

THE SYNTHESIS OF Ag-POLYPYRROLE NANOCOMPOSITE COATED LATEX PARTICLES AND THEIR APPLICATION AS A FLUORESCENT QUENCHING AGENT*

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Abstract Submicron-sized Ag-polypyrrole/poly(styrene-*co*-methacrylic acid) (Ag-PPy/P(St-*co*-MAA)) composite particles were fabricated *via* a redox reaction between pyrrole and AgNO₃ in the presence of P(St-*co*-MAA) soap-free latex. The products are characterized by transmission electron microscopy (TEM), electron diffraction spectra (EDS), Raman spectra, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The results showed that Ag-PPy nanocomposites were *in situ* deposited onto the surface of P(St-*co*-MAA) latex particles tailored by carboxylic-acid groups. The nanocomposites of Ag-PPy distributed on the surface of polymer particles transformed from discretely dots to continuously coating as the reaction temperature increased from 15°C to 60°C. Strawberry-like composite particles were obtained at the reaction temperature of 60°C. The TGA characterization confirmed that the Ag-PPy nanocomposites loading onto the P(St-*co*-MAA) particles were systematically controlled over a range of 6 wt%–42 wt% by changing the reaction temperatures. The fluorescence quenching effect of the Ag-PPy/P(St-*co*-MAA) composite particles was explored on Rhodamine B as a model molecule with the Stern-Völmer quenching constant K_{SV} of 5.9×10^4 (g/mL)⁻¹. It is suggested that the fluorescence quenching effect is caused by the resonance energy transfer mechanism.

Keywords: Nanocomposite-coated latex particles; PPy; Ag nanoparticles; Synthesis; Fluorescence quenching.

INTRODUCTION

The synthesis of conducting polymer-coated colloidal particles has been the subject of numerous studies due to the diverse applications of these particles in the fields of electronics^[1, 2], catalysis^[3, 4], rechargeable batteries^[5], photonic crystals^[6, 7], biomaterials^[8], intelligent materials^[9], fuel cells^[10], biondiagnosis^[11], anti-corrosion and anti-static coatings^[12, 13], heavy metals removal^[14] and sensors^[15] over the last two decades. Encouraged by the attractive properties of noble metal nanoparticles and the possible synergistical properties derived from the nanocomposite of nano-metal and conductive polymers, there has been an increasing interest in the deposition of the composite of nano-metal and conductive polymers onto polymer latex particles. With the surface of noble metal nanoparticles effectively protected from the agglomeration or oxidation, the loading of nanocomposites onto the surface of polymer latex particles can improve the processability, modify the compatibility, and facilitate the storage, dispersion and transport properties of such materials.

Based on the limited reports concerning the synthesis of nanocomposite-coated polymer particles, the

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conductive polymer and the nano-metals can be separately incorporated by multi-stepped electroless coating^[16] or layer-by-layered self-assembly method^[17, 18] onto the surface of latex particles which should be pre-activated. Besides, since our group reported the synthesis of coaxial Ag-PPy nanocables by the one-step chemical oxidative polymerization of pyrrole using AgNO₃ as the oxidant^[19, 20], there have been many reports on the preparation of noble metal-conducting polymer nanocomposites in a one-step reaction. More recently, Fujii *et al.* reported the polypyrrole/palladium nanocomposite-coated latex particles which can be used as the catalyst for Suzuki coupling reaction in aqueous media^[4]. However, the polymer stabilizers such as polyvinylpyrrolidone (PVP) used in such reaction are still inevitable. Further synthesis and application properties of such nanocomposites coated polymer particles are still in need of further explorations.

In this work we concerned on the soap-free deposition of Ag-PPy nanocomposites on the P(St-co-MAA) latex particles. The Ag-PPy nanocomposites were synthesized by the redox reaction of pyrrole and AgNO₃ and stably *in situ* deposited onto the surface of polymer particles tailored by the carboxylic groups introduced by the copolymerization of MAA monomer. The loading amounts as well as the morphology of the Ag-PPy nanocomposites can be controlled by the reaction temperatures. Meanwhile, as the sensitivity of conducting polymers in the application of biosensors can be enhanced distinctly by nano-metals^[21], the application of Ag-PPy/P(St-co-MAA) composite particles as a fluorescent quenching agent was also explored.

