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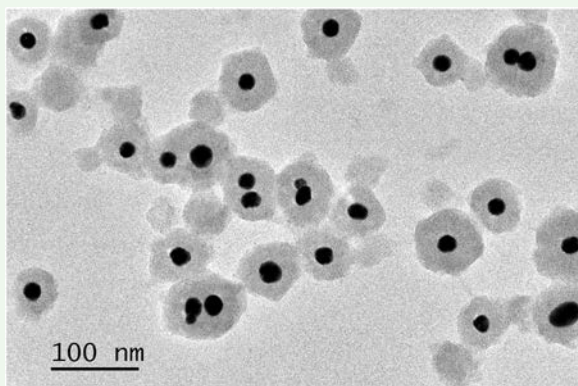
Green synthesis of proanthocyanidins-functionalized Au/Ag bimetallic nanoparticles

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ABSTRACT

Proanthocyanidins-functionalized Au/Ag bimetallic nanoparticles were synthesized by a hydrothermal method. The obtained Au/Ag nanoparticles have been characterized by UV-Vis absorption spectra (UV), Fourier transform infrared spectroscopy (FTIR), Transmission electron microscopy (TEM) and X-ray diffraction (XRD). The UV and FTIR measurement indicated that the as-synthesized colloids have the spherical shapes and the presence of the polymerized proanthocyanidins around metal nanoparticles. TEM and XRD results revealed that the nanoparticles have uniform core-shell structures and the metal core possessed a highly crystalline structure. Furthermore, it was found that the proanthocyanidins-functionalized Au/Ag bimetallic nanoparticles have high removal efficiency for some organic dyes.



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1. Introduction

Noble metal alloy nanomaterials such as Au/Ag bimetallic nanoparticles have attracted considerable attention recently due to their specific optical, electronic, and catalytic properties (1–3). It has been demonstrated that Au/Ag bimetallic nanoparticles show enhanced catalytic activity compared to either Au or Ag nanoparticles, owing to a synergistic effect (4–6). Furthermore, surface plasmon resonance (SPR) characteristic can be tuned systematically from 520 to 400 nm by changing the Au/Ag alloy composition. The plasmonic properties of the alloy nanomaterials have many potential applications such as for imaging, sensing and diagnosis (7,8).

Au/Ag bimetallic nanoparticles can be synthesized by co-reduction of Au and Ag salts in aqueous solution, a galvanic replacement reaction, phase-transfer method, laser ablation and so on (9,10). Recently, green synthesis of noble metal nanoparticles has attracted considerable attention (11–13). For example, Au and Ag nanoparticles can be synthesized by using plant extracts as reducing as well as capping agent (11,14,15).

Proanthocyanidins, one type of natural plant constituent, are present in the fruits, bark, leaves and seeds of many plants (16,17). Proanthocyanidins are well known for their antioxidant activity and increasingly recognized

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as having beneficial effects on human health (17,18). In addition, proanthocyanidins have been reported to possess a broad spectrum of biological, pharmacological and therapeutic activities against free radicals and oxidative stress. Our recent studies have demonstrated that proanthocyanidins can be utilized to syntheses of Au and Ag nanoparticles (14,15). Therefore, proanthocyanidins can be considered as an ideal plant agents using for green synthesis of noble metal alloy nanomaterials. In this study, we explored to use proanthocyanidins as reducing as well as capping agent to synthesize Au/Ag bimetallic nanomaterials by a hydrothermal method.

2. Materials and methods

2.1. Materials

Proanthocyanidins (analytical standard, $\geq 95\%$, molecular weight 594.52) used in the present work was purchased from Aladdin reagent Co., Ltd. (Shanghai, China). Tetrachloroauric (III) acid hydrate was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). AgNO_3 ($\geq 99.8\%$) was used without further purification. All other reagents were of analytical purity grade. Ultra-pure water was used throughout this study, and its resistivity was $>18 \text{ M}\Omega \text{ cm}$.

