, developments of inorganic-organic hybrid materials on nanometer scale have been receiving significant attention due to a wide range of potential applications, the doping inorganic oxides such as TiO_2 [4–6], CdS [7], Silica [8,9], MoS [10], CeO_2 [11], Fe_3O_4 [12], ZnO [13,14], Al_2O_3 [15]. MoO_3 [16] and MnO_2 [17]. These polymer/inorganic hybrids exhibit many new characters, such as electrical, optical, catalytic and mechanical properties that the single material does not have.

The Silica gel material has attracted much attention in the past decades due to its unique properties, such as excellent magnetic responsivity, uniform pore size distribution, high surface area, low cytotoxicity, etc [18–20]. For this purpose, SiO_2 is a preferential choice to separate every single polymer nanoparticles from direct contact. Although the polymerization of aniline and aniline-derived on SiO_2 surface was readily accomplished to achieve polymer/SiO_2, rare encapsulation of SiO_2 on polymer was reported possibly due to their non-compatible interface for the deposition of SiO_2. Furthermore, the fully coating of SiO_2 on polymer limited the application of the cores because the loading target materials do not have effective space to interact with polymer [21].

In this work, we investigate the effect of additives different

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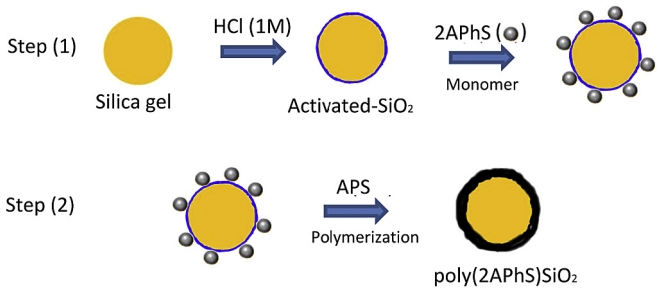

Fig. 1. Scheme of poly(2APhS)SiO_2 nanocomposites preparation.

amounts of SiO_2 nanoparticles (0.5 g, 1.5 g and 2 g) on the properties of composites chemically synthesized by in situ oxidative using 2-aminophenyl disulfide monomer, hydrochloric acid as dopant and ammonium per sulphate as an oxidant. The properties of the nanocomposites were studied and compared with those of poly(2APhS) pure. They were characterized using different techniques: FTIR, UV, XRD, TEM and TGA analysis, the electrical conductivities were measured from the graph using four-point probe method. The electrochemical behavior of the poly(2APhS) separated from the SiO_2 has been analyzed by cyclic voltammetry.

2. Experimental

2.1. Materials

The monomers 2-aminophenyl disulfide (2APhS) (from Aldrich) was used as received. Perchloric acid and hydrochloric acid (from Merck) was ultrapure quality and all the solutions were freshly prepared with distilled-deionised water obtained from an Elga Labwater Purelab Ultra system. Silica gel (SiO_2) (99%) was purchased from the Sigma-Aldrich Company. Ammonium persulfate (APS), methanol (CH_3OH), ammonia solution (NH_4OH) were all of analytical purity and used without further purification.

2.2. Chemical synthesis of hybrid materials

The synthesis of poly(2APhS)/SiO_2 composites was carried out in 100 mL round bottom flask equipped with mechanical stirrer. Firstly, a certain amount of SiO_2 nanoparticles was dispersed in HCl (0.1 M) under simultaneous mechanical stirring and sonication for 1 h, to activate the surface of SiO_2. Then, 0.022 mol of (2APhS) monomer was dispersed in 100 mL of HCl (0.1 M) with SiO_2 nanoparticle (different amounts of SiO_2: 0.5 g, 1.5 g and 2 g). The solution were mixed for 30min, and subsequently appropriate amount of APS in HCl solution was added dropwise to start chemical polymerization of the monomer. The molar ratio of APS to 2APhS was 1:1. Polymerization was carried out at 15–20 °C with 24 h stirring. Black poly(2APhS)/SiO_2 nanocomposites suspensions were filtered out, washed with methanol and then dried under vacuum at 60 °C for 24 h [22,23]. For comparison, a pure poly(2-APhS) was synthesized under the same conditions.

