One-step synthesis of silver-poly(4-vinylpyridine) hybrid microgels by γ-irradiation and surfactant-free emulsion polymerization. The photoluminescence characteristics

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Abstract

Spherical silver-poly(4-vinylpyridine) (Ag-P4VP) hybrid microgels, in which Ag nanoparticles (2–3 nm) were evenly dispersed in P4VP particles (80–120 nm), were successfully synthesized in a single step by γ-irradiation and surfactant-free emulsion polymerization. Both UV–vis spectra and transmission electron microscope (TEM) image reflected that almost all Ag nanoparticles were encapsulated in P4VP particles. More interestingly, this hybrid microgel dispersion exhibited peculiar photoluminescence (PL) phenomenon, which might arise from the monomer emission of the pyridine group enhanced by Ag nanoparticles.
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1. Introduction

In the past two decades, much attention has been paid to the synthesis and characterization of inorganic-polymer nanocomposites for their intriguing optical, electrical, magnetic and catalytic properties [1–6]. As a member of nanocomposite microspheres, hybrid microgels are attractive building blocks for constructing ordered and complex materials. Now, hybrid microgels have been used extensively in the fields of coatings, colloid crystals, catalysis, diagnostics and so forth [1,2,7].

To synthesize the inorganic-polymer nanocomposite microspheres, a variety of methods have been employed, such as ion exchange [7,8], photo-thermal patterning [9], block polymer micelles [10] and surface-graft processing [11]. In these methods, the synthesis of polymer and the preparation of inorganic nanoparticles are operated individually. Thus, inorganic nanoparticles are difficult to be well dispersed in the polymer microspheres. In addition, microemulsions [12–14] and micelles [15] are often used to prepare nanocomposite microspheres, too. Since the surfactants are difficult to be removed

completely, the application of the products is limited [16,17]. Obviously, it is both scientifically and practically important to explore a method of synthesizing inorganic-polymer nanocomposite microspheres, by which inorganic nanoparticles can be evenly dispersed within the polymer microspheres in the absence of the surfactants.

Very recently, we carried out the synthesis of microgels by γ-irradiation and surfactant-free emulsion polymerization, and studied the properties of the obtained microgels systematically [18,19]. The results showed that 4-vinylpyridine (4-VP) was propitious for preparing microgels by the method [18], and the stability of this kind of microgel dispersions mainly arises from the ionization of pyridine groups, resulting in a positively charged surface [19]. Our research group has also successfully synthesized Ag nanoparticles [20] and cuprous oxide octahedron nanocrystals [21] in water-in-oil microemulsions by γ-irradiation. When the Ag clusters or small Ag nanoparticles were protected by dodecyl mercaptan and then dispersed in chloroform, a peculiar PL phenomenon appeared [20]. 4-VP, with the feasible coordination with metal ions [22,23], as well as its easy formation of microgel, has been applied in this work for the preparation of a hybrid microgel through the simultaneous formation of Ag nanoparticles and poly(4-vinylpyridine) (P4VP) microgel by γ-irradiation and surfactant-free emulsion

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polymerization in a single step. It was found that the Ag nanoparticles were well dispersed within the polymer microspheres, but not in the outer layer [24].

It is well known that noble metal clusters and small nanoparticles have fascinating fluorescence or photoluminescence characteristics [20,25–27]. Moreover, Vollath and Szabo [28] found that the metal oxide-poly(methyl methacrylate) nanocomposite, a combinations of two non-luminescent materials, exhibited relatively strong luminescence and suggested that this is due to the energy transfer from metal oxide nanoparticles to the polymer coating via carboxylate bonds. In this paper, the PL enhancement phenomenon of the obtained hybrid microgel dispersion will be reported, as well as a proposed mechanism.