2.2. Synthesis of proanthocyanidins-functionalized Au/Ag bimetallic nanoparticles

Firstly, 50 mL of 0.64 mM proanthocyanidins aqueous solution was prepared by dissolving of pure proanthocyanidins powders with water. In a typical synthesis experiment, 0.30 mL of 2% $\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$ and 0.25 mL of 1% AgNO_3 aqueous solution were added into the as-prepared proanthocyanidins solution. In this case, the participated reactant ratio of Au and Ag is 1:1. The syntheses with different ratio of Au and Ag were also tested. The mixture was stirred together at least 30 min. Then, 40 mL of the final solution was taken out and transferred into a Teflon-lined autoclave of 50 ml, and then sealed and maintained at 140°C for 4 h. Finally, a dark red solution was obtained, which indicated Au/Ag bimetallic colloids were successfully produced. The average solution pH before and after synthetic reaction is lower than 3.0.

2.3. Characterization of Au/Ag bimetallic nanoparticles

2.3.1. UV-Vis absorption spectra

The absorption spectra of Au/Ag colloid were measured by UV-5500 spectrophotometer (Metash, China). The

original Au/Ag colloid solution was diluted to 4-fold and then added into a quartz cuvette for the UV absorption measurement.

2.3.2. Fourier transform infrared spectroscopy

The proanthocyanidins-functionalized Au/Ag nanoparticles (derived from the centrifugation of the Au/Ag colloidal solution) and pure proanthocyanidins were analyzed by Fourier transform infrared spectrometer (IR Affinity-1, Shimadzu, Japan) using KBr pellet method.

2.3.3. Transmission electron microscopy

The transmission electron microscope equipped with energy dispersive spectrometer (EDS, JEOL Ltd., JEM-2100) at 200 kV was used to observe the morphology of the as-synthesized Au/Ag nanomaterials. 5 μl of the Au/Ag colloid solution was dried on a carbon coated copper grid at room temperature and stored in a desiccator prior for TEM imaging. A nickel grid was used for the sample preparation for EDS measurements.

2.3.4. X-ray diffraction

The crystal structure of the Au/Ag nanoparticles was examined by X-ray powder diffraction using Cu K α radiation on a Rigaku D/max 2200 VPC X-ray diffractometer (40 kV/40 mA). The solid Au/Ag nanoparticles sample were collected from the centrifugation of the Au/Ag colloidal solution.

2.4. Removal of organic dyes experiments

20 mg/L of methylene blue or Rhodamine B solution was prepared in the typical experiments. Au/Ag bimetallic nanoparticles (the final concentration of 1 g/L) were then dispersed into the methylene blue solution. After the predefined time, an aliquot solution was taken out, and centrifuged at RCF of 20,000 g for 10 min., the obtained supernatant was used for UV absorption measurement at 664 nm for methylene blue and at 528 nm for Rhodamine B. A series of standard methylene blue or Rhodamine B solution at different concentration were also measured to establish a standard curve. The removal rate of the Au/Ag bimetallic nanoparticles for the methylene blue or Rhodamine B can be obtained according to the standard curve.

3. Results and discussion

3.1. UV-Vis and FTIR absorption spectra characterization

Figure 1 shows the UV absorption spectrum of the proanthocyanidins functionalized Au/Ag bimetallic

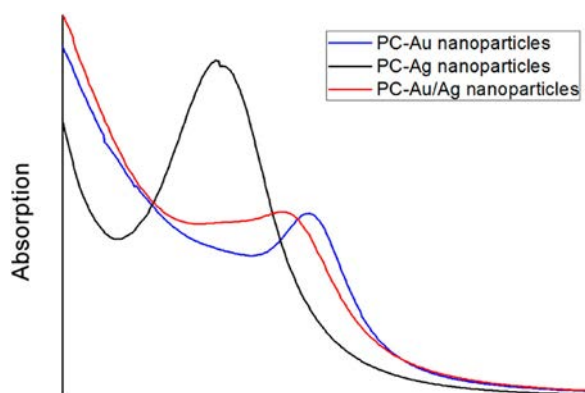


Figure 1. UV-Vis absorption spectra of the proanthocyanidins-functionalized Au/Ag colloidal solution, proanthocyanidins-functionalized Au and Ag colloidal solution.

