



Facile one-pot synthesis of bifunctional magnetic-fluorescent polyvinylpyrrolidone film

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ARTICLE INFO

Article history:

Received 17 January 2014

Accepted 20 March 2014

Available online 26 March 2014

Keywords:

Polymers

Magnetic materials

Composite materials

Fluorescent dye

Polyvinylpyrrolidone

ABSTRACT

A facile one-pot method is developed to produce bifunctional magnetic-fluorescent polyvinylpyrrolidone (PVP) film with excellent superparamagnetism and stable optical property. The optical and magnetic properties and the morphology of the produced PVP film are investigated by fluorescence spectrometry, vibrating sample magnetometer and scanning electron microscopy. The magnetic nanoparticles and the dye molecules are incorporated into the PVP film networks through covalent linkages and the obtained magnetic-fluorescent PVP film exhibits highly stable superparamagnetism and fluorescent property. This facile preparation method can be extended to the fabrication of oxides-doped fluorescent PVP films.

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1. Introduction

Magnetic polymer films have attracted great interest over the last few decades because they were widely used as absorbing materials [1], magnetic recording materials [2] and electromagnetic interference shielding [3]. The reported fabrication of magnetic polymer composite films involved in drop casting [4], spin-coating [5], Langmuir–Blodgett technique [6] and layer-by-layer assembly [7].

Polyvinylpyrrolidone (PVP) has been widely used in various medical and industrial applications because of its excellent water-solubility and biocompatibility [8,9]. Recently our group reported the synthesis of PVP-based fluorescent film and demonstrated the ring-opening and self-crossing mechanism of linear PVP [10]. In addition, Huang and co-workers introduced the interactions between PVP and magnetic nanoparticles (MNPs) [11]. In this work, based on the ring-opening and crosslinking mechanism of PVP and the interaction of PVP and MNPs, we developed a facile one-pot approach for the fabrication of magnetic-fluorescent PVP film by adding MNPs and dye molecules into the reaction system (Scheme 1). The obtained magnetic-fluorescent PVP film exhibited highly stable superparamagnetism and optical property. The facile fabrication of magnetic-fluorescent PVP film in one-pot has not yet been reported in the literature. The one-pot synthesis could be extended to other oxides for the preparation of multi-functional PVP composites.

2. Experiment

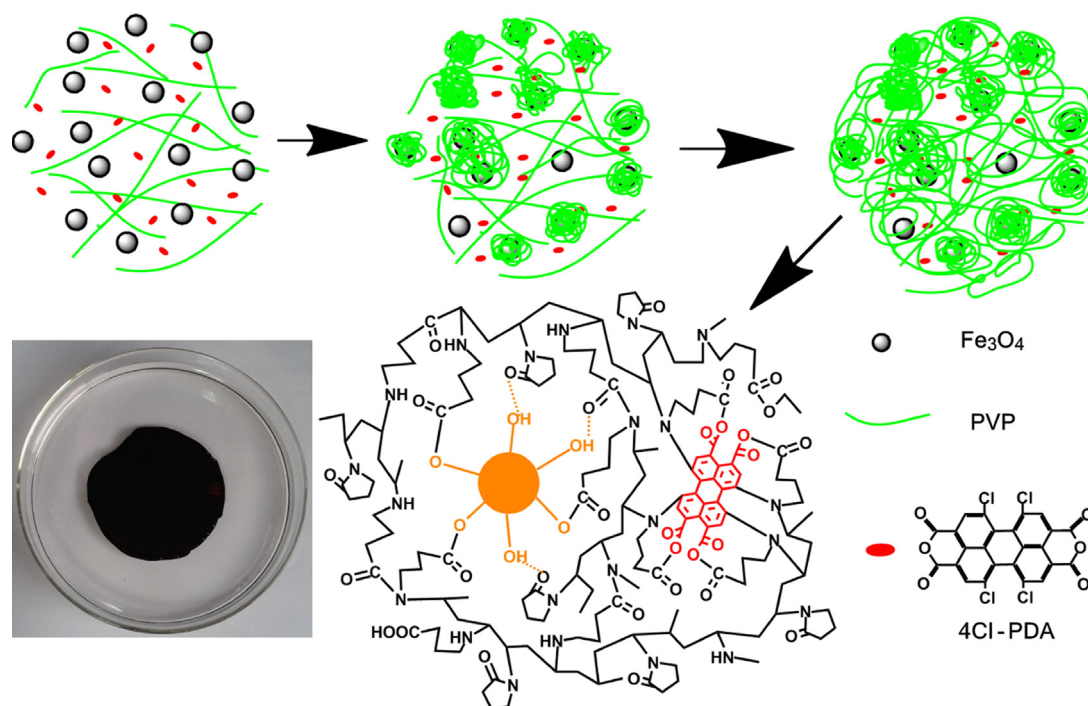
The MNPs with different sizes were synthesized via hydrothermal process according to the literature [12] and the synthesis details were described in Supporting information. To prepare the composite film, MNPs (0.01 g), PVP (0.8 g) and 1,6,7,12-tetrachloro-*p*-erylene tetracarboxylic acid anhydride (4C1-PDA, 0.05 g) were dispersed in the mixture of ethanol (10 mL) and acetone (40 mL) under ultrasonication at room temperature for 30 min. Subsequently, the mixture was put into a teflon-lined stainless steel autoclave and maintained at 160 °C for 30 h. Then the autoclave was cooled to room temperature naturally. The obtained dark red film was washed with ethanol for several times and saved in 30 mL of ethanol.