EXPERIMENTAL

Materials

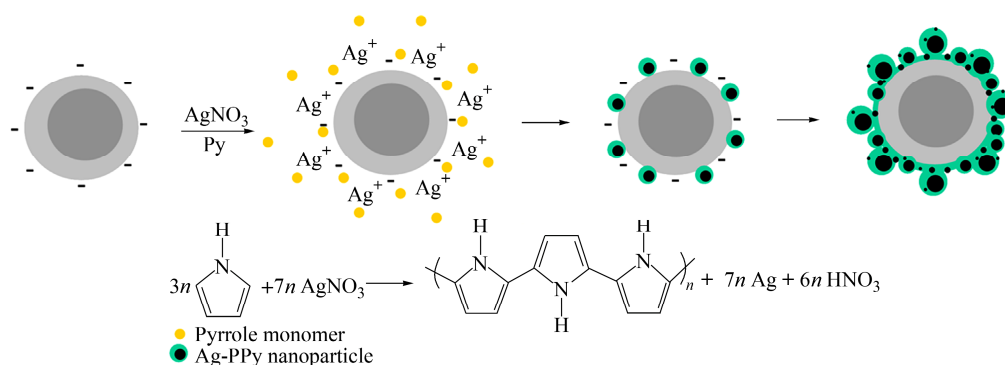
Styrene (St) and methacrylic acid (MAA) were purchased from Fuchen Chemical Reagent. Potassium persulphate (KPS), sodium bicarbonate (NaHCO₃), silver nitrate (AgNO₃) and Rhodamine B were obtained from Beijing Chemical Works. They are all analytical reagents and used without further purification. The pyrrole monomer was purchased from Aldrich, distilled at reduced pressure, and stored in refrigerator before use. All the solutions were prepared with deionized water.

Preparation of Ag-PPy/P(St-co-MAA) Composite Particles

The preparation process is shown in Scheme 1. First, 10 g of monodisperse soap-free P(St-co-MAA) latex synthesized as described in reference^[22] was introduced into a 100 mL mono-neck flask. The aqueous solutions for AgNO₃ (5 mL, 0.56 mol/L) and pyrrole (5 mL, 0.28 mol/L) were sequentially introduced dropwisely into the flask. The reaction mixture was stirred for 48 h at a certain temperature. The color of the system changed from light pink to yellow, yellow grey, dark brown and finally almost black with the reaction proceeded. The composite particles were purified by centrifugation and redispersed with water until the filtrate was colorless.

Characterization

Transmission electron microscopy (TEM) observations were carried out under a HITACHI H-800 instrument operated at 200 kV. Scanning electron microscopy (SEM) characterizations were taken on a HITACHI S-4700 electron microscope with an operating voltage of 20 kV. The high magnification transmission electron microscopy (HRTEM) image was taken on a JEM 3010 instrument at 300 kV. The element microanalysis was performed on an energy dispersive spectrometer (EDS) (EDAX Genesis 30T) coupled to HRTEM operated at 300 kV. The diameter of the latex was measured by dynamic light scattering (DLS) on a Malvern Zetasizer NanoZS instrument. The thermogravimetric analysis (TGA) was carried out on a Perkin Elmer TGA-4000 instrument under a nitrogen atmosphere from 35°C to 800°C at a heating rate of 10 K min⁻¹. The fluorescence emission spectra measurements were carried out on a Cary Eclipse fluorescence spectrometer. The UV-Vis-NIR spectra were recorded on a SHIMADZU UV-3150 UV-Vis-NIR spectroscope.



Scheme 1 The preparation process of Ag-PPy/P(St-co-MAA) composite particles

RESULTS AND DISCUSSION

Figures 1(a) to 1(e) are the TEM images of Ag-PPy/P(St-co-MAA) nanocomposite particles fabricated using the same formulation at reaction temperatures of 0°C, 15°C, 25°C, 40°C, and 60°C, respectively. Ag-PPy nanocomposites were obtained in the redox reaction of AgNO₃ and pyrrole and *in situ* deposited onto the surface of soap-free P(St-co-MAA) latex. It can be observed from the TEM images that many irregular black nanoparticles decorating on the surface of grey spheres which should be the P(St-co-MAA) latex particles with an *z*-average diameter of 318 nm measured by DLS. The HRTEM image of Fig. 1(e) is shown in Fig. 1(f). It is found that the surface of black nanoparticles is encapsulated by a layer of grey polymer which is conjectured to be PPy. The EDS pattern of the rectangular region labeled in Fig. 1(f) is shown in Fig. 1(g). Besides element Cu caused by the copper meshes, elements C, N and Ag are all detected with the atomic contents of 25.7%, 14% and 21.7%, respectively, which confirmed that the composite on the surface of polymer latex particles was composed by PPy and Ag. Therefore, it is reasonable to identify that the black dots in Fig. 1 are Ag nanoparticles and the grey layer absorbed on the surface of Ag nanoparticles is PPy.

