



A novel porous flower-like HA/Ag nanocomposite: One pot preparation and excellent performances as both SERS nanosensor and catalyst



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ABSTRACT

Surface enhanced Raman scattering (SERS) as a powerful analytical tool provides strong enhancement factors, good reproducibility and stability, which has gained good application effect. But single-use or single functional SERS substrate has been limited to the needs of the people. Here, a porous flower-like Hydroxyapatite (HA)/Ag nanocomposite was prepared via one-pot sol-thermal method without any templates. The unique Raman enhancement effect of the HA/Ag nanocomposite as the SERS-active substrate was revealed by the rhodamine 6G (Rh6G) detection at a concentration as low as 1×10^{-10} M. In addition, the as-prepared porous nanocomposite as the catalyst for the reduction of p-nitrophenol (4-NP) can greatly shorten reaction time to 8 min (The rate constant k of the catalytic reaction is 0.426 min^{-1}). Thus, the HA/Ag nanocomposite has wide applications in environmental detection and efficient catalytic degradation for organic pollutants.

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1. Introduction

Raman spectroscopy has attracted a lot of attention since the SERS was firstly reported in 1974 [1]. SERS exhibits several advantages, including abundant material structure information [2], high resolution and sensitivity, and strong anti-jamming capability, which has become a powerful analysis characterization technique [3–5]. People have done a lot of trace detection research to prove that the key of SERS performance is the resonance of plasma to nanostructure and the precious metal signal enhancement effect is particularly significant [6–8]. A SERS substrate with stable enhancement effect and good reproducibility was acquired by preparing the large area of orderly nanostructures or a package of uniformly dispersed gold, silver and copper noble metallic nanoparticles [4,9]. The massive surface with nanoscale roughness, and a variety of nanostructures with various morphologies or compositions were investigated [10–12]. On the one hand, SERS technology has widely applied in environmental monitoring, chemical analysis and biological detection [7,13,14]. Li and coworkers reported the detection of environmental pollutants with SERS [15], while other researchers proposed a chemical detection effect in the

same period [13,16,17]. On the other hand, researchers also have reported a wide variety of catalytic degradation of environmental pollutants [18–20]. With the rapid development of nanotechnology and SERS technique [5,21–23], people were not satisfied with basal material single enhancement effect and would consider other properties including the maneuverability, and price level [4]. For example, Lee reported the functional silver-embedded magnetic nanoparticles as SERS nanoprobe [24]. Yang group designed uniform and optical visualization of SERS substrate for pesticide analysis [25]. Of course, an excellent SERS substrate material could reduce the whole economical cost and extend the application range.

Based on the requirement of environment development, environment-friendly nontoxic materials are becoming more and more popular. It is necessary that SERS substrate is biocompatible and environment-friendly, which could avoid further pollution. Hydroxyapatite (HA) is the main inorganic component of the bones and teeth in the bodies, which has excellent biocompatibility, bioactivity, adsorption and exchange capacity. It has been widely used in protein purification, gas monitoring, drug slow release, catalyst, chemical and environmental engineering, etc. [6,26,27] Moreover, HA can make the noble metal composites distributed uniformly and organic dye adsorbed easily [28,29]. But the porous

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HA-precious metal composites used for SERS detection and catalytic pollutant degradation have not been reported so far.

Phenol contaminants have caused the increasing water pollution, which need to be controlled. The strong toxicity of p-nitrophenol (4-NP) contaminants is difficult to be eliminated, which has received additional consideration. There is a challenge about the purification of wastewater containing phenol and aromatic hydrocarbon compounds in our country even all over the world. The toxicity decreases after 4-NP is reduced to p-aminophenol (4-AP), which is used widely in the photographic developer, corrosion inhibitor, anticorrosion-lubricant and hair-dyeing agent in chemical manufacture and pharmaceutical fields [30–33]. At present, the degradations of some phenol contaminants are still ineffective, including slow degradation rate and secondary pollution. How to put forward the feasible, rapid, efficient, environmental and friend solutions is a problem to be solved. According to our knowledge, the study on the HA/Ag nanocomposite as the environment-friendly efficient catalyst for removing 4-NP has not been mentioned.

Herein, we report a simple one-pot sol-thermal approach for constructing a novel SERS substrate, i.e., porous flower-like HA/Ag nanocomposite. The Ag NPs are distributed on HA nanosheets uniformly. We investigated the detection limit for dye Rh6G and the catalytic reduction for 4-NP by using porous flower-like HA/Ag nanocomposite as both SERS substrate and catalyst, and obtained excellent results. Our work announces an efficient SERS substrate, which may be used in other areas such as medicine or drug carrier.

