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Preparation and optical properties of Ag/PPy composite colloids

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Abstract

Ag/PPy (polypyrrole) composite colloids were prepared through the reaction of silver nitrate with pyrrole solution in DMF either in the dark, or under the irradiation of femtosecond laser (fs) pulse or UV lamp. The UV–vis spectra of the nanocomposite colloid display an intense absorption band around 620 nm, accompanied by a weak one around 470 nm. The colors and optical absorption spectra of as-synthesized colloids can be reversibly tuned between blue and red, corresponding to absorption band of 620 nm and 526 nm, within few seconds by adding base and acid solutions or gases in turn into the composite colloid suspension. In addition, excess of H^+ solution enhanced the absorption band around 470 nm and, at the same time, depressed that around 620 nm. The possible mechanism for the formation and optical absorption properties of the Ag/PPy composite colloid was proposed.

Keywords: Ag/PPy composite colloid; Optical properties; Color; pH Effect

1. Introduction

The composites nanoparticles of metal and electrically conducting polymers (ECPs) nanoparticles have attracted intensive attention in recent years, because of their potential applications in various fields, such as catalysis, chemical sensors and microelectronics [1–5].

Among those composites, noble metals/ECPs, such as Au/PPy and Ag/PPy have been extensively studied because of their unique optical and electronic properties of the metals [6], as well as the high conductivity and good stability of the PPy [7,8].

Up to now, many efficient methods have been employed to prepare Au/PPy composite over the past few years. For example, Au/PPy composite particles were prepared with in situ polymerization [9,10], sonochemical method [11], layer-by-layer (LBL) technique [12,13], soft template technique and others procedures [14–16]. In addition, Au/PPy colloid was obtained [17], and PPy films incorporated by Au nanoparticles were produced under the UV irradiation [18]. It is also found that the conductivities of the conducting polymers could be enhanced by the incorporated gold nanoparticles [5,18,19]. However, little attention has been paid on the preparation of Ag/PPy composite [18], especially those with somewhat different optical properties from either metal nanoparticles or conducting polymers parents [20].

It is well known that the properties, especial conductivity of PPy strongly depend on the pH value of solutions for preparation or post-treatment, i.e., conductive at acidic pH values, while insulative at basic pH values [21,22]. In the case of Ag nanoparticles, it is found that the size of Ag nanoparticles could be controlled to some extent by the base or acid in solution [23,24], and the stable Ag nanoparticles tend to aggregate at higher pH value [25]. For example, Kreibig et al. changed the distance distribution towards the formation of coagulation clusters by changing the pH value of the solution [26].

In this paper, we report the preparation of a blue Ag/PPy composite colloid by a simple wet chemical method. The effects

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of pH value on the color and optical absorption properties of the as-synthesized Ag/PPy colloids were investigated.

2. Experimental

A number of experiments were carried out with varied concentration of both silver ions and pyrrole. Simply mixing $AgNO_3$ solution with pyrrole solution at room temperature led to the slow reduction of silver ions to silver metals and the oxidation of pyrrole, as manifested by a gradual coloration of the solution. As shown below, the time needed for completion of the reaction mainly depends on the silver and pyrrole concentration, as well as temperature, being typically 0.5 M and 0.36 M for Ag and pyrrole, respectively, at 20 °C for 48 h.

For samples irradiation treatment a femtosecond (fs) light (800 nm) from a regeneratively amplified fs Ti:sapphire laser (Spectra-Physics) and a cw UV light (253.7 nm) with an intensity of 8 W were used. After the irradiation, the mixed solution was aged in air in order to form blue colloid.

Effects of pH values were tested through adding dropwise base or acid solutions to the Ag/PPy composite colloid, and corresponding pH values were measured by a pH meter.

The absorption spectra were recorded on a Jasco V-570 Spectrophotometer. When the absorbance exceeded the detection limit of the spectrophotometer the colloids were diluted by the corresponding solvents. The size of particles in colloids was measured by transmission electron microscopy (TEM) and field emission scanning electron microscopy (FSEM). Samples for TEM were prepared by dipping carbon-coated grids in the colloid and drying under the IR light irradiation, while the samples for FSEM were obtained by evaporating drops of the colloid on a silicon substrate in air. Secondary electron imaging mode was used in both SEM and TEM measurements. X-ray diffraction (XRD) measurements were carried out to examine the crystallinity of Ag nanoparticles.

