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Synthesis of noval gold nanomaterials and it's detection of sewage

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Abstract

In this article we report a novel approach to polyvinyl pyrrolidone k-30 (PVP)-templated formation of fluorescent gold nanoparticles (Au NPs) with pore structure and its application to sewage detection. For the first time the method of generating PVP-encapsulated Au NPs in aqueous solution is demonstrated. It was found that the formation of fluorescent Au NPs have highly fluorescent signal. Through the adsorption experiment, it is concluded that the methylene blue is adsorbed on Au NPs. This work successfully develops the capping PVP scaffolds of fluorescent Au NPs with pore structure. This experiment lays a foundation for the application of Au NPs in the field of environmental applications.

Key words: adsorption property, fluorescence, gold nanoparticles, pore structure materials

INTRODUCTION

With the tremendous developments in nanotechnology over recent decades, many researchers have great interest in the application of different nanomaterials in the field of biology, such as bioanalysis, diagnosis, and biomedical treatment (Thakor *et al.* 2011; Sasidharan & Monteiro 2015). China's total sewage discharge accounts for 10% of the total amount of the world's sewage. It is understood that China's urban sewage treatment rate was only 36% (Lin *et al.* 2011). But nanotechnology as a new water treatment technology has made great breakthroughs in recent years (Homberger & Simon 2010). The application of nanotechnology includes the use of engineered nanomaterials to clean-up polluted media such as soils, water, air, groundwater and wastewaters, known as nanoremediation (Karn *et al.* 2009; Lofrano *et al.* 2017; Corsi *et al.* 2018).

Since the 1990s, with the rapid development of nanotechnology, it has made great achievements in the fields of ceramics, catalysis, biology, medicine and so on (Qu *et al.* 2013; Amariei *et al.* 2017; Cheng *et al.* 2017). In 1998, a large number of nanoscale functional materials were prepared by American researchers, and their processing and synthesis are considered as an important basic research project (Amariei *et al.* 2017). Chaudhary was used to study the decolorization and degradation of nine azo dyes under anaerobic conditions; the results showed that the various dyes can quickly degrade (Chaudhary *et al.* 2014). Lawrence Livermore Laboratory of the University of California recently developed a new type of carbon nanotubes (Yu *et al.* 2016), which can reduce the cost of salt removal. China's nanotechnology and nano material development began in the late 1980s, and researchers have made great achievements (Cai *et al.* 2015; Cheng *et al.* 2017), such as: large area directional carbon nanotube array synthesis, long carbon nanotubes (Yu *et al.* 2016), etc. In the field of water treatment, Zhao and his co-workers (Zhao *et al.* 2017) in the treatment of tannery wastewater by nano TiO_2 photocatalytic treatment, found the chemical oxygen demand (COD) and color

Water Practice & Technology Vol 14 No 2
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removal rate of the effluent, as well as its biodegradability were greatly improved. Gu, *et al.* (Gu *et al.* 2017) has successfully demonstrated driving chemical reaction by utilizing solar heat and electricity to minimize the use of fossil fuels. In the future, nanotechnology is an international research hotspot.

In this study, we used PVP as protecting reagent to synthesize gold nanoparticles (Au NPs). Fluorescence spectroscopy was employed to confirm the fluorescence characteristic of the Au NPs. Transmission electron microscope (TEM) was used to characterize the size and morphology of Au NPs. Furthermore, through the adsorption experiment, it is concluded that the methylene blue is adsorbed on Au NPs. At last, EDS was used to detect the adsorption effect of Au NPs in sewage.

MATERIALS AND METHODS

Chemicals and materials

Chlorauric acid ($HAuCl_4 \cdot nH_2O$ (Aldrich)), polyvinyl pyrrolidone k-30(PVP), 1, 2-diaminobenzene, ethanol absolute, distilled water, methylene blue, sewage (Inner Mongolia Normal University sewage plant). All chemical reagents are analytical grade and were used as received without further purification. Phosphate buffered solution (PBS) [10 mM, pH = 7.4] was also prepared. All the solutions were prepared with distilled water and stored at 4 °C before use.

Apparatus

UV/Vis absorption spectra were carried out by a CARY 500 UV/Vis/near-IR spectrophotometer (Varian). Fluorescence measurements were recorded at room temperature using a LS 55 luminescence spectrometer (Perkin-Elmer). Transmission electron microscopy of energy dispersive spectroscopies (TEM-EDS) were recorded to determine the compositions of the obtained products. TEM images were obtained with a JEOL-2100F TEM (Japan), with an operating voltage of 200 kV. The samples for TEM characterization were prepared by placing a drop of colloidal solution on carbon-coated copper grid and dried at room temperature.