2. Experiments

2.1. Instruments and materials

Scanning electron microscopy (SEM) images were obtained by using a S4800 scanning electron microscope operated at 10 kV. The transmission electron microscopy (TEM) images were obtained on a JEM 2100 instrument. X-ray diffraction (XRD) patterns were measured by using a DX-2700 X-Ray Diffractometer equipped with Cu K α sealed tube ($\lambda = 1.5406 \text{ \AA}$), the sample was scanned in the 2θ range of 10° – 80° . Brunauer-Emmett-Teller (BET) surface areas were gotten on a Micrometrics ASAP2020 analyzer. UV–vis spectra of as-prepared products were measured with UV-3900 spectrophotometer (Hitachi, Japan) in the range of 200–800 nm. Raman spectra were acquired by a Renishaw 1000 confocal microscopy. Raman spectrometer was equipped with a CCD detector and a holographic notch filter.

Sodium of polyaspartic acid (PASP), anhydrous calcium chloride (CaCl_2), ammonium dihydrogen-phosphate ($(\text{NH}_4)_2\text{HPO}_4$), silver nitrate (AgNO_3), p-nitrophenol ($\text{C}_6\text{H}_5\text{NO}_3$), hydrochloric acid (HCl), ammonia spirit ($\text{NH}_3 \cdot \text{H}_2\text{O}$) were all supplied by Sinopharm Chemical Reagent Co, Ltd (P. R. China). All the reagents were of analytical grade and used without further purification. Deionized water was also used in the experiment.

2.2. Preparation of porous flower-like HA/Ag nanocomposite

Uniform and porous flower-like HA/Ag nanocomposite was synthesized as follows: 11 g of CaCl_2 and 0.5 g of PASP were co-dissolved in 10 mL of ethylene glycol to form solution A after stirring for 30 min; the solution B was prepared by adding 0.0792 g of $(\text{NH}_4)_2\text{HPO}_4$ to 7.5 mL of ethylene glycol. Then, the solution B was slowly injected into the solution A to form white precipitation, and the pH value of the resultant solution was adjusted to 5 by injecting amounts of diluted $\text{NH}_3 \cdot \text{H}_2\text{O}$ and HCl under stirring. After that,

0.169 g of AgNO_3 was added into the above system under vigorous stirring. The above mixture was transferred to the Teflon-lined autoclave and maintained at 150°C for 24 h, then cooled down to room temperature naturally. After centrifugation, the precipitate was washed thoroughly with deionized water and ethanol four times in turn, and dried in an oven at 60°C for 2 h. Finally, HA/Ag nanocomposite was obtained.

2.3. SERS detection for Rh6G

The tested sample was prepared to be sure that the adsorption-desorption equilibrium of Rh6G on nanocomposite reached. Radiation by a wavelength of 532 nm from a hydrogen ion laser (spectra-Physics model 163-C4260) was used for excitation. The laser power at the sample position was not more than 0.5 mW and the laser beam was focused on the sample at a size of about $2 \mu\text{m}$. The representational summation time used for the research was 2 s. For every specimen, we took three SERS signals in diverse locations to the substrate and then averaged them.

2.4. Catalytic reduction for 4-NP

NaBH_4 (sodium borohydride) was used to reduce 4-NP to 4-AP, as a model to study the catalytic efficiency of HA/Ag. The experiment details are as follows: 162.3 mg of NaBH_4 was dissolved in 11.3 mL of deionized water, then mixed with 15 mL of 4-NP solution (0.18 mM). After magnetic stirring for 20 min, 3.4 mg of catalyst (HA/Ag) was added. Along with the reaction, the bright yellow solution gradually become colorless, reaction process was monitored by UV-vis absorption spectra. For the blank experiment, the method is the same as above without adding the HA/Ag nanocomposite.

3. Results and discussion

The morphology of the as-fabricated flower-like HA/Ag nanocomposite is examined by SEM images, which with different magnification are shown in Fig. 1(a-c). It is observed from Fig. 1a that the prepared product exhibits sphere-like shape with the diameter of about $10 \mu\text{m}$. From Fig. 1b, we can clearly see these spheres were assembled by many lamellar petals, displaying a flower-like morphology (Fig. 1d). Fig. 1c presents the further enlarged SEM image of the porous flower-like HA/Ag nanocomposite, it is found that the lamellar thickness is about 200 nm, there are a few small particles on the flower sheets, which may be Ag NPs.

The further characterization could determine the components of the product. Fig. 2a shows the typical TEM image of as prepared nanocomposite. We can see some relatively uniform particles dispersed on slices of flower-like HA/Ag. The high resolution TEM (HRTEM) image shown in Fig. 2b exhibits the lattice fringes with interplanar spacing of 0.23 nm and 0.28 nm, corresponding to the Ag (111) and HA (211) crystal planes respectively. From above results, we can conclude that the HA/Ag nanocomposite could form in a simple one-pot sol-thermal approach, which can be explained from the interaction between HA and Ag nanoparticles as follows. There are many negatively active groups of OH^- , PO_4^{3-} on HA, which can easily attract positively charged Ag^+ . It created an Ag ion-enriched region on the surface of HA, that is beneficial to increase the saturation of Ag^+ and provide the nucleation site of Ag. And the negatively charged groups adhered to the silver nuclei, leading to a lower surface energy of the crystal lattice. According to the nucleation and growth theory of crystals, the formation of a spherical

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