3. Results and discussion

3.1. Absorption spectra of Ag/PPy colloid during formation

The fs laser irradiation has been reported for photoreduction of Au ion and photopolymerization of photosensitive resin [27,28] due to its two-photon or multiphoton absorption effect. To prepare Ag/PPy nanocomposites, fs laser pulse was used to irradiate $AgNO_3$ (0.5 M) solution containing pyrrole (0.36 M) in DMF. Fig. 1 shows the UV–vis spectra of the Ag/PPy composite colloids formed at different stages. Since the concentrations of the Ag nanoparticles formed at different stages are unknown due to inconstant rate, therefore, absorbance is expressed in the arbitrary unit instead of in the standard format. At the beginning, the colloidal solution exhibits a peak around 420 nm that is enhanced with irradiation duration, as shown in Fig. 1a–c. Afterwards the samples undergo minor visible change, with the slight red-shift to 440 nm, as shown in Fig. 1c–f. The distinct change of color with the further irradiation is reflected in the spectra by the appearance of a broad band around 540 nm and the attenuation of the peak around 440 nm (see curve A in the inset of Fig. 1). After aged in air for 6 h, the peak around 620 nm instead of 540 nm emerges, accompanied by a shoulder around 470 nm (see curve B in the inset of Fig. 1), and a noticeable change of color of the solution from violet to blue occurs. A fully analogous optical absorption property was observed by irradiating under a cw UV light with the wavelength of 253.7 nm, as shown in Fig. 2. The blue colloids were transparent and stable at a temperature lower than 0 °C for a few months.

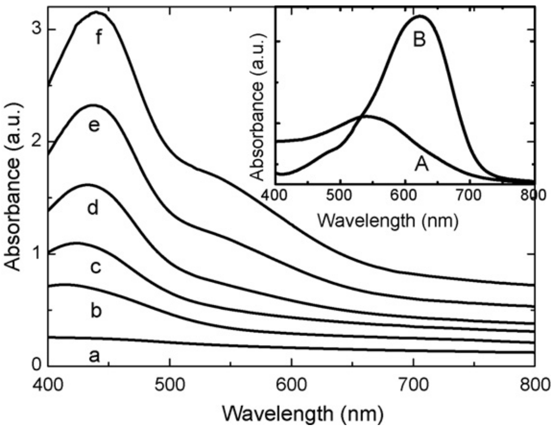


Fig. 1. Absorption spectra of Ag/PPy composite colloid prepared with different fs laser irradiation period for (a) 0 min, (b) 5 min, (c) 15 min, (d) 25 min, (e) 35 min, and (f) 40 min. The inset: (A) 110 min fs laser irradiation and (B) 110 min fs laser irradiation and subsequent 6 h aging.

The shoulder around 470 nm corresponds to the π–π^* transition of the PPy chain [8,16], while the decreased tendency of the absorption in the wavelength close to 800 nm suggests that the PPy is in its reduced state [29], which is consistent with those obtained under sonochemical irradiation [11]. The peak occurring around 420 nm corresponds to the plasma resonance of the small spherical Ag particles [30–32]. As for the peak at around 620 nm, we suppose it due to the surface plasma resonance of Ag nanoparticles. It is known that the plasma resonance absorption is influenced by many factors, such as particle materials, particle size and shape, and the dielectric constant of the host medium [20,33–34]. In the present work, however, the non-spherical Ag