colloidal solution in a typical experiment. The UV absorption of the proanthocyanidins-functionalized Au and Ag colloidal solution were also measured for comparison. As can be seen in Figure 1, there is a broad absorption band ranging from 420 to 550 nm peaked at 509 nm. In comparison with the UV absorption spectra of proanthocyanidins-functionalized Au colloid (peaked at 530 nm) and Ag colloid (peaked at 447 nm), the absorption peak of Au/Ag colloid is located at intermediate positions between the Au and Ag plasmon bands as shown in Figure 1. Therefore, it is attributed to the surface plasmon absorption of Au/Ag composite nanoparticles (4). Furthermore, it is believed that both gold and silver atoms are present on the surface of the nanoparticles. Since its surface plasmon band is more close to that of the gold colloid, it is possible more gold atoms occupied the surface of the bimetallic nanoparticle. It is well known that gold and silver is miscible in all proportions due to the almost identical lattice constants and the unit-cell size of Au–Ag alloys changes by less than 1% over the entire range (19). The different ratio of the surface atoms on nanoparticle are derived from the difference in the reduction rate of the gold and silver salts. As indicated by our primary experiments, tetrachloroauric (III) acid is seemed to be easily reduced as comparison to the silver salts.

Figure 2 shows the FTIR spectrum of the proanthocyanidins-functionalized Au/Ag nanoparticles and pure proanthocyanidins. In the spectrum of pure proanthocyanidins, the broad absorption band ranging from 3400 to 3150 cm^{-1} was ascribed to hydrogen bond effects between phenolic hydroxyl of proanthocyanidins. The absorption band at 1610 and 1105 cm^{-1} were attributed to those of the characteristic functional groups of poly flavonoids moiety in proanthocyanidins. The peaks at 1520 and 780 cm^{-1} were attributed to the skeletal stretching modes of the aromatic ring of

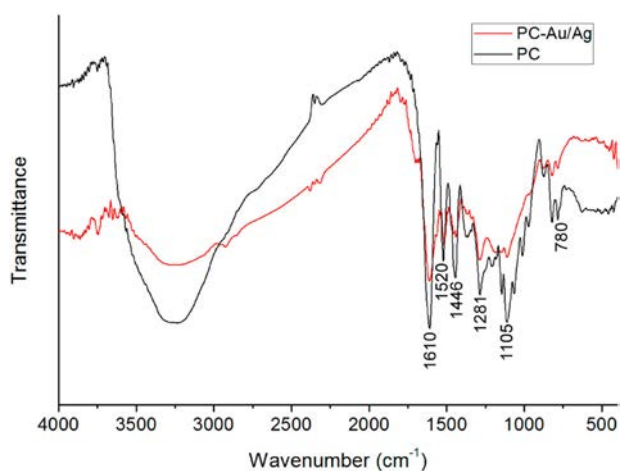


Figure 2. The FTIR spectra of the proanthocyanidins-functionalized Au/Ag nanoparticles and pure proanthocyanidins.

proanthocyanidins structure and CH out-of-plane deformation of the aromatic rings with two adjacent free hydrogen atoms (20,21). In the FTIR spectrum of proanthocyanidins functionalized Au/Ag nanoparticles, the characteristic absorption bands were quite similar to those of pure proanthocyanidins except that the absorption band peaked at 1520 cm^{-1} corresponding to of the aromatic ring moiety of proanthocyanidins shifted to 1515 cm^{-1} , which implied that there are some interactions between the aromatic ring of proanthocyanidins and the surface of nanoparticles. These results indicated that proanthocyanidins were associated with Au/Ag nanoparticles.

3.2. TEM and XRD characterization

The representative TEM images of proanthocyanidins-functionalized Au/Ag bimetallic nanoparticles are showed in Figure 3(a). It can be seen that Au/Ag bimetallic nanoparticles have a very uniform core-shell structures. As judged by the contrast ratio from the TEM image, the core structures is considered to be made up of metal Au and Ag, whereas the shell can be attributed to the organic layers derived from the polymerization of proanthocyanidins. Proanthocyanidins (PA) has been demonstrated as a natural cross-linker, which can be used to improve the resin–dentin bonds of various etch and rinse adhesives (22). Furthermore, proanthocyanidins can be polymerized to high molecular weight polymers by enzyme catalysis under relatively high temperatures (23). In this study, it is believed that proanthocyanidins polymerized to the cross-linked layers under high temperature and high pressure, and finally formed a shell structure around the metal core.

