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One-step synthesis and photoluminescence properties of polycarbazole spheres and Ag/polycarbazole core/shell composites

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ABSTRACT

Polycarbazole (PCz) spheres and Ag/polycarbazole core/shell composites (Ag/PCz) have been successfully synthesized via a Polyvinylpyrrolidione (PVP)-assisted hydrothermal method for the first time. The synthesis is simple, low cost and environment-friendly. The resulting PCz spheres are uniform in dimension with good dispersibility. The shell thickness of the Ag/PCz core–shell nanoparticle is about 30 nm with a powerful light absorption performance. Compared to PCz, the synergistic luminescence behaviors of Ag/PCz were displayed in violet and blue region. The PCz and Ag/PCz can be used as blue and green light-emission materials, respectively. The excellent function of PVP in the process of synthesizing the composites is also discussed rationally.

1. Introduction

Conducting polymers have drawn broad attention due to their important applications in polymeric light-emitting diodes, photovoltaic cells, and field effect transistors [1,2]. Among the conducting polymer families, polycarbazoles (PCz) polymerized through either the 3,6- or 2,7-positions are of particular interest with regards to their photoconductivity [3], electrochromic properties [4] and their application in electroluminescent devices [5]. Generally, PCz can be synthesized by the electrochemical [6,7] and catalytic chemical routes [8]. At present, many studies have focused on chemical synthesis of PCz and composites, and there were extensively investigated for the attractive properties of these materials such as its merits on the improvement of conducting polymer materials [9], well-defined colloidal dimensions or morphologies, intense coloration, biocompatibility, high surface area, efficient radiation absorption, wide spectrum of surface functionalization [10], and so forth. The surfactant-assisted chemical route was of particular interest because the templates could be easily removed after polymerization, and it is readily for scale-up without reducing the size uniformity and shape controllability [11,12].

On the other hand, considerable attention has been paid to metal nanoparticles due to a wide range of potential applications of their remarkable optical, catalytic, electronic and magnetic properties. These properties and applications are strongly dependent on the size and shape of the metal nanoparticles [13]. Silver nanostructures attract great interest because of their unique surface plasmon feature, which enabled their application as optical labels, active substrates for surface-enhanced Raman scattering (SERS), near-field optical probes, and contrast agents for biomedical imaging [14].

Composites from conducting polymers and metal nanoparticles are attractive materials as they combine the properties of low dimensional organic conductors and inorganic materials with high surface area, which enables the resulting composites with unique electrical, thermal, mechanical, and optical properties [15]. Xing and co-workers

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reported a facile colloidal method for synthesizing Au@Ag@ Polyaniline (PANI) nanoparticles, whose eccentric polymer shells were exploited to fabricate eccentric bimetallic cores [16]. Zhang and Wan discovered the self-assembled PANI/TiO_2 composite nanotubes in the presence of β-naphthalenesulfonic acid (NSA) [17]. Kleinermanns and co-workers synthesized PANI–Au composite in the presence of micelles of sodium dodecyl sulfate [18]. Visy and co-workers prepared Polypyrrole (PPy)–Ag nanocomposites via two-step and characterized the composites [19]. Yu and co-workers reported to prepare flexible silver/cross-linked poly(vinyl alcohol) (PVA) nanocables via one-step in situ reduction of Ag^+ and Ag^+-catalyzed cross-linking of PVA chains under hydrothermal conditions [20]. Bhavana and Rajiv synthesized polycarbazole in HCl solutions at room temperature [21] and Zahoor et al. synthesized Ag@PCz nanocomposite material and Ag@PCz coaxial nanocables using the oxidative polymerization method [22,23]. Ag/PCz nanocomposite as a new class of material has attracted considerable attention due to its excellent electrical conductivity and photoluminescence properties. However, the traditional preparation methods often require accurate and complicated conditions. Therefore, developing a new and simple route to synthesis polycarbazole and its nanocomposites is desirable.