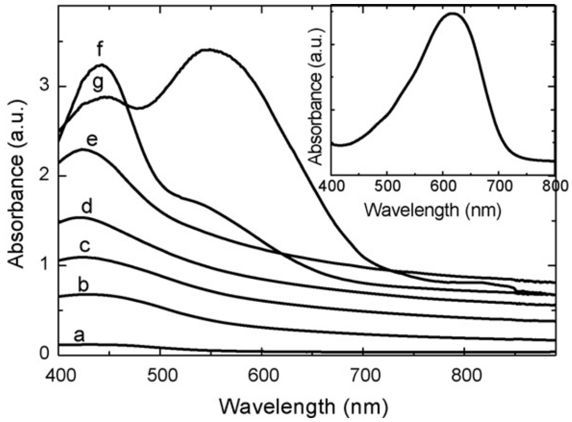


Fig. 2. Absorption spectra of Ag/PPy composite colloid prepared by UV irradiation, down to up: (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min, and (g) 60 min. The inset: after 60 min UV irradiation and subsequent aging in air for 6 h.

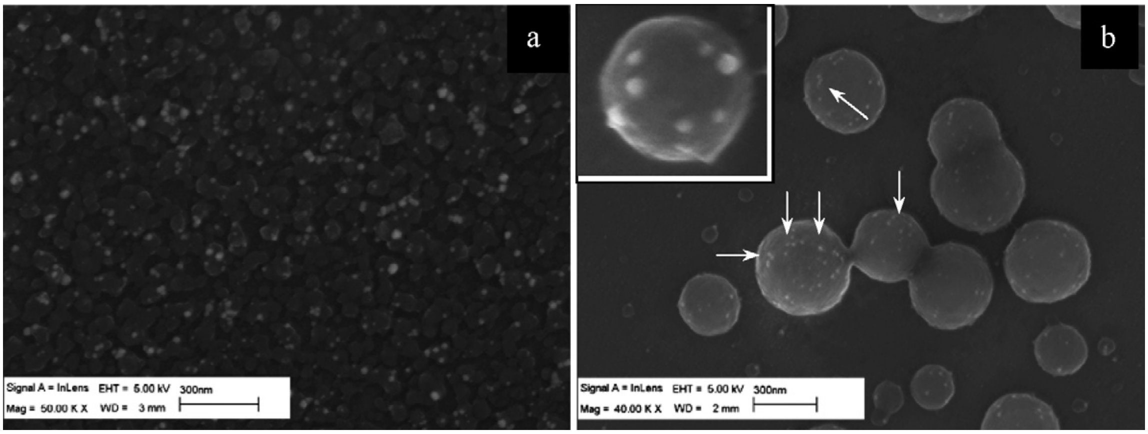


Fig. 3. FSEM photographs of Ag/PPy composite nanoparticles induced by (a) irradiation of fs laser pulse for 110 min and further aging in air for 6 h and (b) in the dark.

particles were seldom seen and no obvious aggregates of colloidal Ag nanoparticles were observed in the subsequent TEM or SEM images. For comparison, PPy–Ag nanoparticles parasite structures are seen everywhere in the TEM and SEM images. Therefore, the band around 620 nm may be attributed to the surface plasma resonance of Ag nanoparticles affected by the dielectric constant of the PPy medium.

3.2. FSEM photographs and XRD analysis

Fig. 3a and b shows the FSEM images of the Ag/PPy composite colloids prepared by fs irradiation for 110 min followed by 6 h aging, and prepared in the dark, respectively. In Fig. 3a, it is observed that there are lots of smaller bright nanoparticles on the surface of the larger grey-black particles. According to secondary electron imaging mode we used, we believe undoubtedly the bright dots are silver which was also confirmed by elemental analysis, while the grey-black particles are PPy or oligomer. The size of Ag nanoparticles is ca. 20–30 nm, while the size of PPy particles is on the order of 100 nm. Breimer et al. found the bright Ag nanoparticles on the surface of amorphous PPy film when they mixed Ag ions with aqueous pyrrole solution and irradiated it using UV light [18]. A typical graph for identifying Ag nanoparticles is shown in inset of Fig. 3b, and some Ag nanoparticles formed on the polypyrrole particles are denoted by the arrows. It is observed that the bright smaller Ag nanoparticles denoted by arrows disperse on the surface of the spherical PPy particles with the size on the order of 200–400 nm, and the Ag nanoparticle-dispersed PPy surface structure can be clearly seen in inset of Fig. 3b. The size of PPy particles in Fig. 3a is smaller than that in Fig. 3b (100 nm versus 200–400 nm), and this is maybe attributed to laser ablation effect of ultra-short fs laser on reduction of the particles size [35,36].