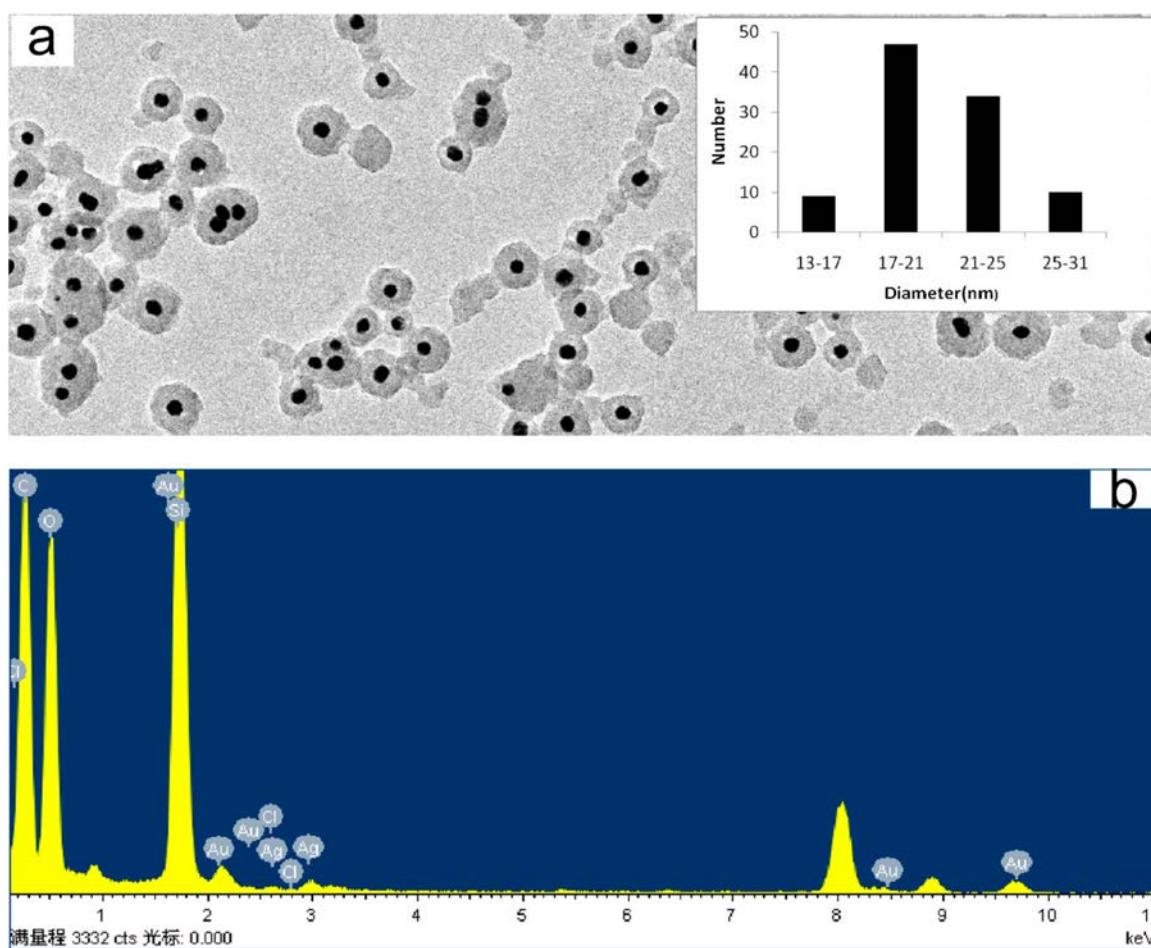


Figure 3. (a) The representative TEM image of the obtained Au/Ag nanoparticles. (b) The EDS spectrum of the Au/Ag nanoparticles.

Under hydrothermal conditions, transformation from phenols to O-quinones might be the first step of polymerization. The formed quinones will react with other phenols with an electron-rich ring. When the reaction occurs, a new bond is formed between the two phenolic compounds resulting in the generation of a highly polymerized proanthocyanidins.

The average core size of bimetallic nanoparticles was 20.8 ± 3.0 nm ($n = 100$). The average shell size was 23.2 ± 4.8 nm ($n = 100$). The core-shell structures in this study is actually an inorganic-organic structure, which is different from the Au@Ag or Ag@Au core-shell structures as reported in recent literatures. The elemental composition of the metal core was further analyzed by energy-dispersive spectroscopy (EDS) spectra as shown in Figure 3(b). The EDS spectrum confirmed the presence of Ag and Au content of the nanoparticles. The atomic ratio of Au to Ag was approximately 0.7 based on the elemental measurement (AuM and AgL). The crystalline characterization of Au/Ag bimetallic nanoparticles was analyzed by XRD. Figure 4 shows XRD patterns of the Au/Ag bimetallic nanoparticles, which

are consistent with fcc Au (or Ag). The crystal grain size estimated from XRD peak was 17.7 nm, which is close to that of TEM measurement.