2. Experimental

2.1. Materials

Silver nitrate (GR, Shanghai Chemical Reagents Inc.), isopropanol (AR, Beijing Chemical Reagent Inc.), methanol (spectroscopically pure reagent, Tianjing Shield Company) and dodecyl mercaptan (CP, Fine Chemical Reagent Factory of Nankai University) were used as received. 4-VP (Merck, >96%) was purified by vacuum distillation. N,N'-methylenebisacrylamide (Bis, AR, Beijing Chemical Reagents Inc.) was purified by recrystallization and dried in vacuum. Deionized and tridistilled water was used in the experiments.

2.2. Instruments

All the solutions were irradiated in the filed of a ^{60}Co γ-ray source whose dose rate was determined by Fricke dosimeter. The UV–vis spectra were recorded by a U-3010 Spectrometer. TEM images were obtained on a JEOL JEM-200CX transmission electron microscopy, operating at 120 kV. The dynamic light scattering (DLS) experiment was carried out at 25 °C via a ALV/DLS/SLS-5022F laser light scattering spectroscopy (wavelength: 632.8 nm) with the scattering angle of 90°. The intensity autocorrelation functions were analyzed to obtain the hydrodynamic radii (R_h) of particles with methods of Contin and Cumulant. The PL spectra were measured on a F-4500 Fluorescence Spectrometer. The excitation and emission slit widths were 10 nm and the scanning speed was 240 nm/min.

2.3. Methods

An aqueous solution containing 4 mmol/L AgNO$_3$, 0.045 mol/L 4-VP, 2.0 mol/L isopropanol and 0.45 mmol/L Bis was prepared. After bubbling with high purity N$_2$ and being sealed, the solution was irradiated for 3 h and 20 min with a dosage of 24 kGy. After irradiation, a stable, brown and translucent microgel dispersion was obtained. Thin-layer chromatography analysis (silica thin-layer plate, ethyl acetate/petroleum ether = 9/1, v/v) showed that almost all 4-VP was involved in the polymerization. The obtained microgel dispersion was dropped onto a Formvar-covered copper grid that was placed on filter paper and evaporated in air before

characterization by electron microscopy. Before the DLS measurements, the microgel dispersion was diluted by water and centrifuged at 12,000 rpm. After being diluted 50-folds by water, the UV–vis and PL spectra were measured.

Similar procedure was used to synthesize the P4VP microgel, except that AgNO$_3$ was not added.

3. Results and discussion

3.1. Formation and characterization of Ag-P4VP hybrid microgel

The TEM image of the Ag-P4VP hybrid microgel is shown in Fig. 1. It can be seen that the diameters of spherical P4VP particles range from 80 to 120 nm and monodispersed Ag nanoparticles with diameters of 2–3 nm are evenly dispersed in the polymer particles. Because the Ag nanoparticles are distributed at various depths in the P4VP particles, not all of them are observed at a given focus. In the field of vision, there are no Ag nanoparticles existing outside the P4VP particles. This result suggests that almost all Ag nanoparticles are encapsulated in P4VP particles. DLS Analysis shows that the R_h of the microgel is in the range of 53.7–79.2 nm. This indicates that the size detected by DLS is larger than that by TEM. Such discrepancy may be ascribed to the shrink of P4VP particles during the preparation of TEM samples [29].