Synthesis of the multifunctional Au NPs

In a typical synthetic procedure, 25 mM $HAuCl_4 \cdot nH_2O$ solution (2 mL) was added dropwise into PVP solution (1 M). The $HAuCl_4$/PVP molar ratio was 1:1, 5:1 or 20:1. The resulting solution was diluted to 7.5 mL and then 1, 2-diaminobenzene solution (0.5 mL, 0.1 M) was added dropwise into the mixture solution. After a few hours of stirring at room temperature, the mixture solution was centrifuged with distilled water and ethyl alcohol absolute (ethanol/water volume ratio of 1:1) three times.

Adsorption experiment

PBS [10 mM, pH = 7.4] was prepared with KH_2PO_4 and Na_2HPO_4. Methylene blue (0.075 g) was dissolved in distilled water (50 mL) to form 0.08 mM methylene blue reagent. The as-prepared methylene blue reagent (5 mL) was added into PBS (5 mL) and centrifuged for 15 min, the rotational speed was 8,000 r/min. The prepared Au NPs (20:1, 5:1, 1:1; 5 mL) were added to the methylene blue reagent (5 mL), the sample was separated by centrifugation and centrifuged for 15 min, with a rotational speed of 8,000 r/min. The absorbance was measured at a wavelength of 660 nm and a diameter of 1 cm.

The Au NPs (20:1, 5:1, 1:1) were added dropwise into sewage (the volume ratio of Au NPs solution/sewage is 1:1), the sample was separated by centrifugation and centrifuged 15 min at the rotational speed of 5,000 r/min, by using EDS to detect the adsorption effect of Au NPs in sewage.

Water Practice & Technology Vol 14 No 2
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RESULTS AND DISCUSSION

Analysis of fluorescence of Au NPs

In this work, Au NPs has excellent fluorescence properties, therefore, we can apply it in the field of biomedicine. For example, researchers can use gold nanoparticles to fluorescently label cancer cells for further treatment.

Firstly, the absorption peak of Au NPs (20:1, 5:1, 1:1) was measured by UV/Vis absorption spectrum. As shown in Figure S1. The absorption peak of Au NPs was 400 nm–520 nm. Because of the different molar ratio of PVP to $HAuCl_4$•nH_2O, the fluorescence intensity of Au NPs is also different. It can be seen from Figure 1. The molar ratio of $HAuCl_4$/PVP was 1:1 and the fluorescence intensity was the strongest. With the increase of $HAuCl_4$/PVP molar ratio, the fluorescence intensity of Au NPs decreases, and the molar ratio of $HAuCl_4$/PVP is negatively correlated with fluorescence intensity. It can be seen in Figure 1 that the excitation wavelength of Au NPs (1:1, 5:1, 20:1) is 375 nm, 378 nm, and 377 nm, respectively. The emission wavelength of Au NPs (1:1, 5:1, 20:1) is 570 nm, 574 nm, and 571 nm, respectively.

