PAA/ZnO Raspberry-Shaped Composite Microspheres Decorated with Ag Nanoparticles as Cleanable SERS Substrates

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ABSTRACT: A PAA/ZnO/Ag heterostructure composite material was prepared by a reduction method. The properties of composite particles are analyzed by transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), UV–visible spectroscopy, and Raman spectroscopy. Ag nanoparticles play an important role in PAA/ZnO/Ag composite microspheres, conferring new SERS properties and functions to PAA/ZnO/Ag. The intensity of the SERS signal of PAA/ZnO/Ag irradiated with UV light decreased from 10 000 to below 500. The SERS detection limit of R6G obtained was reduced to $1 \times 10^{-6}$ M. The PAA/ZnO/Ag composite particles show a very good degradation effect on R6G under UV light irradiation. This study has developed a new synthesis method to prepare SERS signal enhancement materials with self-cleaning effects. According to the experimental results, the PAA/ZnO/Ag composite material has higher sensitivity than the PAA/ZnO composite material.

INTRODUCTION

Composite particles of different types and controllable chemical compositions are the sources of advanced materials because they are used in solar cell materials,1 drug testing,2 photocatalysis,3,4 chemistry, and other fields. They also have potential application prospects in sensors.5 In addition, by changing and controlling the size, shape, and composition of composite particles, new optical, electronic, and photocatalytic properties can be obtained. Various techniques have been used to achieve coating of core particles with inorganic or organic layers.6 In addition, inorganic and hybrid coatings are usually prepared by surface-functionalized deposition to form a coating on the core. Moreover, organic–inorganic composite particles are prepared by first functionalizing the surface of the core particles and then combining them.9 Recently, in our research group, PAA/ZnO composite particles were prepared on the basis of the hybrid coagulation method.8 Compared with surface modification methods,9,10 this method can be used for facile synthesis of composite particles without any surface modification. In addition, great efforts have also been devoted to the preparation of composite particles to fabricate various multicomponent composite materials.11 CdS/SiO$_2$/sulfonated PS multicomponent composite microspheres have been synthesized with controllable multiple properties.12 It is mentioned in the literature that adding nano-Ag particles can make composite particles recyclable with self-cleaning ability.13−15

In this paper, PAA/ZnO composite particles were used as host particles for the preparation of PAA/ZnO/Ag multicomponent composite particles with Ag nanoparticles coated on PAA/ZnO particle surfaces. Herein, PAA/ZnO composite particle surfaces were modified with SnCl$_2$ reduction of Ag particles that effectively self-assembled onto the PAA/ZnO composite particle surface. The next step was to grow silver nanoparticles based on the nucleation sites of Ag seeds. Then, hydroquinone was used as a reducing agent. The effect of PAA/ZnO on the SERS signal and cleanability after adding silver nanoparticles is reported in this study.

RESULTS AND DISCUSSION

Surface Morphology of PAA/ZnO/Ag Composite Microspheres. The PAA/ZnO/Ag composite particles showed a shape resembling that of a raspberry, with an average diameter of about 1 μm (Figure 1a,b), and the surface of ZnO was rough (Figure 1c). As a result of constructing Ag nanoparticles on ZnO particles by the reduction method, the obtained PAA/ZnO/Ag composite microspheres with an average diameter of about 1 μm exhibited a raspberry morphology with a clear raspberry structure, on which there were dark-colored nanoparticles. In the images of dark-colored nanoparticles, Ag, ZnO, and gray PAA microspheres can be identified (Figure 1a,b).
Because of the electrostatic interaction between Ag(TEA)_2^{2+} and Sn^{2+}, Ag(TEA)_2^{2+} ions are reduced in situ by SnCl_2, and Ag NPs can easily grow on PAA/ZnO microspheres. Therefore, the surface of the resulting PAA/ZnO/Ag composite microspheres is relatively rough, and Ag NPs are uniformly formed on the PAA/ZnO microspheres (Figure 1c). In addition, the EDS spectrum showed the presence of C, Zn, O, and Ag elements (Figure 1d).

**Elemental Mapping Analysis.** Figure 2a–f shows the scanning TEM (STEM) and EDS mapping images of PAA/ZnO/Ag. In the EDS mapping image, Zn, Ag, C, and O show different colors individually, which confirms the formation of PAA/ZnO/Ag composite microspheres. Different colors are displayed as different elements, where blue, green, red, and purple indicate the presence of Zn, Ag, C, and O, respectively. Interestingly, the EDS mapping results reveal that the distribution of carbon and oxygen is uniform throughout the whole particle, which confirms the presence of PAA particles. They confirmed the co-presence of ZnO and Ag nanoparticles in PAA particles.