Fig. 2a shows the UV–vis spectrum of the obtained hybrid microgel dispersion after dilution with water. The absorption band with a maximum at ca. 420 nm can be ascribed to the surface plasma (SP) band of Ag nanoparticles [7,30], further confirming the formation of Ag nanoparticles. As well known, unprotected Ag nanoparticles display an absorption band with a maximum at ca. 390 nm [31,32]. Here, the red shift of SP band can be attributed to the strong interaction between Ag nanoparticles and the pyridine groups of P4VP [33]. However, after refrigeration, ablation and centrifugation, the supernatant with the same dilution is colourless and no absorption band around 390 nm was observed (Fig. 2b). These results suggest that almost
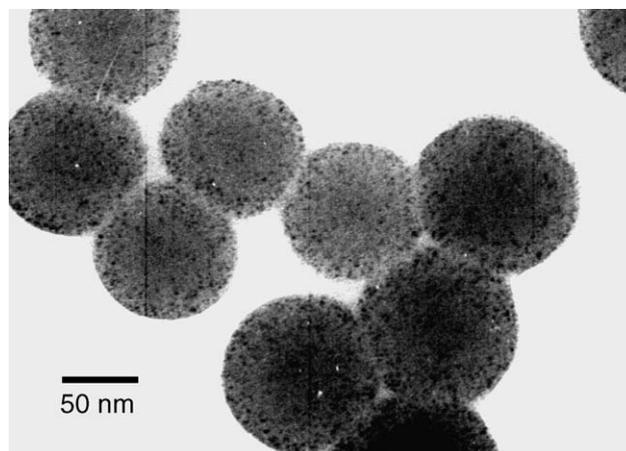

Fig. 1. TEM image of Ag-P4VP hybrid microgels prepared by γ-irradiation and surfactant-free emulsion polymerization in a single step.
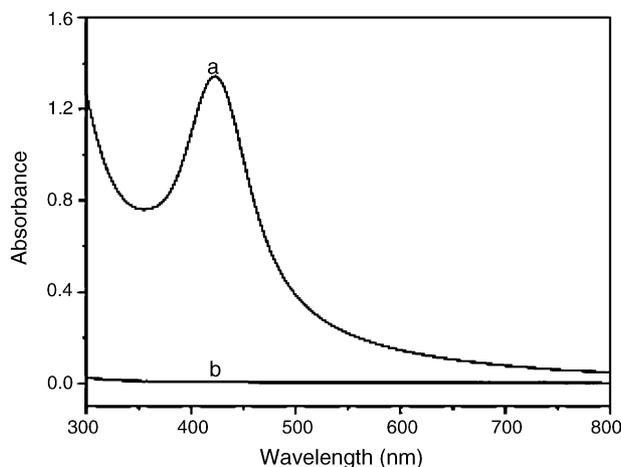
Fig. 2. UV–vis spectra of the Ag-P4VP hybrid microgel dispersion (a) and the supernatant after refrigeration, ablation and centrifugation (b).

all Ag nanoparticles are encapsulated in P4VP particles, which is consistent with the result of the TEM observation.

In the aqueous solution, 4-VP monomers and Ag^+ coordinate complexes were mixed homogeneously at the molecular level. When the solution was irradiated by γ-ray, water absorbed most of the irradiation energy and generated many reactive species, such as hydrated electrons (e_{aq}^-), H_3O^+, H and $^\bullet OH$ (Eq. (1)) [34]:

$$H_2O \xrightarrow{\text{irradiated}} e_{aq}^-, \ H_3O^+, \ H, \ ^\bullet OH, \ldots \qquad (1)$$

The produced radicals could induce the copolymerization of coordination compounds and 4-VP monomers, and it was the reducing species, especially e_{aq}^-, that reduced Ag^+ to Ag (Eq. (2)) [34,35].

$$Ag^+ + e_{aq}^- \rightarrow Ag \qquad (2)$$

Then, silver mono-atoms and Ag^+ aggregated to form silver clusters [36] and nanoparticles. Because the rate of polymerization was faster than that of reduction, almost all silver clusters, Ag nanoparticles and Ag^+ were collected by P4VP microgel through coordination interaction, in which Ag^+ was reduced further. It was the formation of P4VP microgel that confined the further growth of Ag nanoparticles. According to the principal of charge conservation, small amount of H_3O^+ produced by γ-ray irradiation could be reserved because of the reduction of Ag^+. The reserved H_3O^+ reacted with pyridine groups on the surface of the P4VP microgel to make it more stable. Thus, the stable microgels containing small size Ag particles were formed. On the contrary, in the absence of Ag^+, the H_3O^+ would be consumed through a series of other reactions [37]. Furthermore, isopropanol, a scavenger of oxidative radicals (Eq. (3)) [34,38]