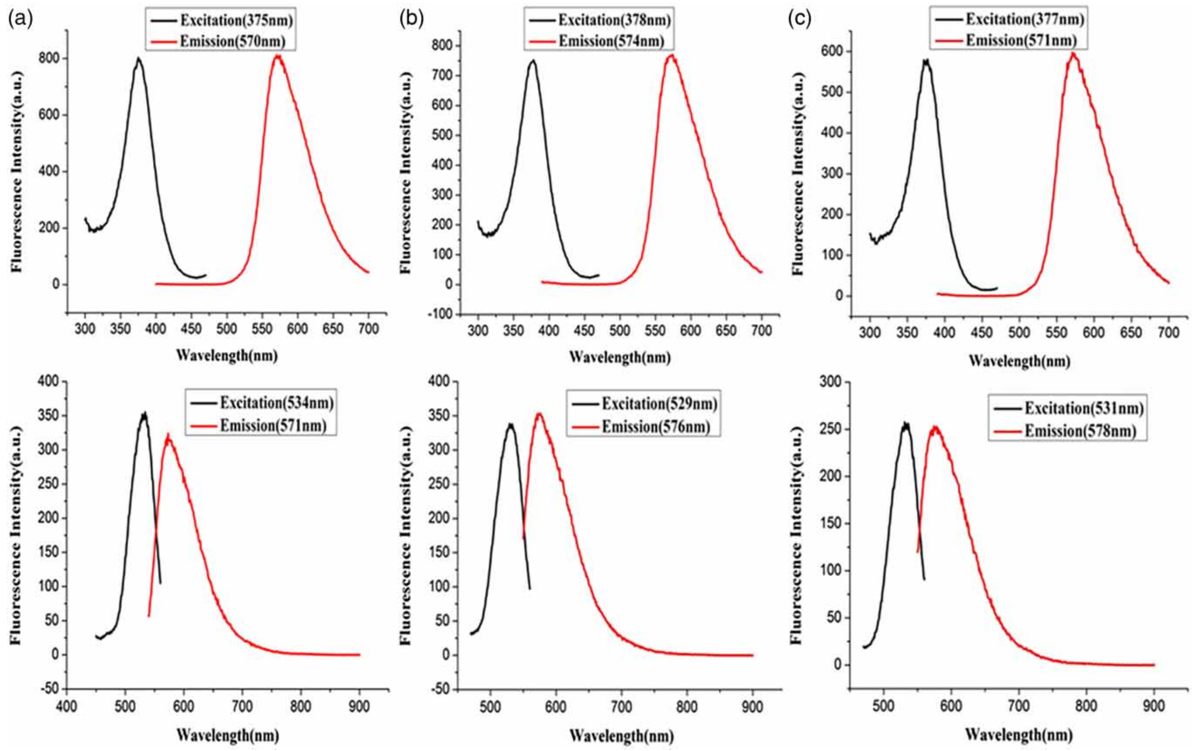

Figure 1 | Fluorescence spectrum of Au NPs (1:1(a); 5:1(b); 20:1(c)).

Characterization of Au NPs

The molar ratio of PVP to $HAuCl_4$•nH_2O has a significant effect on the size and morphology of the gold crystals. The corresponding enlarged images reveal that the surface of these spheres is nearly smooth. PVP is a major protective agent, affecting the morphology of the product. If there is no PVP regulation, only irregular Au NPs aggregates can be obtained.

Moreover, the Au NPs obtained from the images have a pore structure. As shown in Figure S2. The Au NPs showed better pore structure, and can be used in the monitoring of environmental pollutants. Therefore, the Au NPs can be used in the adsorption of organic pollutants or other adsorption experiments. Thus, the nano materials are used in the adsorption experiments.

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The size and shape of the fluorescent Au NPs were examined using transmission electron microscopy (TEM). Figure 2 shows the TEM size of PVP-protected Au NPs. PVP-templated Au NPs have the pore structure shown in Figure 2(a) and 2(b), respectively and the sizes of these particles are from 42.8 nm to 142.8 nm. The results reveal that the spherical PVP-templated Au NPs can be clearly distinguished due to the high electron density of the molecule. Compared with Figure 3(a)–3(c), PVP-templated Au NPs applied to sewage could induce its aggregation.

From the data shown in Figure 4(a) and 4(b), the result of uptake of metal cations in sewage showed that the PVP-templated Au NPs were adsorbent, indicating that Au NPs can be utilized for sewage disposal. Figures S3 and S4 show that the Au NPs adsorbed a number of elements in the sewage, including Mg, Si, K, Al, Ca, Ti, Fe and other elements. The morphology of Au NPs have been imaged by EDS tomography, shown in Figure 4(c). From the EDS image, PVP-templated Au NPs confirmed that using PVP as framework does work.