The deposition amounts as well as the morphologies of the nanocomposite particles were different by varying the reaction temperatures. When the reaction temperature is 0°C, only a few of polymer latex particles are decorated with Ag-PPy nanoparticles (Fig. 1a). As shown in Fig. 1(b), uniform Ag nanoparticles are evenly distributed on the surface of latex at a reaction temperature of 15°C. Moreover, the PPy coating layer can hardly be distinguished in both Figs. 1(a) and 1(b). It can be inferred that the loadings of Ag-PPy nanocomposites are low for the products prepared at both 0°C and 15°C. The phenomena consist with the slow reaction rates at low reaction temperatures which were suggested by the slow color transition of the reaction solution by naked-eye observation. The color of both the reaction mixture and the final product was faint compared with the dark color of that obtained at a reaction temperature above 25°C. It can be observed from Figs. 1(c) to 1(e) that both the amount and the average sizes of deposited silver nanoparticles increased obviously in comparison with Figs. 1(a) and 1(b). The PPy layers coating on silver particles are obvious in the magnified TEM images of inset of Figs. 1(c), 1(d), and 1(e). In addition, many tiny silver particles are observed embedded in the PPy phase even in the corresponding low magnification images. By comparing the TEM images in Figs. 1(c) to 1(e), the average size of silver particles decreased from *ca.* 40 nm to *ca.* 25 nm as the reaction temperature increased from 25°C to 60°C. The increasing reaction temperature would cause the increasing rates for the formation of Ag nucleus, however, the accelerated formation and deposition rate of PPy should effectively inhibit the further growth or aggregation of Ag nanoparticles.

The TEM picture of the product obtained using PS soap-free latex without functional monomer MAA as template is shown in Fig. 1(h). It can be observed that most of Ag nanoparticles aggregated and isolated in the system. Therefore, we suppose that the functional group of -COOH on the surface of soap-free P(St-co-MAA) latex is the key parameter for the tailored deposition of formed Ag-PPy nanocomposites onto latex particles.