$$(CH_3)_2CHOH + {}^\bullet OH \rightarrow (CH_3)_2\dot{C}OH + H_2O \qquad (3)$$
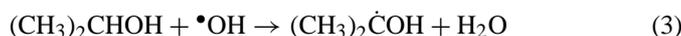
and chain-transfer reagent [38], was added into the solution to eliminate the influence of oxidative radicals on the reduction of Ag^+ and control the rate of polymerization. At the same time, $(CH_3)_2\dot{C}OH$, with the reduction potential of -1.5 V [39],

could also reduce Ag^+ [38,40], leading to an increased Ag yield.

3.2. Photoluminescence characteristics

When water-diluted Ag-P4VP hybrid microgel dispersion was excited at 260 nm, the excitation wavelength of P4VP [41], fluorescence quenching took place. This phenomenon is similar to the situation that a fluorophore directly binding to the metal surface, where both energy and electron transfer processes were considered to be the major deactivation pathways for excited fluorophores [42,43]. Thus, to avoid the quenching phenomenon, all samples were excited at 220 nm, which is the excitation wavelength of Ag nanoparticles [20]. Fig. 3A shows that the PL spectra of Ag-P4VP hybrid microgel dispersion diluted by water is similar to that of P4VP microgel dispersion with the same dilution. Obviously, the PL intensity of the former is stronger than that of the latter. Both the Ag-P4VP and P4VP microgels were also treated with plenty of dodecyl mercaptan, and then diluted by methanol. Since methanol, a good solvent for P4VP, enforced the P4VP chains unfold, Ag nanoparticles were exposed to the solvent and protected by dodecyl mercaptan. In this case, however, the PL spectra are different (Fig. 3B). The latter shows weak PL emission, while the former displays an emission peak at ca. 300 nm and a shoulder peak at ca. 350 nm, which are close to the PL emission peak positions of Ag clusters or small Ag nanoparticles protected by dodecyl mercaptan [20]. Therefore, it can be concluded that the PL emission of Ag-P4VP in water with a main peak at ca. 340 nm (Fig. 3A) results from the monomer emission of the pyridine group.

As mentioned above, small amount of H_3O^+ was produced in the presence of Ag^+. The possibility that the increase of acidity enhances the PL emission can be excluded from Fig. 4A, which shows that the PL intensity of P4VP microgel dispersion is reduced with the increased concentration of HNO_3. In order to answer the question of whether the residual Ag^+ enhances the PL emission or not, a control experiment was performed, in which 8 and 24 μmol/L Ag^+ were added into the diluted P4VP microgel dispersion, corresponding to the condition that 90 and
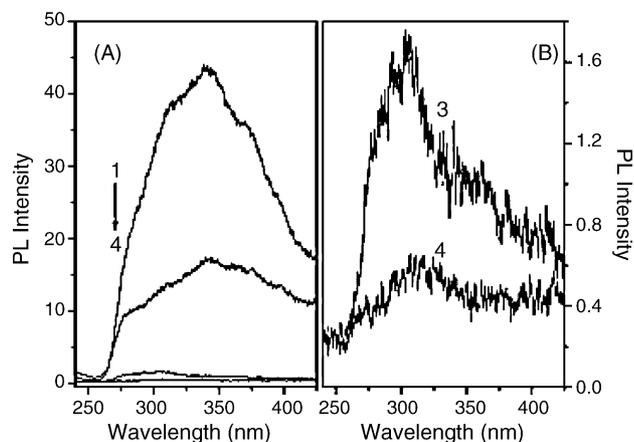