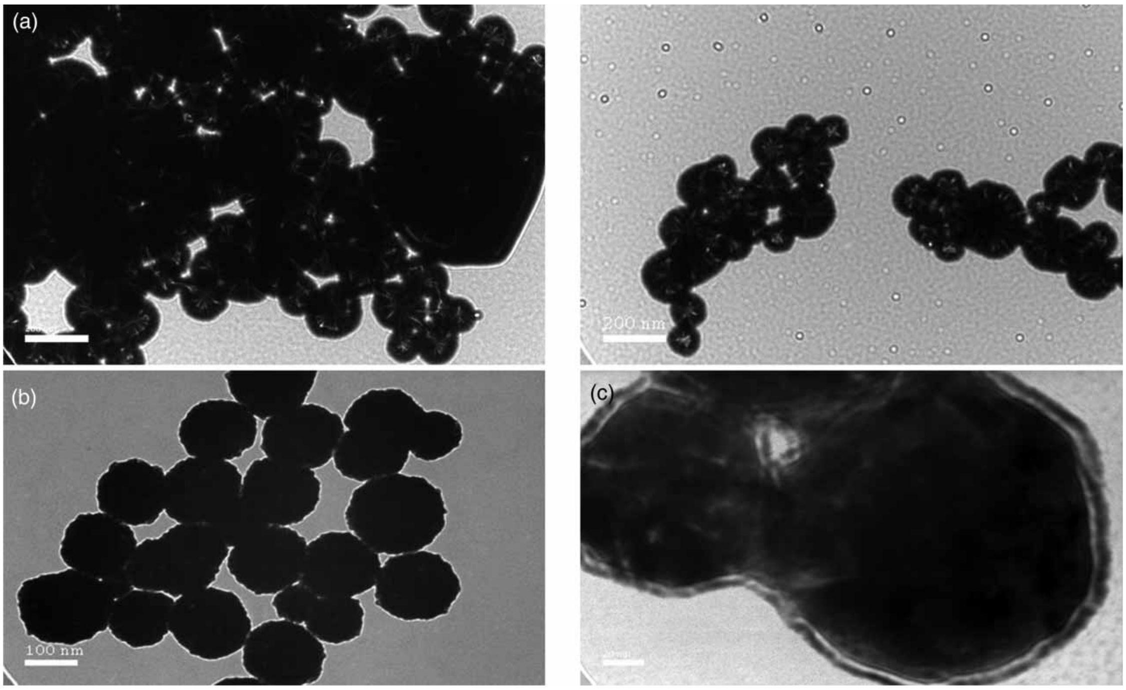

Figure 2 | TEM of PVP-templated Au NPs.

Discussion and results of adsorption experiments

From Table 1, we can see that the prepared Au NPs have a certain adsorption to methylene blue. The adsorption of methylene blue on Au NPs (20:1) was the best, which also verified that the Au NPs (20:1) have a pore structure.

CONCLUSION

In summary, we used a simple, convenient and rapid synthesis method to prepare Au NPs. Through the study of the fluorescence spectra of Au NPs, it is found that the fluorescence properties of the Au NPs are excellent, the excitation wavelength of Au NPs (1:1, 5:1, 20:1) is 375 nm, 378 nm, and 377 nm, and the emission wavelength of Au NPs (1:1, 5:1, 20:1) is 570 nm, 574 nm, and 571 nm, respectively. It can be used to label cancer cells, for biological imaging and further study. The Au NPs were observed by transmission electron microscopy, and the pore structure of Au NPs was

Water Practice & Technology Vol 14 No 2
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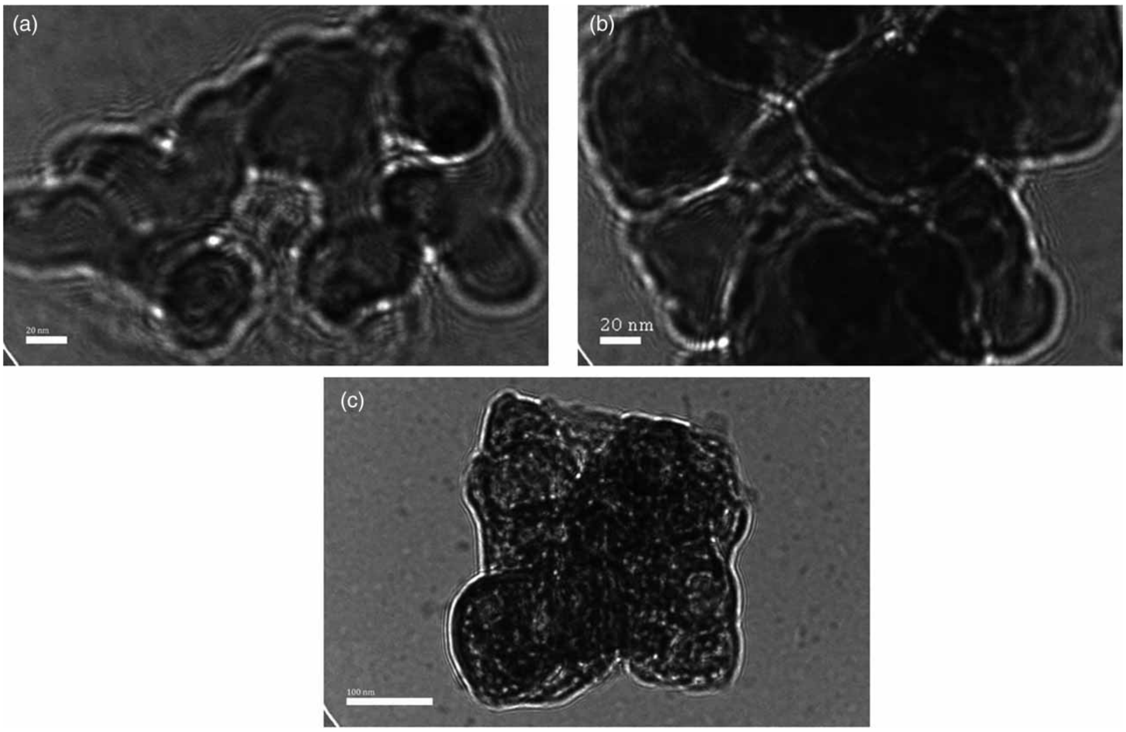