In both Fig. 3a and b, coagulations and other shapes of Ag nanoparticles are hardly observed. And the Ag nanoparticles are so small that those larger PPy particles can be regarded as their host medium. Therefore, the absorption band around 620 nm can be attributed to the surface plasma resonance of Ag nanoparticles, which was affected mainly by dielectric constant of the PPy medium [20].

X-ray diffraction (XRD) measurements were performed to examine the crystallinity of Ag particles in the composites. Obtained XRD patterns (omitted herein) show four characteristic peaks of the face-centered cubic (fcc) crystalline structure of Ag, namely (1 1 1), (2 0 0), (2 2 0), and (3 1 1) (JCPDS file no. 04-0783), which confirms the formation of the Ag nanoparticles in the colloid.

3.3. pH tunable optical absorption properties

A systematic investigation on changes of pH values has carried out, and an interesting optical absorption band was observed for the as-synthesized Ag/PPy composite colloid. When base solutions, e.g., $NH_3{\cdot}H_2O$ was added into the blue Ag/PPy colloid, the colloid turned into red within few seconds, and the absorption band around 620 nm attenuated but an extra band around 526 nm appeared, as shown in Fig. 4a and b. On the other hand, when acid solutions, e.g., HCl solution were added into the above red solution, a faster reverse process occurred, i.e., its color changed from red back to blue within few seconds, and the absorption band reverted to around 620 nm. The pH values corresponding to Ag/PPy colloids at different stages are listed in Table 1 where, the Ag/PPy-1, Ag/PPy-2, Ag/PPy-3, Ag/PPy-4, Ag/PPy-5 are designated to Ag/PPy colloids of as-synthesized, 10-fold-diluted, base-added, base–acid-added and excess acid-added, respectively, and the wavelengths of the intensive absorption band at different stages are also included. The pH value increases from ca. 3.30 to 4.80 after adding base solution at the first time, and decreases from ca. 4.80 to 4.20 after adding acid solution and so on. The amount of base solution needed to tune the blue Ag/PPy colloid to red is more at

Table 1
pH values corresponding to Ag/PPy colloids at different stages

Ag/PPy colloid state	pH values
Ag/PPy-1 (620 nm)	2.20
Ag/PPy-2[a] (620 nm)	<3.30
Ag/PPy-3[a] (526 nm)	>4.70
Ag/PPy-4[a] (620 nm)	<4.20
Ag/PPy-5[a] (470 nm)	<0 (out of the range of PH meter)

[a] Ten-fold dilutions.