Fig. 3. (A) PL spectra of Ag-P4VP hybrid microgel dispersed: in water (1) and in dodecyl mercaptan/methanol (3), P4VP microgel dispersed: in water (2) and in dodecyl mercaptan/methanol (4). (B) Enlargement of (3) and (4).
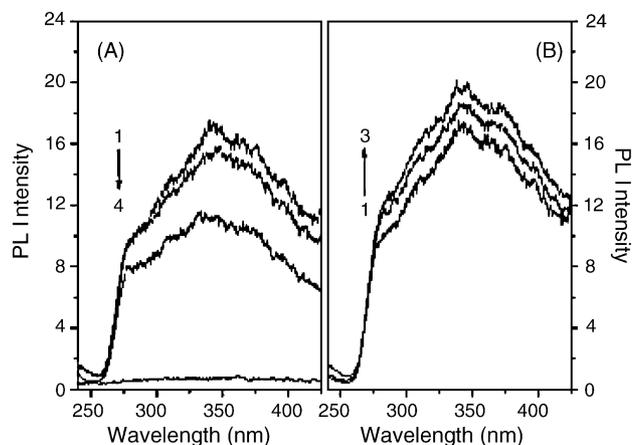
Fig. 4. The effects of acidity (A) and Ag^+ (B) on the PL spectra of water-diluted P4VP microgel dispersion. (A) [HNO_3] = 0, 0.08, 0.18, 0.45 mmol/L (from 1 to 4). (B) [Ag^+] = 0, 8, 24 μmol/L (from 1 to 3).

70% of Ag^+ was reduced in hybrid microgel system, respectively. Though an emission enhancement was observed in both situations, the extent is minor (Fig. 4B). Fig. 5 illustrates that the PL intensity of the diluted Ag-P4VP hybrid microgel dispersion is decreased with the increase of the concentration of HNO_3. This is because HNO_3 can react with pyridine groups and unfolds the P4VP chains, which can weaken the interaction between Ag nanoparticles and pyridine groups. Especially, when the concentration of HNO_3 is 0.45 mmol/L, the PL spectrum of Ag-P4VP hybrid microgel dispersion is similar to that of P4VP microgel dispersion (Fig. 3A). It is suggested here that such a large emission enhancement (Fig. 3A) may be explained in terms of the interaction between Ag nanoparticles and pyridine groups. The possible mechanism is that Ag nanoparticles transfer the absorbed energy to pyridine groups [28]. The detailed mechanism is worthy of further study.
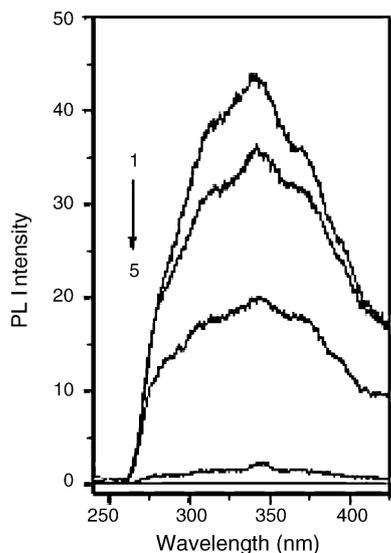

Fig. 5. The effect of acidity on the PL spectra of water-diluted Ag-P4VP hybrid microgel dispersion. [HNO_3] = 0, 0.18, 0.45, 0.90, 1.35 mmol/L (from 1 to 5).

4. Conclusions

Spherical Ag-P4VP hybrid microgels, with Ag nanoparticles (2–3 nm) dispersed evenly in P4VP particles (80–120 nm), were successfully synthesized in a single step by γ-irradiation and surfactant-free emulsion polymerization. UV–vis spectra and TEM image demonstrated that almost all Ag nanoparticles were encapsulated in P4VP particles. More interestingly, the hybrid microgel dispersion exhibited peculiar photoluminescence phenomenon, which might arise from the monomer emission of the pyridine group enhanced by Ag nanoparticles.

Acknowledgments

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