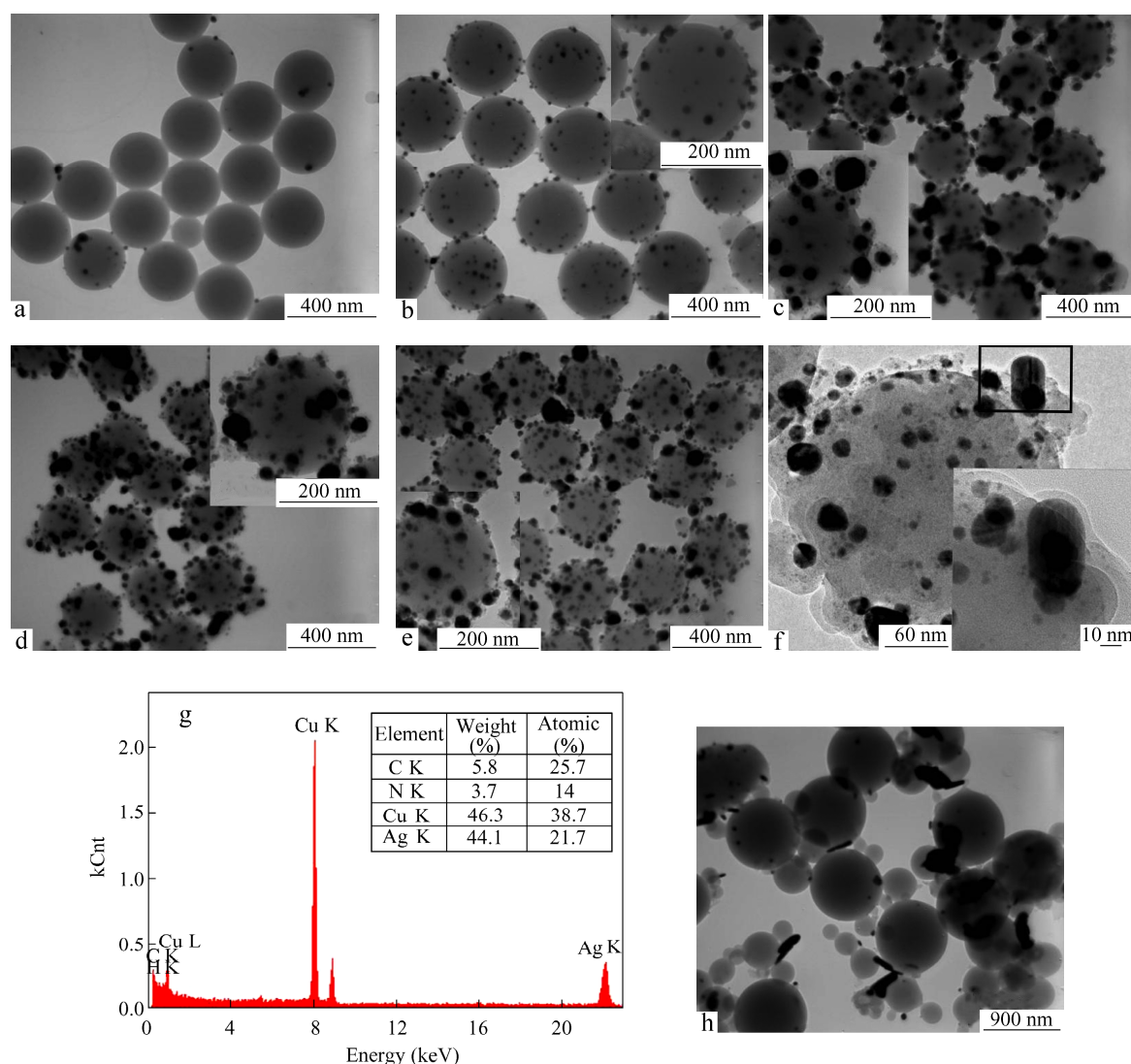


Fig. 1 The TEM pictures of Ag-PPy/P(St-co-MAA) nanocomposite particles synthesized at temperatures of (a) 0°C, (b) 15°C, (c) 25°C, (d) 40°C and (e) 60°C, respectively (Insets of the pictures are the high magnified TEM images.), (f) the HRTEM image of Ag-PPy/P(St-co-MAA) nanocomposite particles (Inset of (f) is the enlarged image of the part labeled by black rectangle.), (g) the EDS pattern and the element content of the part labeled by the black rectangle in (f), (h) the TEM picture of the product obtained using PS soap-free latex as template

Figures 2(a) to 2(d) are the SEM images of Ag-PPy/P(St-co-MAA) composite particles prepared at the reaction temperature of 15°C, 25°C, 40°C, and 60°C, respectively. The SEM image of the particles prepared at 15°C shown in Fig. 2(a) is distinctly different from others. The surface of the particles is smooth except some irregular plate-like bumps distributed sparsely on the surface. It is speculated that those irregular depositions are composed by small Ag-PPy nanocomposite particles. When the reaction temperature increased to 25°C, the surface roughness of the product increased distinctly, implying that the amount of Ag-PPy nanocomposites decorating on the surface of P(St-co-MAA) particles increased. But the Ag-PPy particles were accumulated together with bare smooth surfaces of the latex particles observed in the high magnified SEM image shown in the inset of Fig. 2(b). The distribution of Ag-PPy particles on the latex surface became denser as shown in Fig. 2(c) as the reaction temperature further increased. Especially, strawberry-like Ag-PPy/P(St-co-MAA)

particles were prepared and observed in Fig. 2(d) with the whole surface of the products coated by Ag-PPy composites. The coherent coating structure can be confirmed by the figure shown in Fig. 2(e). Intact hollow composite particles were observed after the composite particles prepared at 60°C had been extracted by THF for 48h. However, only broken aggregated structures can be observed after the composite particles prepared at 25°C had been extracted by THF (Fig. 2f).

