

Preparation, characterization and photoluminescence activity of Rhodamine B doped silver nanoparticles/poly (vinyl alcohol) nanocomposite films

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The Rhodamine B doped silver nanoparticles/poly(vinyl alcohol) nanocomposite films were prepared by using poly (vinyl alcohol) as a stabilizing and reducing agent. The silver nanoparticles were directly synthesized in the poly(vinyl alcohol) matrixes based on the reduction of the AgNO₃ inorganic precursor through heat treatment. The active nanocomposite films were prepared by doping Rhodamine B into the silver nanoparticles/poly(vinyl alcohol) nanocomposites. These nanocomposite films were characterized using UV-vis spectroscopy, transmission electron microscopy and photoluminescence spectroscopy. The effects of heat treatment temperature on the properties of the silver nanoparticles/poly(vinyl alcohol) nanocomposite films have been studied. In addition, a largely enhancement of photoluminescence intensity of Rhodamine B has been observed.

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1. Introduction

Synthesis and assembly of noble metallic nanoparticles are central themes in developing science and technology of the specific class of nanomaterials. Especially, noble metallic nanoparticles combined with polymers have attracted much attention because of their distinct optical, electrical and catalytic properties, which have potential applications in the fields of catalysis, bioengineering, photonics and electronics [1–5], especially sensor applications [6,7]. The common approaches to such materials are casting of films from a mixture of preformed noble metallic nanoparticles and polymers [8], plasma deposition techniques [9] and in situ growth [10]. A successful preparation of noble metallic nanoparticles is determined by the ability to produce nanoparticles with uniform distributions and long stability, given their tendency to rapidly agglomerate in aqueous solution [11]. Among the noble metallic nanoparticles, silver nanoparticles are one of the most fascinating metals. Researchers have demonstrated that optimal concentration of silver ions and heat treatment temperature are shown to lead to a homogeneous dispersion of silver nanoparticles in polymer matrix [12]. Beside the parameters of the synthesis process, polymer matrixes are one of the factors to be considered. Polyphosphate, polyacrylate, poly (vinyl sulfate), poly(vinyl alcohol) (PVA) and poly(ethyleneimine), have been used to stabilize the silver nanoparticles [13,14]. In particular, the

biologically friendly PVA with low cytotoxicity and excellent thermal stability has been employed to design silver nanoparticles/PVA composites [15,16].

Recently, there has been an increasing interest in the synthesis of the silver nanoparticles stabilized in dye doped polymers, which have the potential for their applications in laser devices [17]. In these active materials the silver nanoparticles have been used as an effective means for improving spectroscopic properties. The enhanced spectroscopic properties are due to the surface plasmon resonance (SPR) of the silver nanoparticles. It is believed that the proper formulation of dye doped polymer matrixes, in which the silver nanoparticles are dispersed, can modulate the spectroscopic properties. The most reported laser dye used in the silver nanoparticles/polymer composites is Rhodamine 6G [18]. However, Rhodamine B (RB) is less studied in polymers for its laser action due to its deactivation processes [19].

In this paper, in order to design a metal enhanced fluorescence system based on the RB doped Ag-PVA nanocomposite films, we report the effect of heat treatment temperature and the SPR of the silver nanoparticles on the properties of the RB doped Ag-PVA nanocomposite films. In the system, the silver nanoparticles are used as the origin of the SPR absorption. The RB molecules are used as the gain medium, whose peak of photoluminescence wavelength is located outside the SPR absorption band of the silver nanoparticles.

2. Materials and methods

2.1 Preparation of the RB doped Ag-PVA nanocomposite films

The RB doped Ag-PVA nanocomposite films were synthesized from PVA (average molecular weight 500 g, alcoholysis degree 87.0~89.0%), distilled water, silver nitrate (AgNO_3) and Rhodamine B. The pure chemical reagents were obtained from aladdin chemical reagent corporation and were used without any further purification.

The RB doped Ag-PVA nanocomposite films were prepared by using the following procedure [12]. First, 1 g of PVA was dissolved into 10 ml of distilled water to obtain PVA aqueous solution. Then, aqueous solutions of silver nitrate, RB and PVA prepared beforehand were mixed at different silver nitrate weights of 0.031, 0.063 and 0.094, respectively. The mixtures were stirred for about 20 minutes using magnetic stirrer at 60~110°C. Finally, the resulting solutions were spincoated on glass slides at 900 r/s. Before spinning, the glass slides were sonicated sequentially in acetone and distilled water for three times, followed by heat treatment at 100°C. Then, the obtained nanocomposite films were heated for 5 minutes at 50°C, 70°C, 90°C, 110°C, respectively. The obtained Ag-PVA nanocomposite films without RB were yellow and transparent. However, the nanocomposite films appeared to be yellow after heat treatment, then changed into deep yellow, because larger amounts of silver nanoparticles were synthesized after heat treatment.

