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Preparation and Fluorescence Properties of Co-doped Nanocomposite Film Based on Supra Molecular Structure

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A novel materials design procedure based on the co-doping of metal nanoparticle and azo dye compound (MNPADC) is developed to improve the properties of functional molecules. The synthesized materials were characterized by transmission electron micrograph (TEM), ultraviolet-visible absorption spectra (UV-Vis) and fluorescence spectra (FS). It was found that the fluorescence intensity of methyl orange (MO) was enhanced by 5 times in the aqueous composite system doped with silver nanoparticles whereas it was reduced by 15% and 20% in composite films with co-mixing and coating structures, respectively. The results indicate that the properties of functional molecules can be greatly improved in composite film with supra molecular structure and that the procedure presented here is effective.

Key words: Supra molecular structure, Nanocomposite film, Silver nanoparticles, Methyl orange, Fluorescence properties

I. INTRODUCTION

Since Creighton *et al.* reported on the surface-enhanced Raman scattering (SERS) of adsorbed molecules in silver sol system [1], many researches have been carried out on the mechanism and physicochemical properties [2-6]. Silver sol has been widely employed as the active substrate for SERS because of the simplicity of preparation, the convenience of monitoring the sol, the possible control of particles, and the tremendous enhancement factor of resonance local field of silver particles [7,8]. However, a major disadvantage is the continuous aggregation of the sol particles in solution system. As an accompanying effect of SERS, the fluorescence enhancement and quenching provides an effective means for studying the interaction between particles and adsorbed molecules [9]. Recently, it was reported that the fluorescence quenching has a significant prospect in the fields of sensors and biomedicine [10]. However, to date, the researches on fluorescence enhancement and quenching effect mostly focused on solution systems. Little attention was paid to solid films.

Based on the SERS theory and literatures' results, we proposed a novel design procedure for materials with supra molecular structure. When two kinds of dopant such as metal nanoparticles and dye molecules are co-doped in polymer matrix, the interactions between nanoparticles and dye molecules might be capable of improving the properties of functional molecules. Recently, we have successfully synthesized a new opto-

electronic material based on supra molecular structure of MNPADC by co-doping, which behaves excellent optical and thermal properties and thus meets the requirements of short-wavelength optical storage [11,12].

In order to understand the mechanism of the interactions between silver particles and MO molecules, we measured the FS of composite system in solution and film states, respectively. When silver sol was added into MO solution, the fluorescence intensity of MO was enhanced obviously; however, when the liquid coating system composed of silver nanoparticles and MO molecules was doped into polymer matrix to form nanocomposite film, the fluorescence intensity of MO was reduced. We also analyzed the mechanism of fluorescence properties in detail.

II. EXPERIMENTAL

A. Reagents

The reagents in the experiments were as follows: silver nitrate (Beijing Chemical Factory, China), sodium boro-hydride (MERCK-Schuchardt, Germany), methyl orange (Tianjin Chemical Factory, China), polyvinyl alcohol (PVA) (Xi'an Chemical Factory, China). All reagents used were of analytical grade without any further purification. De-ionized water was used in the experiments as solvent.

B. Apparatus and measurements

The morphologies of samples were observed using a transmission electron microscope (Hitachi H-600, Japan), operated at 100 kV. The absorption spectra

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of samples were measured with UV-Vis spectrometer (Hitachi U2001, Japan) in range of 300–800 nm. The FS of samples were determined using a luminescence spectrometer (Perkin-Elmer LS50B, USA) with an excitation wavelength of 350 nm.

C. Preparation of samples

Silver sol was used as the source of silver nanoparticles in our experiment. It was prepared by the colloidal chemistry method reported previously [11]. Since the color of colloid prepared is brown, it is denoted as BSC sol. In general, there are two methods of adding two kinds of dopant into the same matrix: one is that two kinds of dopant are doped into the same matrix in turn (denoted as co-doping with co-mixing structure), and the other is that two kinds of dopant are mixed together first and then the mixture is doped into the matrix (denoted as co-doping with coating structure).