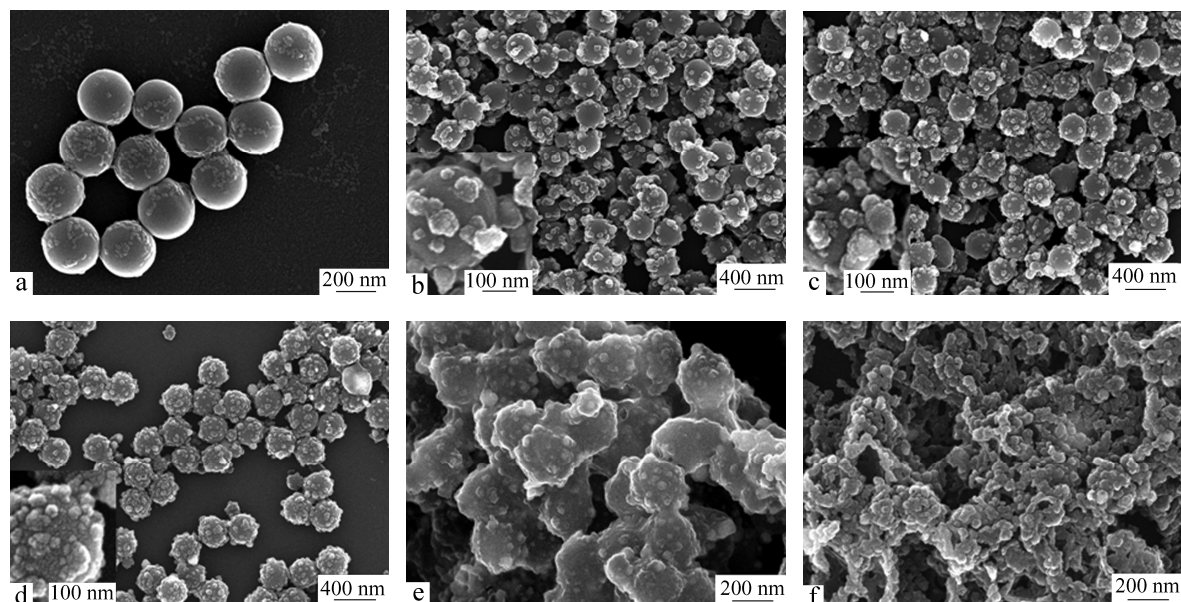


Fig. 2 The SEM pictures of Ag-PPy/P(St-co-MAA) nanocomposite particles synthesized at the temperatures of (a) 15°C, (b) 25°C, (c) 40°C, and (d) 60°C, respectively (Inset of pictures are the high magnified SEM images of single nanocomposite particles.), (e) and (f) respectively the SEM images of the product obtained at 60°C and 25°C extracted by THF

The actual mass loadings of Ag-PPy nanocomposites on the polymer particles fabricated at different temperatures can be estimated roughly from the TGA curves (Fig. 3). It is observed from Fig. 3 that the Ag-PPy mass loadings of Ag-PPy/P(St-co-MAA) composite particles fabricated at 25°C, 40°C, and 60°C are almost the same, which are 41.8 wt%, 39.8 wt%, and 38.8 wt%, respectively, whereas that of nanocomposite particles fabricated at 15°C is only 6.1 wt%, which falls in line with the inferences obtained from the TEM characterization. Furthermore, the thermal stability of Ag-PPy/P(St-co-MAA) particles was improved in comparison with pure P(St-co-MAA) and PPy.

Further characterization of the composite particles was carried out by surface enhanced Raman resonance (SERS) which provided us a convenient method to confirm the chemical structures of PPy coated on the surface of Ag nanoparticles in this work. The Raman spectra of P(St-co-MAA), Ag-PPy/P(St-co-MAA) and pure PPy doped by Cl^- (PPyCl) are shown in Fig. 4. The characteristic peaks of P(St-co-MAA), such as the breath vibration of phenyl ring at 1002 cm^{-1} and $=\text{C}-\text{H}$ stretching vibration on the phenyl ring at 3052 cm^{-1} , totally disappeared in the case of Ag-PPy/P(St-co-MAA), which should be due to the precipitation of Ag-PPy nanocomposite on the surface. It is obvious that the Raman intensity for Ag-PPy/P(St-co-MAA) is greatly enhanced compared to that for pure PPyCl. The inset of Fig. 4 is the magnified Raman spectrum of pure PPyCl, which exhibits characteristic bands of PPy for a $\text{C}=\text{C}$ backbone stretching at 1586 cm^{-1} , pyrrole ring stretching peaks (double) at 1322 and 1376 cm^{-1} , $-\text{C}-\text{H}$ in-plane deformation vibration peaks (double) at 1056 and 1083 cm^{-1} [23]. As shown in spectrum, these corresponding peaks respectively locate at 1596 , 1317 , 1384 , and 1048 cm^{-1} , proving that the polymer layer coating on the surface of Ag nanoplates is PPy [24]. But it is found that the $\text{C}=\text{C}$ backbone stretching shifts to higher frequency. Moreover, the peaks at 1384 and 1083 cm^{-1} ,

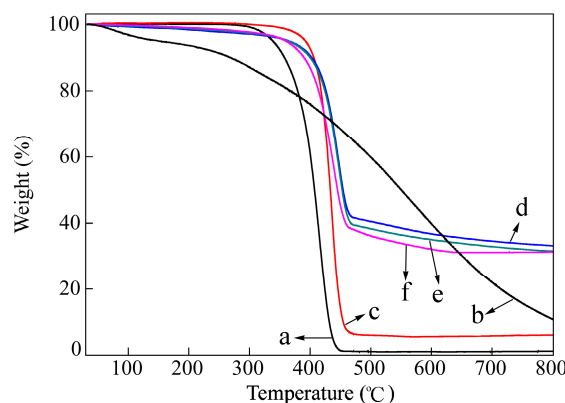


Fig. 3 TGA curves obtained in nitrogen atmosphere for (a) pure P(St-co-MAA) latex particles, (b) pure PPy, and Ag-PPy/P(St-co-MAA) nanocomposite particles prepared at (c) 15°C, (d) 25°C, (e) 40°C, and (f) 60°C, respectively

respectively attributed to the pyrrole ring stretching and —C—H in-plane deformation vibration of oxidized PPy, are greatly damped. Consequently, it can be concluded that the oxidation level of PPy in Ag-PPy/P(St-co-MAA) is lower than that in the pure PPyCl^[25–27], which is in conformity with the fact reported in the literatures that the doping degree of NO_3^- (0.21) is lower than that of Cl^- (0.33)^[28].