2.2 Characterization of the RB doped Ag-PVA nanocomposite films

The shape and size of silver nanoparticles synthesized in the Ag-PVA nanocomposite films were measured by Transmission Electron Microscopy (TEM) (Model JEM 2100 JEOL, Japan). TEM samples were prepared using carbon coated copper grids. The copper grids were coated by heat treated Ag-PVA aqueous solution. UV-visible optical absorption spectra of the RB doped Ag/PVA nanocomposite films were recorded by UV-visible absorption spectroscopy (Model TU-1901 UV-vis spectrometer, Beijing Purkinje General Instrument Co. Ltd, P.R.China). The properties of photoluminescence activity were displayed by Fluorescence spectrometer (Model a Fluorolog FL3-211-P spectrofluorometer equipped with a Xe flash lamp, Jobin Yvon, France). The same excitation area was taken for all the RB doped Ag-PVA nanocomposite films.

3. Results and discussion

3.1 UV-visible optical absorption and structural characterization of the PVA based nanocomposite films

The UV-visible optical absorption spectra of the RB doped PVA nanocomposites with silver nanoparticles and without silver nanoparticles heated at 110°C are shown in Fig. 1. The curve (a) and (b) are the spectra of sample 1 ($\text{AgNO}_3/\text{RB}=0.031 \text{ g}/0.96 \text{ g}$) and sample 2 ($\text{AgNO}_3/\text{RB}=0 \text{ g}/0.96 \text{ g}$), respectively. The appearance of the broad peak in the curve (a) at about 415 nm indicates the formation of silver nanoparticles in sample 1. The broad peak is due to the SPR in the conduction bands of silver nanoparticles [20]. The curve (b) shows that there is an absorption peak located at about the wavelength of 555 nm due to the RB molecules for sample 2. However, the absorption peak due to the RB molecules for sample 1 is located at the wavelength of 562 nm, which has a red shift compared with the absorption peak of sample 2. The red shift is due to the local field by silver nanoparticles. This also indicates some RB molecules adsorb preferentially onto silver nanoparticles. Furthermore, the absorption intensity due to the RB molecules for sample 1 is larger than that for sample 2. Compared with the curve (a) and (b), we conclude that it is caused by the SPR of the silver nanoparticles.

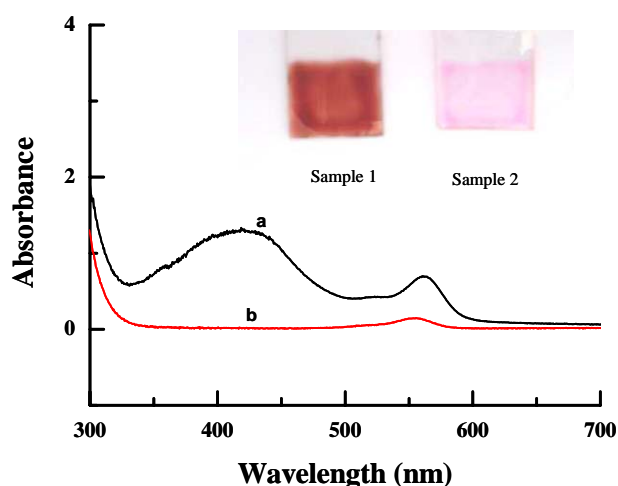


Fig. 1. UV-vis optical absorption spectra of the RB doped Ag-PVA nanocomposite films heated at 110 °C with different contents. (a) Sample 1: $\text{AgNO}_3/\text{RB}=0.031 \text{ g}/0.96 \text{ g}$, (b) Sample 2: $\text{AgNO}_3/\text{RB}=0 \text{ g}/0.96 \text{ g}$. The inset is the photographs of the two samples.

Both the transmission electron microscopy image and energy dispersive spectrometer of the formed silver nanoparticles in the Ag-PVA aqueous solution (Sample 3: $\text{AgNO}_3/\text{RB}=0.031 \text{ g/0 g}$) are presented in Fig. 2. Fig. 2 (a) shows the silver nanoparticles are spherical and the size of the silver nanoparticles is from 10 to 30 nm. Moreover, Fig. 2 (b) confirms the silver nanoparticles by exhibiting a peak at approximately 3 keV, which is typical for the absorption of the silver nanoparticles due to the SPR.