The polymerization procedure for the preparation of poly(2-APhS)/SiO_2 composites is shown in Fig. 1 [24]. Since the surface charge of SiO_2 is positive in acidic conditions, an amount of Cl^- is adsorbed on the surface of nanoparticles to compensate the positive charges. In the same acidic conditions the monomers; (2APhS) are converted to cationic anilinium ions. This leads to electrostatic interactions between the adsorbed anions and cationic anilinium ions.

2.3. Physicochemical characterization

The X-ray diffraction of the powder nanocomposites were obtained using a Bruker CCD-Apex equipment with a X-ray generator (Cu K_α and Ni filter) that has worked at 40 kV and 40 mA. A Hitachi U-3000 spectrophotometer was used for recording the UV–Vis spectra. The poly(2APhS) were separated into *N*-methyl-2-pyrrolidone (NMP). Fourier transform infrared (FT-IR) spectra was recorded using a Bruker Alpha.

For Transmission Electron Microscopy (TEM) observations, the samples were dispersed in ethanol and deposited on TEM grids. The images were collected using a JEOL (JEM-2010) microscope, working at an operation voltage of 200 kV.

Thermogravimetric analysis (TGA) was performed with a Du Pont thermogravimetric analyzer at a heating rate of 20 °C/min under nitrogen. About 10 mg of sample was heated up to 900 °C.

2.4. Electrochemical characterization

The following analysis methods were used to analyze the electrochemical characteristics of the fabricated samples. Electrochemical workstation (VERSASTAT II) was used to carry out the cyclic voltammetry (CV). Three-electrode measuring method was used for analyzing the performance of the electrode wherein the fabricated working electrode, the platinum electrode used as the counter electrode, and the reversible hydrogen electrode (RHE) used as the reference electrode were used inside a beaker with 1 M

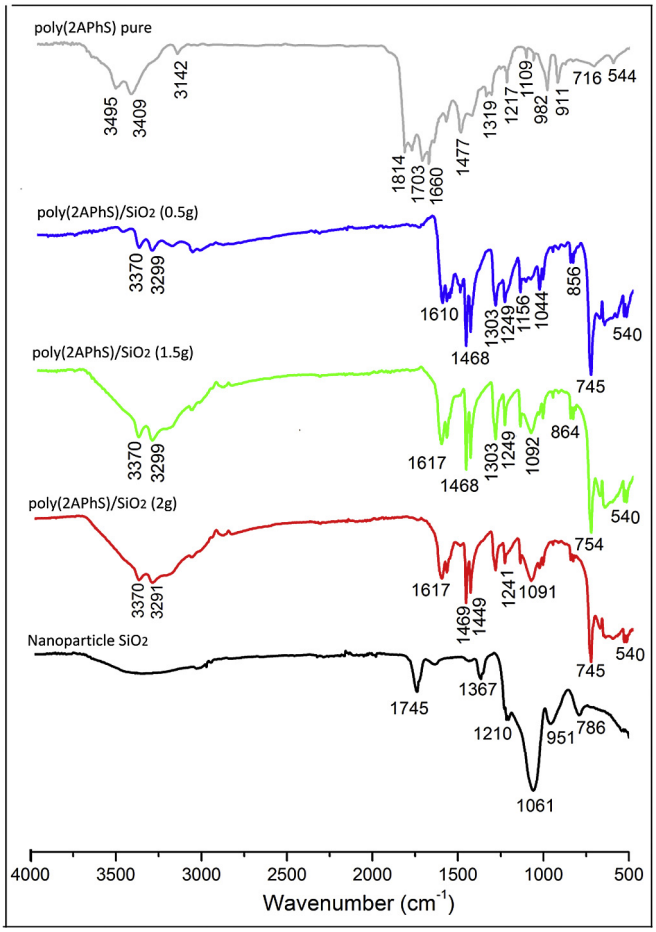

Fig. 2. FT-IR absorption spectra of poly(2APhS)/SiO_2 (with different amounts of SiO_2: 0.5 g, 1.5 g and 2 g) and their SiO_2 nanoparticle.