Figure 3 | TEM of PVP-templated Au NPs acting on sewage.

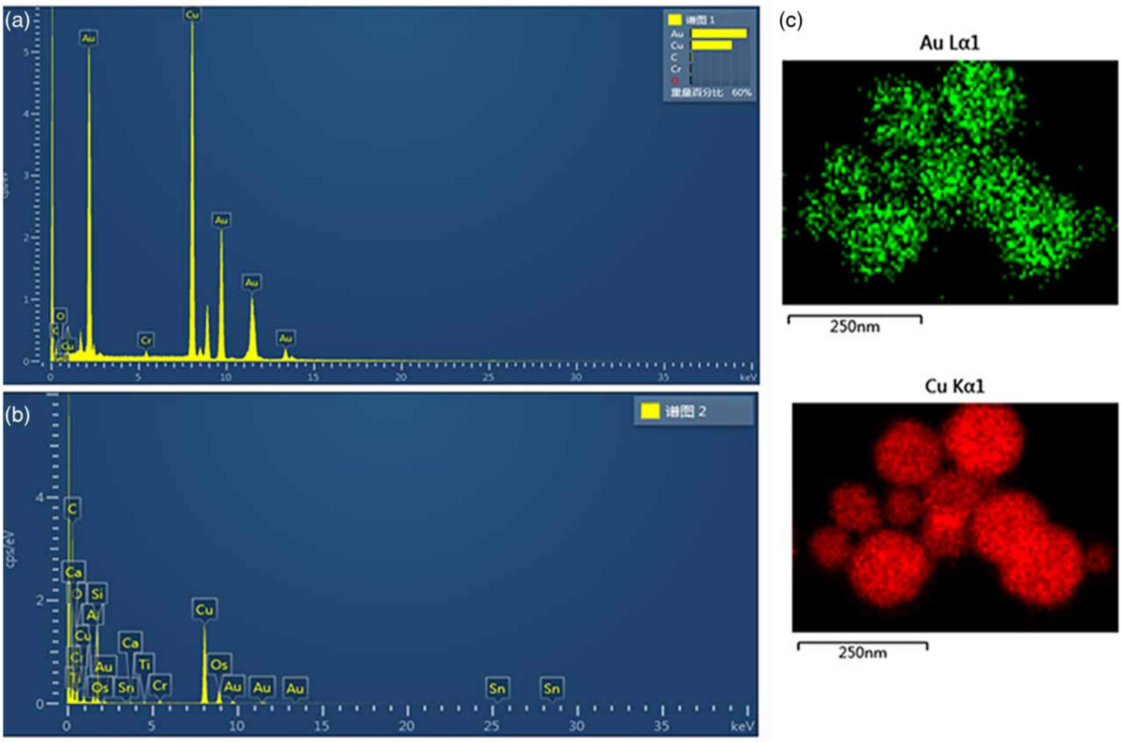

Figure 4 | TEM-EDS of PVP-templated Au NPs acting on sewage (each sample was added to the copper mesh for testing).

obtained, the sizes of these particles are from 42.9 nm to 142.8 nm. Au NPs were applied to sewage detection and the methylene blue is adsorbed on Au NPs. In recent years, more and more researchers have studied the application of Au NPs in the field of medicine. In the future, gold nanoparticles have a good prospect in the field of biology and the environment.

Water Practice & Technology Vol 14 No 2
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Table 1 | Adsorption of methylene blue by Au NPs

Project	Molar ratio of $HAuCl_4$ to PVP	Blank (water)	Methylene blue-buffer solution	Gold nanoparticles-Methylene blue
Abs	20:1	0	0.57	0.21
Abs	5:1	0	0.34	0.33
Abs	1:1	0	0.47	0.24

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