In this paper, we synthesized PCz by a facile PVP-assisted hydrothermal method using ammonium persulfate (APS) as oxidant. The sample was composed of spherical particles and grew to larger particles via Ostwald ripening processes. When we changed the oxidant to $AgNO_3$, as expected, we got the PCz-coated Ag nanocomposites, through the redox reaction of $AgNO_3$ and carbazole monomer, in the presence of PVP by a "one-pot" synthesis. Ag nanoparticals were encapsulated by PCz, well-proportioned thickness of coating agent is about 30 nm. Surprisingly, the nanocomposites showed good light absorption and photoluminescence properties.

2. Experimental section

2.1. Materials

Carbazole (chemical grade, Shanghai yuanhang Reagent Plant). Acetic acid (analytical grade, Beijing Chemical Plant). $AgNO_3$ (analytical Chengdu Chemical Reagent Plant). Polyvinylpyrrolidione (PVP) (Sinopharm Chemical Reagent Co., Ltd.). Ammonium persulfate (APS) (analytical grade, Beijing Chemical Plant). Ethanol (analytical grade, Beijing Chemical Plant). Distilled water was used throughout the work. All of the materials were used as received.

2.2. Synthesis

2.2.1. Synthesis of polycarbazole spheres

0.2 g PVP was dissolved in 20 mL ethanol, and then 0.1672 g carbazole monomer was added to the mixture under stirring. When the mixture solutions turned transparent, 15 mL of aqueous solution of APS was added. At the same time, the color of the solution turned milky. Keeping stirring for 10 min, the solution was loaded into a 50 mL Teflon-lined stainless steel autoclave, which was sealed and maintained at 180 °C for 24 h. Then, the products were cooled to the room temperature, centrifuged, washed with distilled water and ethanol for several times, and finally dried in a vacuum at 60 °C for 24 h.

2.2.2. Synthesis of Ag/polycarbozole composites

0.2 g PVP was dissolved in 30 mL ethanol, followed by addition of 0.2508 g carbazole monomer under stirring (Solution A). $AgNO_3$ (0.1698 g) and acetic acid (1 mmol) were dissolved in 10 mL distilled water (Solution B). After Solution A turned transparent, Solution B was added in one portion. The resulting solution was stirred for 30 min. Then the mixture solution was loaded into a 50 mL Teflon-lined stainless steel autoclave, sealed, and kept at 180 °C for 24 h. The products were centrifuged, washed with distilled water and ethanol several times, and finally dried in a vacuum at 60 °C for 24 h.

2.3. Characterization

The morphologies of the polymer and nanocomposites were examined by transmission electron microscope (TEM, HITACHI-600) operation at 80 kV and field emission scanning electron microscopy (FE-SEM; XL30 ESEM-FEG). The samples used for TEM were prepared by placing one drop of the particle suspension on the carbon coated copper grid and leaving to dry. Infrared spectra of the samples were measured on KBr pellets on a MAGNA560 Fourier transform IR spectrophotometer. The UV–vis spectra of the samples were measured on a SHIMADZU UV-2550 UV–visible spectrophotometer. The components of the composites were detected by X-ray photoelectron spectroscopy (VG ESCALAB MK II spectrometer). Molecular weights were determined on a Waters Alliance Gel permeation chromatography (GPC) 2000 system. Photoluminescence spectra were recorded on a Hitachi F-4500 spectrophotometer. The 1H nuclear magnetic resonance (NMR) spectra of the samples were collected by using an AVANCE 400M spectrometer (Bruker, Germany) and the solution was prepared in $CDCl_3$ solution.

3. Results and discussion

In our work, polycarbazole spheres have been successfully synthesized by a hydrothermal method in the presence of PVP, using APS as oxidant. The morphology of polycarbazole particles were observed by the TEM and SEM. As shown in Fig. 1, the sample prepared at 180 °C (Fig. 1a and b) was composed of spherical with uniform dimension. The average diameter of the spherical nanoparticles was in the range from 500 nm to 1 μm. The molecular weight of PCz was measured using Gel permeation chromatography (GPC), tetrahydrofuran (THF) was used as an eluent at a flow rate of 1.0 mL/min at 30 °C. The M_n, M_w, and M_z of PCz were identified to be 262512, 329366 and 398745, respectively. When the reaction was carried out at 100 °C under otherwise the same conditions, the products showed anomalous shapes (Fig. 1c), which were unstable under TEM beam. Besides, the products pre-