3. Results and discussion

Synthesis of magnetic particles: When $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was used as the sole iron source, the MNP size can be tuned rationally by adjusting the volume ratio of glycol/diethylene glycol (V/V in mL). As shown in Table S1 and Fig. S1, the size of MNP increased with the increasing volume ratio of EG/DEG. A typical TEM image of the MNPs is given in Fig. 1A. The obtained MNPs keep the spherical shape with uniform size (ca. 270 nm in diameter). Fig. 1B displays the XRD pattern of the obtained MNPs. All diffraction peaks of Fe_3O_4 in face-centered cubic crystal (JCPDS card no. 19-0629) can be detected, indicating the successful synthesis of Fe_3O_4 nanoparticles. As shown in Fig. 1C, the Fe_3O_4 nanoparticles exhibited

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Scheme 1. Schematic representation of the formation of magnetic-fluorescent PVP film.

excellent colloidal dispersity and can be easily isolated by an external magnet within 10 s.

Preparation of magnetic PVP film: MNPs with the size of 270 nm and 30 nm were separately dispersed with linear PVP in the mixed solvent to produce the magnetic PVP film with black color (Scheme S1). The obtained magnetic PVP film was washed with ethanol and acetone and also isolated by external magnet for several times until the MNPs could not be washed out from the film. The magnetic property of the produced PVP film was investigated by a vibrating sample magnetometer. As shown in Fig. S2A, the prepared magnetic PVP film exhibited the excellent superparamagnetism owing to the incorporation of MNPs inside the PVP film. To confirm the composition, the obtained magnetic film was characterized by Fourier transform infrared (FTIR) spectroscopy (Fig. S2B). The IR spectrum of the obtained magnetic film was almost the same as that of PVP. The reason is explained by the high content of PVP, thus, the characteristic peaks of Fe_3O_4 nanoparticles were overlapped by those of PVP. While the black color and the superparamagnetism of the produced PVP film indicated the successful incorporation of MNPs into the film. In contrast, the blank PVP film exhibited light yellow without superparamagnetism (Fig. S3).

As shown in Fig. S2B(c), the surface of the achieved MNPs possesses hydroxyl groups because the MNPs were prepared by the polyol process [13]. Yang [14] reported the esterification between Fe_3O_4 nanoparticles surface and carboxymethylated chitosan at 85 °C. In the previous work, it has been demonstrated that the ring-opening process of PVP chains generated $-\text{COOH}$ groups [10]. Therefore, the esterification between the hydroxyl groups located on MNP surface and the $-\text{COOH}$ groups derived from the ring-opened PVP chains must occur under higher temperature and pressure. This is indeed the case. The MNPs can not be separated from the magnetic PVP film by external magnet and the film showed excellent superparamagnetism, suggesting the tight conjugation of MNPs in the PVP film. The proposed reaction mechanism is presented in Scheme S1. Consequently, the magnetic PVP film was successfully prepared by incorporating MNPs into the cross-linked PVP film.

In order to investigate the effect of these MNPs on the morphology of the PVP film, scanning electron microscopy (SEM) was performed. The magnetic PVP film was found to be composed of many microspheres and the diameter of microspheres appeared to be highly size-dependent (Fig. 2). Big size of MNPs usually led to the formation of large microspheres in the PVP film. The interface between the microspheres was unobvious, which was explained by the chemical reaction between PVP chains and the surface of MNPs.

Preparation of magnetic-fluorescent PVP film: As 4Cl-PDA was added during the preparation of magnetic PVP film, bifunctional magnetic-fluorescent PVP film with dark red color was fabricated (Scheme 1). The obtained magnetic-fluorescent PVP film was washed with ethanol and acetone for several times until the MNPs and dyes could not be extracted by solvents. The dark red color and FTIR spectra verified that the produced film was composed of MNPs, PVP and 4Cl-PDA (Fig. S4). The thickness of the magnetic-fluorescent PVP film was about 0.15 mm. The UV-vis absorption and the fluorescence emission spectra of the obtained magnetic-fluorescent film are shown in Fig. 3A. The room-temperature magnetization of the prepared magnetic-fluorescent PVP film exhibited excellent superparamagnetism (Fig. 3B). The content of the MNPs in the film was about 6 wt%, which was characterized by TG analysis in an air atmosphere (Fig. S5). The fluorescence intensity and the superparamagnetism of the film remained unchanged under natural light even after 2 weeks of storage, indicating that both the MNPs and dyes were stably embedded in the film. Yin and Roberts reported that the 4Cl-PDA dye containing two anhydrides and four chloride atoms reacted with the ring-opened PVP [10,15–17]. Therefore, the 4Cl-PDA dye was covalently bound to the PVP chains, resulting in the formation of PVP film with highly stable optical property. SEM was performed subsequently to visualize the morphology of the magnetic-fluorescent PVP film. The film surface was smooth and many microspheres inside the surface can be observed clearly (Fig. S6). Since 4Cl-PDA could react with the PVP chains which might locate in different microspheres, the shape of microspheres became relatively irregular by comparison with that in the pure magnetic PVP film. Nevertheless, the magnetic-fluorescent PVP film was successfully prepared by the incorporation of MNPs and dye molecules into the cross-linked PVP network.

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