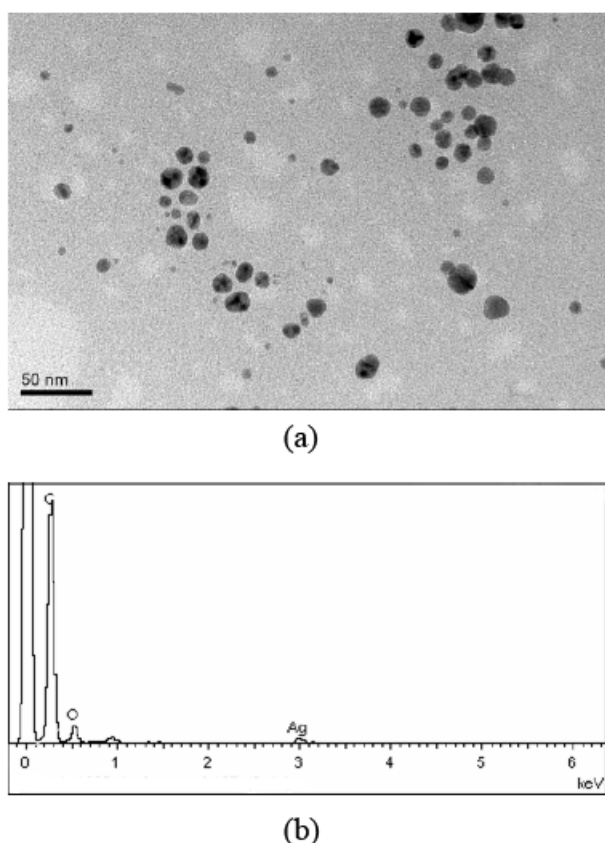


Fig. 2. (a) TEM image of the Ag-PVA aqueous solution ($\text{AgNO}_3/\text{RB}=0.031 \text{ g/0 g}$) heated at $110 \text{ }^\circ\text{C}$. (b) EDS analysis of the Ag-PVA nanocomposite film.

3.2 The effect of heat treatment temperature on the UV-visible optical properties of the RB doped Ag-PVA nanocomposite films

The silver nanoparticles were obtained by heating the RB doped PVA nanocomposite films. All the contents of AgNO_3 and RB in the three samples were 0.094 and 0.96, respectively. The heat treatment temperatures were 50°C (Sample 4), 70°C (Sample 5) and 90°C (Sample 6), respectively. Fig. 3 indicates that the SPR absorption intensity of the silver nanoparticles is strengthened by increasing the heat treatment

temperatures from 50 to 90°C . It demonstrates that the quantity of the silver nanoparticles in sample 4, sample 5 and sample 6 is increased with increasing the heat treatment temperature. With different heat treatment temperatures, the wavelengths of the SPR absorption peaks of the silver nanoparticles have little change. It indicates that the average sizes of the silver nanoparticles have little change. This is also demonstrated in Ag-PVA nanocomposite films without doping the RB [12]. Furthermore, the intensity of the absorption peak due to the RB molecules at about 562 nm is strengthened with increasing the heat treatment temperature. This also demonstrated that the SPR of the silver nanoparticles can strengthen the optical absorption of the RB molecules.

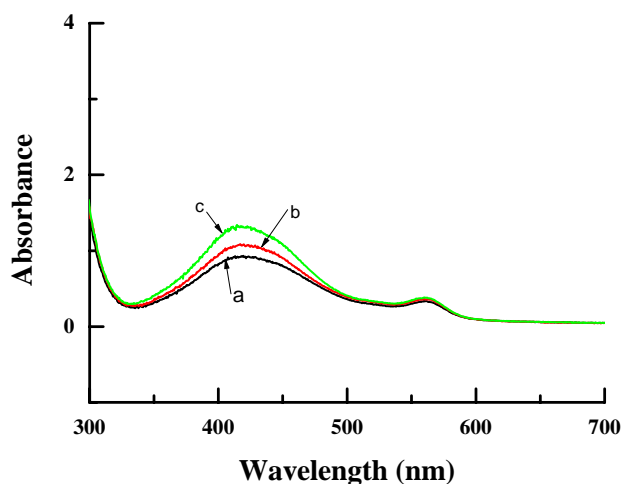


Fig. 3. UV-vis optical absorption spectra of the RB doped Ag-PVA nanocomposite films ($\text{AgNO}_3/\text{RB}=0.094 \text{ g/0.96 g}$) heated at various temperatures: (a) $50 \text{ }^\circ\text{C}$, (b) $70 \text{ }^\circ\text{C}$, (c) $90 \text{ }^\circ\text{C}$.