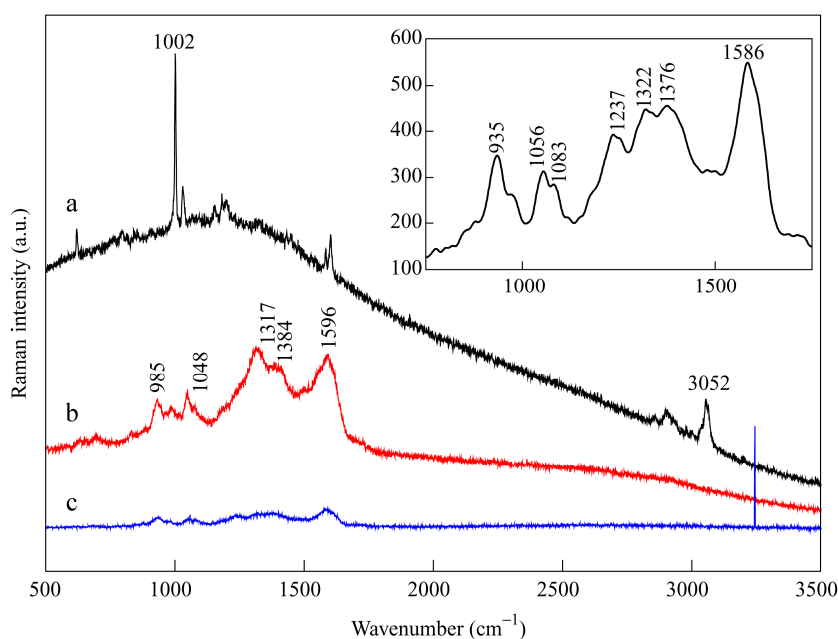


Fig. 4 The Raman spectra of (a) P(St-co-MAA), (b) Ag-PPy/P(St-co-MAA) nanocomposite particles and (c) pure PPyCl

Besides temperature, the amount of AgNO_3 , pyrrole and latex added can also be changed to adjust the loading amount of Ag-PPy nanocomposites. Herein, the amount of P(St-co-MAA) was changed while the amount of AgNO_3 and pyrrole was fixed. The reaction temperature was 25°C. The theoretical loading amounts of Ag-PPy nanocomposites were adjusted to be 24.94%, 52.26% and 66.09%, respectively. The TEM images of the products are shown in Fig. 5. It can be observed that the size of Ag nanoparticles increased as the theoretical amount of Ag-PPy composites increased. And aggregated and isolated Ag-PPy composites appeared as the theoretical loading amount of Ag-PPy increased to 66.09%. TGA curves of these composite particles are shown

in Fig. 6. It is found that the loading amounts of Ag-PPy composites obtained from TGA curves are respectively 20.7%, 35.6% and 54.5% when the theoretical loading amount are 24.94%, 52.26%, and 66.09%.

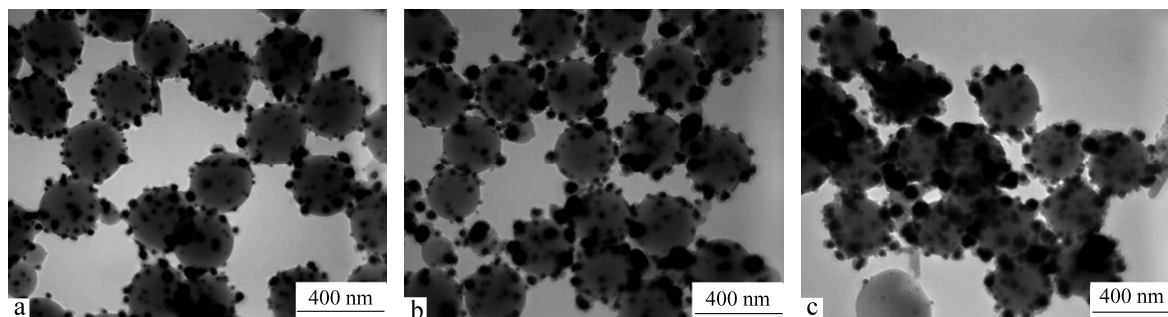


Fig. 5 The TEM images of Ag-PPy/P(St-co-MAA) nanocomposite particles with theoretical Ag-PPy loading of 24.94% (a), 52.26% (b), and 66.09% (c)