**UV–Vis Analysis.** Figure 3 shows the UV–visible optical properties of Ag nanoparticles, ZnO nanoparticles, ZnO/Ag composite particles, PAA/ZnO composite particles, and PAA/ZnO/Ag composite particles. The PAA/ZnO/Ag and PAA/ZnO composite particles show high-intensity absorption signals in the UV–visible diagram in Figure 3. PAA/ZnO and PAA/ZnO/Ag composite particles have higher absorption signals than ZnO nanoparticles, ZnO/Ag composite particles, and Ag nanocrystals. There is a strong coupling reaction between PAA/ZnO composite particles and Ag particles, resulting in a red-shift phenomenon.

**SERS Effect of PAA/ZnO/Ag and PAA/ZnO Composite Particles.** SERS performance was evaluated by immersing PAA/ZnO/Ag and PAA/ZnO composite microspheres into a
solution of rhodamine 6G (R6G) with a fixed concentration of $10^{-5}$ M and exciting at a laser wavelength of 514 nm, as shown in Figure 4a, b. PAA/ZnO/Ag composite particles show the best SERS performance. PAA/ZnO/Ag particles show high-intensity SERS signals at positions 611, 744, 1190, and 1315 cm$^{-1}$, which are attributed to the inward bending of the C–C–C plane, outward bending of the C–H plane, inward bending of the C–H plane, and C–O–C tensile vibration, respectively. Figure 4a also shows peaks at 1362, 1511, and 1650 cm$^{-1}$ attributed to the C–C stretching mode of the aromatic ring. In
this study, it is difficult to calculate the accurate SERS surface topography enhancement factor. PAA/ZnO/Ag has a better SERS signal enhancement effect than PAA/ZnO, so adding silver nanoparticles can effectively enhance the SERS signal of PAA/ZnO.

It is recognized that both electromagnetic and chemical mechanisms help to enhance SERS. Figure 4a shows that PAA/ZnO/Ag exhibits a high-intensity SERS signal under a laser wavelength of 514 nm. Under 514 nm wavelength laser irradiation, Ag nanoparticles can be excited by resonance and can generate local electromagnetic oscillations. Through this local surface plasmon resonance (LSPR), the Raman signal is fully enhanced. In addition, the Fermi level of Ag nanoparticles is higher than that of ZnO nanoparticles, and the Fermi level of ZnO nanoparticles is higher than than that of PAA microspheres. Electrons of Ag nanoparticles are easily transferred to the conduction band of ZnO nanoparticles at the PAA/ZnO interface. In this case, the accumulation of negative charges on the side closest to the PAA/ZnO, and positive charges accumulate on the other side. A local electric field is formed around the particles.

Figure 5 shows the SERS spectrum analysis of PAA/ZnO/Ag composite microspheres at different R6G concentrations. The experimental results show that the detection limit of PAA/ZnO/Ag composite microspheres for trace pollutants can reach $10^{-6}$ M. This composite material is capable of detecting trace pollutants.

**Self-Cleaning of PAA/ZnO/Ag Composite Particles.** In this work, the SERS signal enhancement and cleanability of PAA/ZnO/Ag in the presence of trace pollutants are presented as practical applications. A very interesting phenomenon is that the trace pollutant signal of PAA/ZnO/Ag is close to zero after UV light irradiation as shown in Figure 6b. In this step, the nanosilver is irradiated with UV light to generate electrons and holes, which can degrade trace R6G. The PAA/ZnO/Ag composite particles that had been used for SERS detection were cleanable by photodegradation of R6G under UV irradiation.

**CONCLUSIONS**

In summary, this study successfully prepared a new PAA/ZnO/Ag multifunctional composite material. This composite material shows a good effect on the SERS signal enhancement and cleanability in the presence of R6G trace pollutants.

**EXPERIMENTAL SECTION**

**Materials.** Zinc acetate and sodium hydroxide were purchased from Aldrich and used directly. Ethanol was used as the solvent for the synthesis of ZnO nanoparticles. PMDA (pyromellitic dianhydride) and ODA (oxydianiline) were purchased from Aldrich, while acetone and methanol were used as solvents for the preparation of PAA particles. Ag(TEA)$_2$ and SnCl$_2$ and hydroquinone were purchased from Aldrich and used for the synthesis of Ag nanoparticles.
Synthesis of PAA Particles. Using a homogenizer (8000 rpm, room temperature), 0.625 g of PMDA (pyromellitic dianhydride) and 0.575 g of ODA (hydroxydiphenylamine) were reacted to prepare PAA particles in an acetone (90 mL)/methanol (30 mL) solution.

Synthesis of ZnO Particles. For the synthesis of ZnO nanoparticles, 0.5 g of zinc acetate and 0.16 g of sodium hydroxide were added to ethanol for reaction. The zinc acetate solution was placed in a flask, mixed with an equimolar ethanolic solution of sodium hydroxide, and refluxed at 65 °C for 1.5 h. After the reaction, ZnO particles were then separated from the mixture by centrifugation at 10,000 rpm for purification. Finally, the ZnO particles were redispersed in ethanol to obtain a ZnO suspension.