3.3 Photoluminescence activity of the RB doped Ag-PVA nanocomposite films

Fig. 4 shows the photoluminescence activity of the RB doped Ag-PVA nanocomposite films. The curve (c) is the photoluminescence in the Ag-PVA nanocomposite films without doping the RB, which indicates that for the Ag-PVA nanocomposite films there has no photoluminescence activity. The curve (b) is the photoluminescence in the RB doped PVA without doping silver nanoparticles (Sample 2). It shows that the RB molecules have the maximum photoluminescence peak at the wavelength of 574 nm . The curve (a) is the photoluminescence in the RB doped Ag-PVA nanocomposite films with doping silver nanoparticles

(Sample 1). The maximum photoluminescence peak for sample 1 is located at the wavelength of 587 nm. There is a red shift of the excitation peaks for sample 1 and sample 2. It is shown in the curve (d) and (e) of Fig. 4, respectively. Moreover, the curve (a) and (b) show that about twice enhancement of the photoluminescence intensity can be obtained by the silver nanoparticles in the RB doped Ag-PVA nanocomposite films. This is attributed to the silver nanoparticles enhanced fluorescence associated with the electromagnetic field enhancement caused by the indirect interaction between silver nanoparticles and RB molecules. This result demonstrates that a majority of RB molecules are not in a direct contact with silver nanoparticles, only a few RB molecules are adsorbed onto the surface of silver nanoparticles.

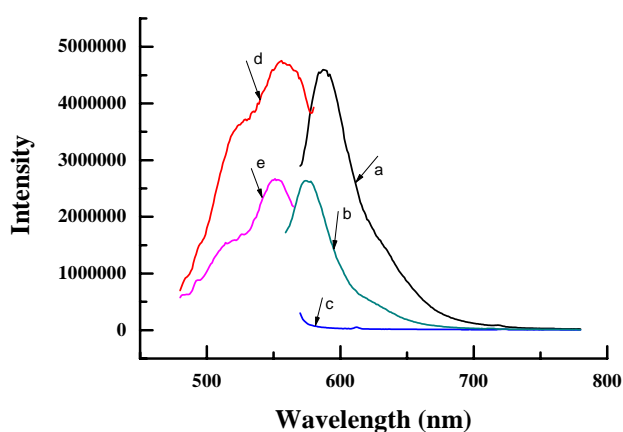


Fig. 4. Photoluminescence intensity of the RB doped Ag-PVA nanocomposite films. (a) $\text{AgNO}_3/\text{RB}=0.031$ g/0.96 g, (b) $\text{AgNO}_3/\text{RB}=0$ g/0.96 g, (c) $\text{AgNO}_3/\text{RB}=0.96$ g/0 g. The excitation spectra of the RB doped Ag-PVA nanocomposite films. (d) $\text{AgNO}_3/\text{RB}=0.031$ g/0.96 g, (e) $\text{AgNO}_3/\text{RB}=0$ g/0.96 g.

The ratio of the quantum yields for the two samples with or without doping silver nanoparticles can be determined by $\Phi_u/\Phi_s = (Y_u/Y_s)(A_s/A_u)$, where Y_u and Y_s represent the integral areas of photoluminescence spectra, A_u and A_s represent the absorption values at the excited wavelengths. For the two samples with or without doping silver nanoparticles in this experiment, Y_u/Y_s and A_s/A_u are 2.2 and 0.6, respectively. So, the ratio of the quantum yields for the two samples are about 1.3. This demonstrates that by doping silver nanoparticles the quantum yield is increased. This also shows that the surface plasmon resonance absorption of the silver nanoparticles strengthens the photoluminescence of the RB.

4. Conclusion

In conclusion, about twice enhancement of the photoluminescence intensity by the surface plasmon resonance absorption of the silver nanoparticles was demonstrated. The effect of heat treatment temperature on the UV-visible optical properties of the RB doped Ag-PVA nanocomposite films were carried out systematically. It was found that by increasing the heat treatment temperature, both the intensity of the surface plasmon resonance absorption and RB absorption were strengthened.

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