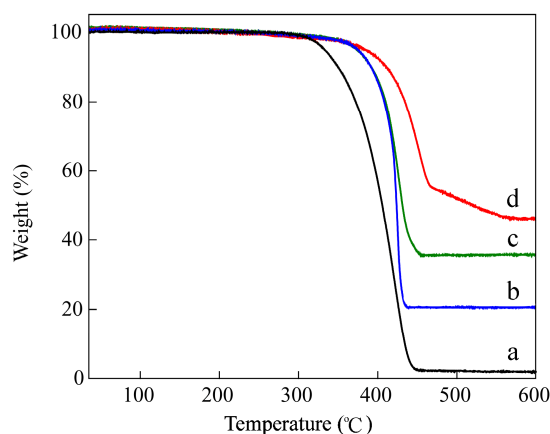


Fig. 6 The TGA curves of P(St-co-MAA) latex (a) and Ag-PPy/P(St-co-MAA) composite particles with theoretical Ag-PPy loading amount of 24.94% (b), 52.26% (c) and 66.09% (d)

The synthesized Ag-PPy/P(St-co-MAA) composite particles have been redispersed into P(St-co-MAA) latex emulsion. Ultrasonic was applied on the mixture for 20 min/day for one week. The SEM image of the mixture is shown in Fig. 7. It is observed that no Ag-PPy nanoparticles were isolated or transferred onto the surface of un-coated P(St-co-MAA) latex. The stable decoration of Ag-PPy nanocomposites onto the latex particles indicated the strong interactions between $-\text{COOH}$ and PPy which was proposed to be caused by hydrogen interactions between $-\text{COOH}$ and $-\text{NH}-$ ^[1].

The fluorescence intensity of Rhodamine B in the presence of different concentrations of Ag-PPy/P(St-co-MAA) composites particles was recorded, and the results are shown in Fig. 8. It can be found that the fluorescence of Rhodamine B was efficiently quenched by the Ag-PPy nanocomposites loaded polymer particles in a concentration-dependent way. Although the emission intensity of Rhodamine B decreased, the maximum emission peak was fixed. The absorbance spectrum of Ag-PPy/P(St-co-MAA) particles and emission spectrum of Rhodamine B are shown in Fig. 9. It can be found that overlap exists between the two spectra, suggesting that the fluorescence quenching effect might be induced by the resonance energy transfer from the excited Rhodamine B to Ag-PPy/P(St-co-MAA) composite particles.

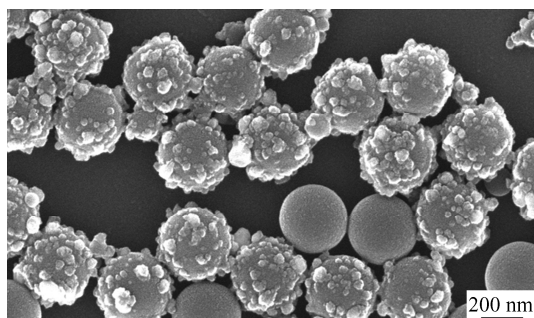


Fig. 7 The SEM image of the mixture of P(St-co-MAA) and Ag-PPy/P(St-co-MAA) after ultrasonic radiation 20 min/day for one week

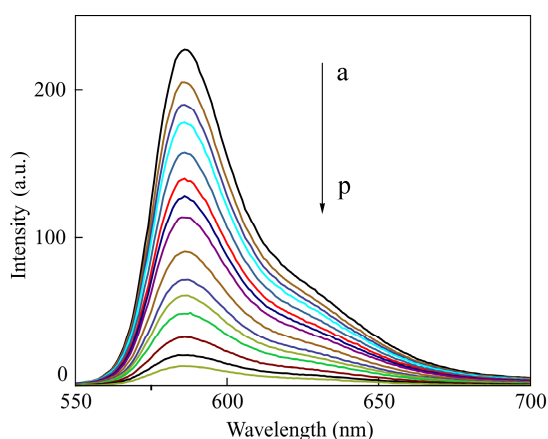


Fig. 8 The emission spectra of Rhodamine B in the presence of different concentrations of Ag-PPy/P(St-co-MAA) composite particles ($\times 10^{-5}$ g/mL): (a) 0, (b) 0.20, (c) 0.40, (d) 0.54, (e) 0.84, (f) 1.14, (g) 1.44, (h) 1.73, (i) 2.48, (j) 3.22, (k) 3.71, (l) 4.46, (m) 5.94, (n) 7.92 and (p) 9.90