To obtain the co-doped mother solution with coating structure, 9 mL of MO solution (5 mmol/L) was added to 25 mL of fresh BSC sol (1 mmol/L) and the mixture was dispersed by ultrasonic. Then the mixture was put aside still for about 1 h, added to 10 mL of PVA solution (5wt%), and dispersed further by ultrasonic for a few minutes. Finally, the resulted mixture was filtered, and the co-doped mother solution with coating structure was obtained. The mixture was denoted as coating MBP solution.

As for the co-doped mother solution with co-mixing structure, 25 mL of fresh BSC sol was added to 10 mL of PVA solution and the mixture was dispersed by ultrasonic. Then 9 mL of MO solution was added to the above mixture and dispersed by ultrasonic. After the mixture was filtered, the co-doped mother solution with co-mixing structure was obtained. The mixture was denoted as co-mixing MBP solution. For comparison, the MO-doped PVA solution (denoted as MP solution) and the BSC-doped PVA solution (denoted as BP solution) were also prepared.

To fabricate the composite films by spin-coating, the mother solution was dripped onto a neat k9 glass plate at room temperature, and the wet film was dispersed on the substrate plate by spin-coating. Then, the wet film was dried at 40 °C for 5 min. Above procedure could be repeated many times to prepare the films with various thicknesses. The resulting film was dried at 100 °C for 1 h to completely remove solvent, and then cooled down to room temperature. The composite films resulted from the two co-doped mother solutions were denoted as coating MBP film and co-mixing MBP film, respectively.

III. RESULTS AND DISCUSSION

A. TEM images of silver nanoparticles

The TEM images of silver particles in colloid and silver particles coated with MO in composite film are shown in Fig.1 and Fig.2, respectively. It can be seen

from Fig.1 that the silver particles are almost spherical, and well dispersed. The average size of particles is about 11–12 nm. It can be observed in Fig.2 that the shapes of particles coated with dye are sphere or ellipsoid-like. The average size of particles in Fig.2 is larger than that in Fig.1. These size and shape changes of particles could be attributed to the aggregation and growth of particles resulted from the adsorption of dye molecules onto the surface of silver particles.

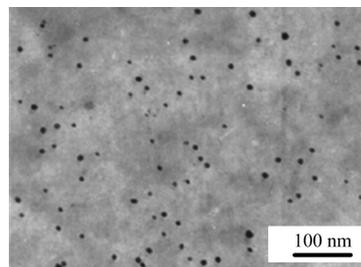


FIG. 1 TEM images of silver nanoparticles in colloid.

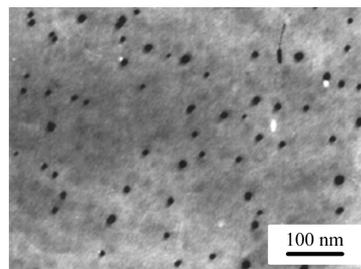


FIG. 2 TEM images of silver nanoparticles coated with dye in film.

B. UV-Vis absorption spectra of samples in aqueous system

Figure 3 shows the absorption spectra of MO, BSC, MP and BP in aqueous solution, respectively. The absorption band (curve a) is attributed to plasma resonance of silver nanoparticles. Compared curve b with curve a, we can see that the absorption bands of BSC sol and BP solution have the same maximum absorption wavelength. The absorption band (curve c) is attributed to the intramolecular π - π^* electron transition of MO. Again, we can see that the absorption bands of MO solution and MP solution have the same maximum absorption wavelength. The absorption spectra in Fig.3 indicate that the PVA in aqueous system is an inert medium and has no influence on the absorption peak of silver nanoparticles and MO molecules.