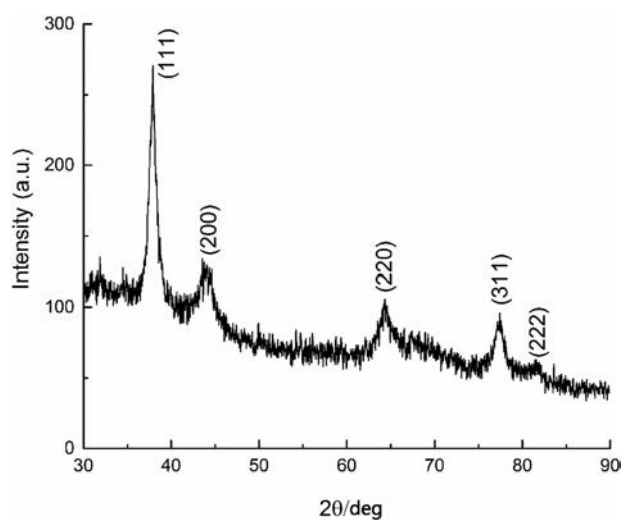


Figure 4. XRD pattern of the proanthocyanidins-functionalized Au/Ag nanoparticles.

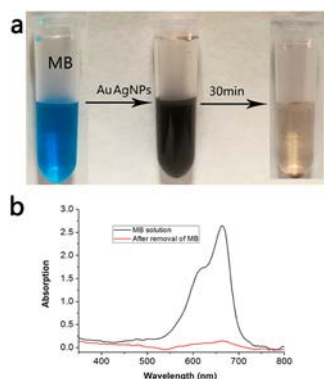


Figure 5. (a) The photographs of the removal process for methylene blue (MB) by Au/Ag bimetallic nanoparticles. (b) UV-Vis absorption spectra of methylene blue (MB) solution before and after interaction with Au/Ag bimetallic nanoparticles.

3.3. Removal of organic dyes by Au/Ag bimetallic nanoparticles

Recently, nanomaterials have been explored to apply for water treatment such as removal of heavy metal ions and harmful organic dyes (24). In this study, we investigate the interactions of the as-synthesized proanthocyanidins-functionalized Au/Ag bimetallic nanoparticles with the organic dyes methylene blue and Rhodamine B. Figure 5(a) shows the photograph of the removal process by Au/Ag bimetallic nanoparticles for methylene blue. It can be seen that the blue color is almost disappeared after 30 min incubation with the nanoparticle. UV-Vis absorption spectra of methylene blue (MB) solution before and after interaction with Au/Ag bimetallic nanoparticles were showed in Figure 5(b). The removal rate of Au/Ag bimetallic nanoparticles for methylene blue is high than 96% via UV absorption measurement. Removal of other organic dyes such as Rhodamine B has also been tested. The removal ratio of Au/Ag bimetallic nanoparticles for Rhodamine is 92.7% under the same test conditions as for methylene blue. Therefore, a proanthocyanidins functionalized Au/Ag bimetallic nanoparticle is an alternative agents using for removal of some organic dyes. The removal mechanism of proanthocyanidins-functionalized Au/Ag bimetallic nanoparticle to methylene blue or Rhodamine B is still not very clear. It is considered that proanthocyanidins shell and the core-shell structures are critical to the interactions with the organic dyes.

4. Conclusion

In this study, we developed a hydrothermal method to synthesize the proanthocyanidins-functionalized Au/Ag bimetallic nanoparticles. These nanoparticles have

perfect core-shell structures wherein proanthocyanidins oligomers form outer organic shell and Au/Ag atoms make up of metal core. XRD characterization confirmed that the Au/Ag metal core possessed a highly crystalline structure. Furthermore, the proanthocyanidins-functionalized Au/Ag bimetallic nanoparticles have high removal efficiency for organic dyes such as methylene blue and Rhodamine B. Further potential applications of these novel proanthocyanidins-functionalized Au/Ag bimetallic nanoparticles are underway.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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