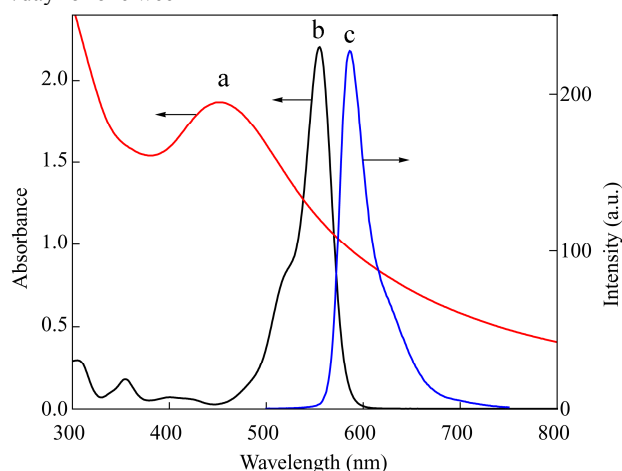


Fig. 9 The absorbance spectra of (a) Ag-PPy/P(St-co-MAA) composite particles and (b) Rhodamine B; The fluorescent emission spectra of Rhodamine B (c)

The fluorescence quenching data in Fig. 8 was re-plotted based on Stern-Völmer equation^[29]:

$$\frac{f_0}{f} - 1 = K_{SV} C_Q$$

where f_0 is the fluorescence intensity in the absence of quencher, f is the fluorescence intensity in the presence of quencher, K_{SV} is the Stern-Völmer fluorescence quenching constant, which measures the efficiency of the fluorescence quencher, and C_Q is the concentration of fluorescence quencher (Ag-PPy/P(St-co-MAA) composite particles). The relationship between f_0/f versus C_Q is shown in Fig. 10. From the linear region of plot of f_0/f versus C_Q , fluorescence quenching constant K_{SV} for composite particles is calculated to be 5.9×10^4 (g/mL)⁻¹. Herein, the K_{SV} of Ag nanoparticles is calculated to be *ca.* 3.54×10^4 (mol/L)⁻¹. As the concentration of Ag-PPy/P(St-co-MAA) composite particles increased above 3.07×10^{-5} g/mL, a positive deviation (concave toward Y-axis) in the Stern-Völmer plot was observed. This superlinear behavior indicates the presence of mixed quenching in the present system^[30]. The zeta potential of Ag-PPy/P(St-co-MAA) composite particles is -21.5 mV implying that their surface is negatively charged. Rhodamine B, on the other hand, is positively charged in the water phase. Therefore, it is considerable that the attractive electrostatic interaction, in conjunction with resonance energy transfer, is responsible for the quenching of Rhodamine B in the presence of Ag-PPy/P(St-co-MAA) composite particles.

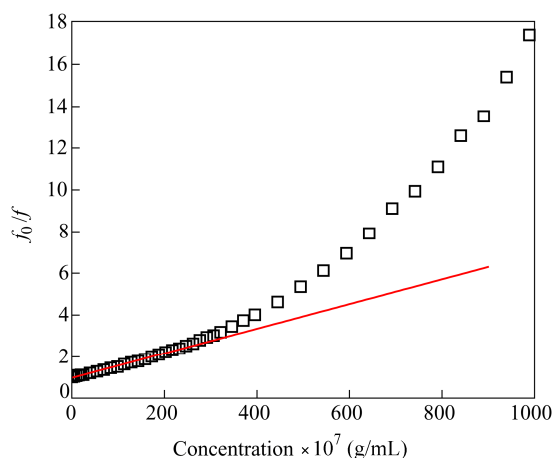


Fig. 10 The Stern-Völmer plot for the quenching of Rhodamine B by Ag-PPy/P(St-co-MAA) composite particles

CONCLUSIONS

The Ag-PPy/P(St-co-MAA) composite particles were prepared by the *in situ* deposition of Ag-PPy nanocomposites produced by the redox reaction of pyrrole and AgNO₃ onto the surface of submicron latex particles of P(St-co-MAA) under soap-free conditions. The structures of the products were characterized by TEM, EDS, Raman spectra, TGA and SEM. The loading amounts as well as the distribution of the nanocomposites on the polymer particles were affected by the reaction temperature. The reaction rate at 0°C was so slow that only little Ag-PPy nanocomposites formed which was too little to deposit on all latex particles. The distribution manner of Ag-PPy nanoparticles transformed gradually from discrete to continuous as the reaction temperature increased from 15°C to 60°C. The precipitated Ag-PPy nanocomposite particles have strong interactions with the latex substrate, which is valuable in further applications. The strawberry-like composite particles showed excellent fluorescence quenching effect on Rhodamine B. It is suggested that the synthesized Ag-PPy nanocomposite coated polymer particles have potential applications as fluorescent sensors.

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