Synthesis of PAA/ZnO Composite Particles. The ZnO particle suspension in ethanol was ultrasonicated for about 30 min at room temperature. PAA solution (2 mL) was added to ZnO solution, and ultrasonic oscillation was performed for 1 h. The resulting suspension was mixed with 2 mL of PAA in 0.4 mL of ZnO suspension; afterward, it was ultrasonicated for another 3 h at room temperature. The final mixture is the PAA/ZnO composite.

Synthesis of PAA/ZnO/Ag Composite Particles. The Ag nanoparticle coating of PAA/ZnO cores was performed according to ref 16. First, the PAA/ZnO particle was dispersed in 6 mL of methanol–acetic acid–ethanol medium (methanol 30/acetate 90/ethanol 100 wt/wt). Under vigorous stirring at room temperature, 2 mL of ethanol solution containing 0.03 g of SnCl2 was added for about 30 min to obtain activated PAA/ZnO composite particles. Second, PAA/ZnO composite particles were dispersed in 3 mL of ethanol solution containing Ag(TEA)2+; stirred for about 30 min, and then filtered to obtain PAA/ZnO/Ag seed composite particles. Third, the PAA/ZnO/Ag seed MS was redispersed in 50 mL of Ag(TEA)2+ solution and stirred. In another flask, 4 mL of hydroquinone solution and 96 mL of ethanol were mixed. Two milliliters of the mixture was added dropwise to the Ag(TEA)2+ solution of the PAA/ZnO/Ag seed MS as described above. The solution mixture was stirred for another hour. The reaction solution turned brown, indicating that Ag was produced. The product was filtered and washed with ethanol. Finally, the PAA/ZnO/Ag powder obtained after filtration was put into a vacuum drying oven and dried at 500 °C for 1 day to obtain PAA/ZnO/Ag powder.

The carboxyl groups on the surface of PAA are prone to condensation reactions with hydroxyls on the surface of ZnO, so PAA and ZnO can easily combine together.

In our synthesis method, the surface morphology and optical properties of PAA/ZnO/Ag composite materials were studied. First, PAA/ZnO composite particles were added into an ethanol solution containing SnCl2 with vigorous stirring at room temperature, and then filtered to obtain activated PAA/ZnO composite particles. Second, the activated PAA/ZnO composite particles were dispersed in Ag(TEA)2+ solution and stirred and then filtered to obtain PAA/ZnO/Ag composites containing Ag seeds. Third, the Ag-seeded PAA/ZnO composites were redispersed in Ag(TEA)2+ solution and stirred. In another flask, hydroquinone solution and ethanol were mixed. The hydroquinone/ethanol solution was added into the above PAA/ZnO/Ag-seeded composite solution. The above solution was stirred. During the reaction, the PAA/ZnO/Ag-seeded composite solution turned brown, indicating that Ag nanoparticles have been produced. The product was filtered and washed with ethanol. Finally, the obtained PAA/ZnO/Ag composite microsphere product was placed in a vacuum drying oven for one day. The synthesis mechanism diagram of PAA/ZnO/Ag composite microspheres is shown in Scheme 1. PAA/ZnO composite microspheres were first synthesized using a heterogeneous agglomeration method.

Scheme 1. Schematic Process for PAA/ZnO/Ag Microspheres

SERS Spectral Measurements. The PAA/ZnO/Ag composite microsphere material was used as a substrate for SERS measurements. The R6G solution was diluted to 10−5 and 10−6 M with ethanol. For the PAA/ZnO/Ag composite to reach an equilibrium with adsorbed analyte R6G, the composite must be immersed in the R6G solution for 30 min. Then, the soaked PAA/ZnO/Ag composite microspheres were kept in vacuum desiccators at room temperature ready for SERS measurements.

Characterization. The synthesized PAA/ZnO/Ag composite material was analyzed by TEM and high-resolution TEM (HRTEM) (Tecnai F20) under a 200 kV operating voltage. The high-angle annular dark-field (HAADF) image and elemental mapping image were obtained under an American FEI Tecnai G2 F30 S-TWIN field emission transmission electron microscope (at 300 kV). The optical properties were determined using a Lambda 35 UV–vis spectrometer. The SERS signal was recorded using a Thermo Nicolet Almega XR with 514 nm laser excitation with an integration time of 0.2 s.

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Y. Fabrication of tri-layer structured CdS/SiO₂/sulfonated PS
evolution by water splitting.

CuO photocatalysts to increase photoactive electrons in hydrogen

with Dye Molecules.

scopic, Structural, Morphological Characterization and Interaction

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Notes
The authors declare no competing financial interest.

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