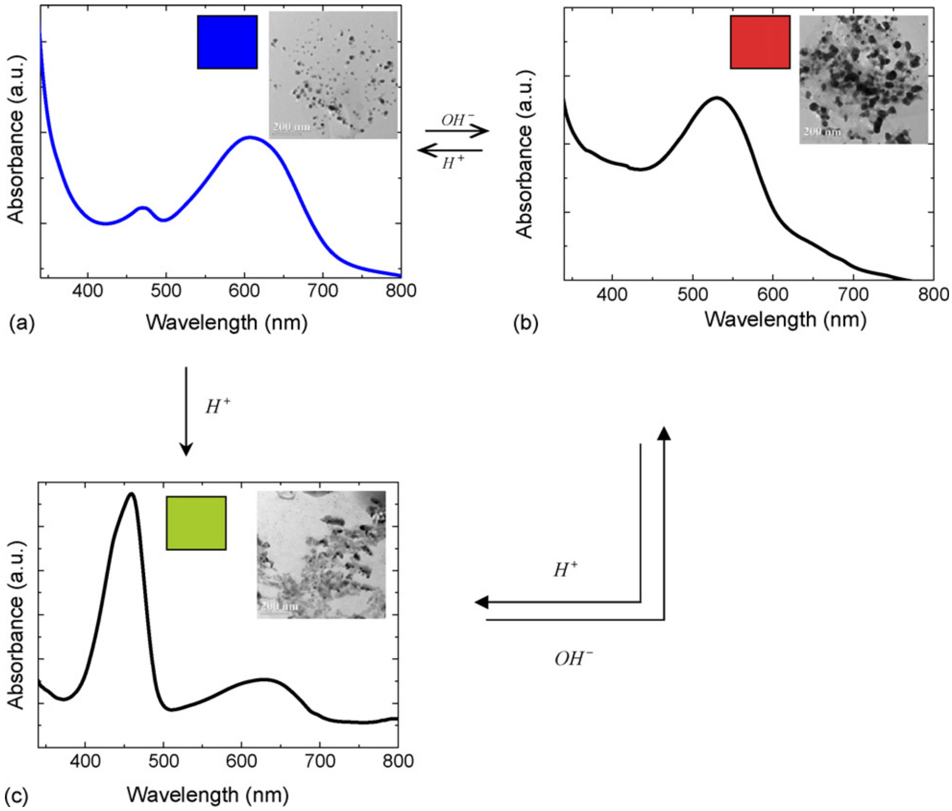


Fig. 4. Absorption spectra of: (a) blue Ag/PPy composite colloid, (b) red Ag/PPy composite colloid by adding $NH_3{\cdot}H_2O$ into the as-synthesized Ag/PPy colloid, and (c) colloid by adding excess of HCl solution. The inset: TEM images.

the first time than the subsequent ones, which is consistent with the variation of pH values. Besides solutions, the gaseous bases and acids, e.g., NH_3 and HCl could also be used to tune the colors and absorption spectra of blue Ag/PPy colloid. The color and the absorption spectra of the Ag/PPy colloid could change between the two states reversibly when the base and acid gases were added.

Another observation on optical absorption for the as-synthesized Ag/PPy colloid is the variations of spectra and color within a few seconds after excess of acid was added into the blue colloid. The pH value of the Ag/PPy colloid is out of the range of pH meter (<0), as listed in Table 1. Fig. 4c shows the absorption spectra of acid-added Ag/PPy colloid. Comparing with those in Fig. 4a, the intensity of the band around 620 nm decreased while that around 470 nm increased. In addition, tunable color and absorption with the pH value was also observed between the states in Fig. 4b and c by adding base and acid solutions in turn.

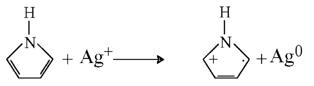
In Fig. 4a–c, three intensive absorption bands around 470 nm, 526 nm, and 620 nm are observed for the Ag/PPy colloid, suggesting that the colloid may be used as a photothermal materials, for its absorption bands are very close to laser lights of 488 nm, 532 nm, and 632 nm, respectively.

3.4. Mechanism for the formation of Ag/PPy composite and its optical properties

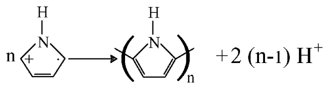
For comparison, Ag/PPy colloid was prepared with a mixed solution of 0.5 M $AgNO_3$ and 0.36 M pyrrole by holding in the dark for more than 48 h. This fact suggests the availability of Ag/PPy colloid in the absence of light irradiation. However, with the help of fs laser pulse or UV light irradiation, formation of the blue colloid was achieved within a few hours (0.5 h irradiation + 6 h aging process). In other words, the reaction rate was accelerated by the presence of fs pulse or UV light irradiation which introduced additional reactions such as photochemical reduction of Ag ions and polymerization of pyrrole on the basis of original redox reaction between Ag ions and pyrrole.

Although DMF is an effective reducing agent [37], the change of color and absorption spectra for the solution of $AgNO_3$ in DMF was too little to be observed. Therefore, we reckon that Ag ions were reduced mainly by pyrrole instead of DMF.