C. UV-Vis absorption spectra of co-doped composite system

The absorption spectra of co-doped composite system are shown in Fig.4. We can see that the absorption band of the co-mixing MBP solution (curve a) almost has the same shape as the coating MBP solution (curve

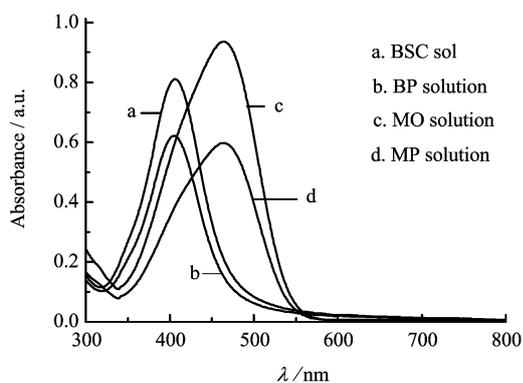


FIG. 3 Absorption spectra of BSC sol (a), BP solution (b), MO solution (c) and MP solution (d), respectively.

b) in aqueous composite system. It is mainly because both absorption bands, in essence, were formed by the superposition of BSC absorption and MO absorption in PVA solution. Compared with the aqueous composite system, the absorption bands of co-mixing MBP film (curve c) and coating MBP film (curve d) show changes in the intensity and shape, respectively. Especially, not only the peaks of the “single-peak” bands in composite films behave a blue-shift compared with the “double-peak” bands in aqueous system, but also the peak of coating MBP film behaves a blue-shift of 7–8 nm compared with co-mixing MBP film. The mechanism of the absorption blue-shift was discussed in detail in the reference [11].

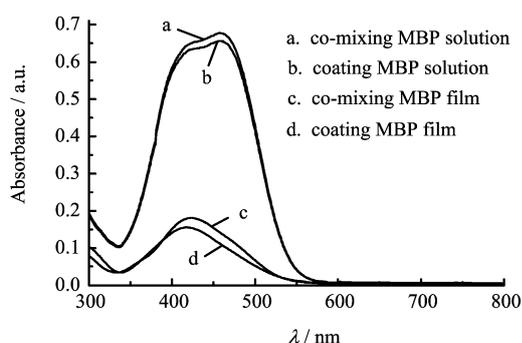


FIG. 4 Absorption spectra of co-mixing MBP solution (a), coating MBP solution (b), co-mixing MBP film (c) and coating MBP film (d), respectively.

D. Fluorescence enhancement and quenching of MO

9 mL of MO aqueous solution (5 mmol/L) was added to 10 mL of PVA solution (5wt%), then oscillated (MP solution) in order to form homogeneous mixture. Figure 5 shows the FS of MP solution and coating MBP solution. It can be seen clearly from the profiles of FS that the fluorescence intensity of MO in coating MBP solution (curve b) was enhanced by about 5 times compared with that in MP solution (curve a). It is noteworthy that the fluorescence peak of coating MBP solution should be attributed to MO, not to silver, be-

cause the fluorescence peak of silver particles locates at about 480 nm, which has been confirmed experimentally. Therefore, we conclude that the doping of silver nanoparticles in aqueous system leads to the fluorescence enhancement of MO.

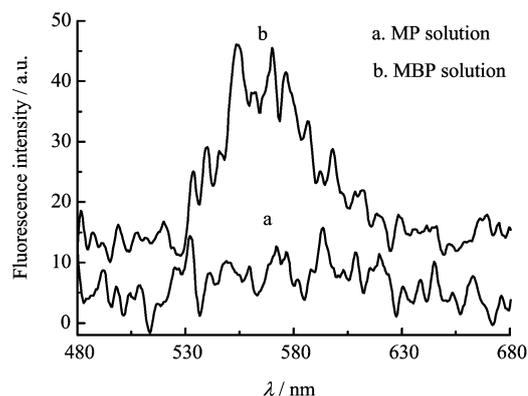


FIG. 5 Fluorescence spectra of MP solution (a), coating MBP solution (b), excited at 350 nm.

Figure 6 shows the FS of composite films. Compared with MP film (curve a), the fluorescence intensities of co-mixing MBP film (curve b) and coating MBP film (curve c) were reduced by about 15% and 20%, respectively. The results indicate that the doping of silver nanoparticles in composite films gives rise to the fluorescence quenching of MO.