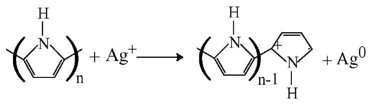
Thus, by referring to the literatures [16,17], formation of Ag/PPy composite can be expressed briefly as follows



(1)



(2)



(3)

$$mAg^0 \rightarrow (Ag)_m \tag{4}$$

The silver ions were reduced to silver atom by pyrrole monomer, and at the same time, the latter were oxidized to pyrrole radicals cations (Eq. (1)), which then combined to form polymer (Eq. (2)). The silver ions near or on the surface of polypyrrole could also be reduced to atoms by polypyrrole (Eq. (3)) [15,16,38] while the Ag atoms aggregated to form silver nanoparticles (Eq. (4)). Finally, Ag nanoparticles–PPy particles parasite structures were produced and Ag/PPy composite was formed.

The insets in Fig. 4a–c show the TEM images of as-synthesized Ag/PPy colloids, $NH_3{\cdot}H_2O$, and excess H^+ solution, respectively. In Fig. 4a, some well-separated black nanoparticles and grey particles are observed, while aggregation of larger-sized black nanoparticles on the grey amorphous substance is clearly seen in Fig. 4b, and a few small black nanoparticles on the grey amorphous block are observed in Fig. 4c. As mentioned above, secondary electron imaging mode was used in TEM measurement, so the black dots correspond to Ag nanoparticles, while the grey substance PPy particles. For the silver nanoparticles, which usually carry positive surface charges [39], a lower pH value favors the stability of its colloid [25], as shown in Fig. 4a. However, the colloidal nanoparticles tend to aggregate when the pH value increases [25], as shown in Fig. 4b. The effect of base solution on the Ag nanoparticles was balanced out when the acid solution was added to the base-added colloid. Hence, it is the congregation and larger size of metal nanoparticles that result in the color change and appearance of absorption band around 526 nm. As a result of coagulation, the Ag/PPy colloid becomes less stable in Fig. 4b than that in Fig. 4a. In the case of absorption band around 470 nm, its intensity decreases with base solution addition, which is consistence with the behavior of PPy films at the pH of 3–6 [40]. Compared with Fig. 4a, amorphous PPy with small Ag nanoparticles are formed in Fig. 4c. Since the pH value was lower than 0, the pyrrole remains polymerized in the colloid due to catalysis effect from acid [8,16]. On the other hand, decrease of absorption band around 620 nm implies that the Ag nanoparticles are covered entirely by freshly formed PPy or partially solved under this acidic condition. This indicates that the ratio of Ag to PPy in the composite can be controlled to some extent by adjusting the pH value of the colloid.

Based on the reaction mechanism of as-prepared Ag/PPy colloid with the excess H^+ solution, we suppose that a similar process will occur when the concentration of the pyrrole is high. As presented in Eq. (2), when a new bond form between two pyrrole radical cations during polymerization process, two protons produce, which means that, to synthesize one PPy molecule consisting of n pyrrole monomer, $2(n-1)$ protons produce. Thereby, if 0.36 M pyrrole monomer are entirely polymerized, an equivalent $[H^+]$ of 0.36–0.72 M will form. This indicates that resultant Ag/PPy colloid is at acidic pH, although the initial mixed solution of $AgNO_3$ and pyrrole is basic. The experimental results proved the validity of our hypothesis.

The effect of the experimental parameters such as concentration of $AgNO_3$, and temperature was also studied. The higher the concentration of $AgNO_3$, and the temperature, the faster the formation rate of the Ag/PPy. However, the stability decreases with increasing temperature.

Other noble metal salt, such as chloroplatinic acid, and chloroauric acid were also tried as metal source in an attempt to prepare other metal/PPy colloid. Yet we failed to obtain the Pt/PPy and Au/PPy colloids. However, a new approach was proposed by reacting other metal salts with the Ag/PPy to form different metal/PPy colloid, which is now in progress.

4. Conclusions

Blue Ag/PPy colloid was prepared in the dark, and under irradiation of either fs laser pulse or cw UV at room temperature. The color and absorption spectra of the as-synthesized Ag/PPy can be tuned between two states reversibly within few seconds by changing the pH of the colloid suspensions, which is correlated with the aggregation of the silver nanoparticles in the colloid. For the Ag/PPy colloid, three intensive absorption bands around 470 nm, 526 nm, and 620 nm can be tuned.

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