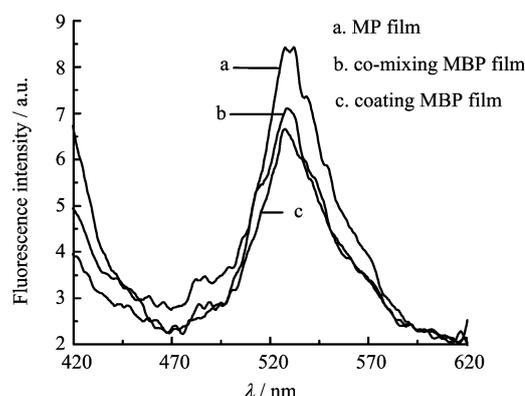


FIG. 6 Fluorescence spectra of MP film (a), co-mixing MBP film (b), and coating MBP film (c), excited at 350 nm.

E. Mechanism of fluorescence properties of MNPADC composite films

To discuss the mechanism of fluorescence properties of MO, it is necessary to understand the formation of nanocomposite film with supra molecular structure. It is known that the large specific surface and strong surface energy of silver nanoparticles make it carry positive charge on the surface of particles. According to the prepared process of coating MBP film, when MO molecules

were adsorbed onto the surface of silver particles by Coulomb interaction between silver particles and anion groups ($-\text{SO}_3^-$) of MO, the dye layer around silver particles and the supra molecules with coating structure were formed [13]. Therefore, the supra molecules were composed of silver particles and MO molecules, marked by $[(\text{Ag})_n]_{\text{core}}[(\text{MO})_m]_{\text{shell}}$. When the aqueous composite system with supra molecular structure was doped into polymer PVA matrix, the supra molecules were immobilized in matrix and formed a MNPADC nanocomposite film after the evaporating of water.

The major difference between the aqueous composite system and the corresponding composite film is that no water exists in composite film. In aqueous system, MO and silver are surrounded by many water molecules and form the hydrated ions and particles, respectively, which results in the interval between silver particles and the adsorbed MO molecules in supra molecular structure. However, in composite film, the interval is greatly reduced because of the removal of water molecules. In other words, compared with the aqueous system, MO molecules are nearer to the surface of silver particles in composite film with supra molecular structure. Thus, the adsorption between MO and silver particles in aqueous system belongs to the loose physisorption, but belongs to the close physisorption in composite film with supra molecular structure.

In the theory of the fluorescence enhancement and quenching, Weitz concluded that it depends on the competition between the enhancement of local field around the surface of metal particles and the non-radiate energy transfer from the adsorbed molecules to the surface of particles [14]. It is well known that there is enormous local field around spherical metal nanoparticles in the light of the local field effect near the surface plasmon resonance [15], and that the local field falls off swiftly with the increase of the distance away from the surface of particles. Due to the excitation of local field of silver particles, the fluorescence intensity of MO molecules around silver particles enhances in aqueous system compared with MO in MP solution without silver. So the fluorescence enhancement of MO resulted from the doping of silver particles in aqueous and solid composite system, naturally, should both exist in MBP solution and MBP film. However, for MBP film, besides the contribution from the fluorescence enhancement of MO, the fluorescence quenching of MO is also an important influence factor, especially for coating MBP film. Although the close physisorption can lead to the fluorescence enhancement of MO because of MO near to silver particles in composite film, the strengthened interaction between silver particles and MO molecules can also lead to the non-radiate energy transfer from the adsorbed MO molecules to the surface of silver particles. Thus the result of the competition between fluorescence enhancement and quenching leads to the fluorescence quenching of MO in composite film. The degree of quenching in coating MBP film is stronger than that in co-mixing MBP owing to the direct interactions be-

tween MO molecules and silver particles.

IV. CONCLUSIONS

We have prepared the nanocomposite film with supra molecular structure based on the co-doping of MNPADC. The fluorescence properties of the films were discussed by comparison with the aqueous composite system. It was found that the doping of silver nanoparticles can lead to the fluorescence enhancement of MO in aqueous system and the fluorescence quenching of MO in composite film. By analyzing the mechanism of the fluorescence properties, we conclude that the effects of metal nanoparticles on the adsorbed functional molecules in composite film with supra molecular structure should be capable of improving the functional properties of molecules.

V. ACKNOWLEDGMENT

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