Construction of Ag spherical micro/nanostructures as SERS-active substrates

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Abstract. The silver spherical micro/nanostructures were fabricated by the electrochemical deposition technique. Many silver nanosheets build the spherical microstructures. Confirmed by XRD, UV-VIS and SEM characterization measures, the Ag spherical micro/nanostructures were synthesized on the ITO conductive substrates. Furthermore, different current densities were selected to investigate the growth of Ag microspheres. As the gaps between the nanosheets formatted the “hot spots”, which can effectively enhance the Raman signal, we chose the R6G molecule as the probe molecule to evaluate the SERS performance. The experiment results prove that the Ag spherical micro/nanostructures obtained by the simple electrochemical techniques can be used as high-performance SERS-active substrates.

1. Introduction

The Au, Ag and Cu nanoparticles and nanocomposites have been widely used in surface-enhanced Raman scattering spectroscopy [1, 2], catalysis [3], and biochemical sensors [4]. Generally, high-performance SERS substrates should have enough density of “hot spots”, which from gaps and tips between the rough surface materials [5, 6]. These special Raman-enhanced spots attributed to localized surface plasmon resonances (LSPR) in the surface of metal nanoparticles [7, 8]. Thus, these nanostructures brings about very strong enhancement of the electromagnetic (EM) field on the metal surface [9]. The Nanoparticles has extensively applied in surface-enhanced Raman scattering (SERS) since the core-shell nanoparticles with their unique strategies and functions based on the LSPR properties [8]. Up to now, multiple functional nanorods [10, 11], nanospheres [12], nanowires [13, 14], nanostars [15] and other nanostructures have been applied to SERS-based detection.

Although the nanoscale structures have a good Raman-enhanced effect, the structural stability is poorer, and the structure of the micron-scale despite the enhancement effect is weak, but the structural stability is good. Therefore, the micro/nanostructures having the two advantages will be very suitable to be used as the SERS-active substrate [16]. The nanosheets provide many SERS “hot spots” and the microsphere-like structures have stable properties [17], which makes the characterization of substrates more convenient.

In this paper, we have adopted a simple galvanostatic deposition method to fabricate the Ag spherical micro/nanostructures on the ITO glass for SERS. The different scales of nanostructures were obtained by changing the current density and the prepared Ag micro/nanostructures show good Raman-enhanced effect while choosing the Rhodamine 6G molecules as the probe molecule.
Therefore, the Ag spherical micro/nanostructures were expected to be as good SERS-active substrates in various SERS-based detection and monitoring.

2. Experiment

2.1. Materials
Silver nitrate (AgNO$_3$), sodium citrate, Acetone, ethanol, Hydrogen peroxide (30%) and aqueous ammonia obtained from Gaojing Chemical Reagent Co. Ltd. Rhodamine 6G (R6G) was purchased from Mike Chemical Reagent Co. Ltd. All the reagents (analytical grade) used as received without further purification. All solutions were prepared in Deionized water (DI water).

2.2. Synthesis of Ag spherical micro/nanostructures
The mixed aqueous solution of AgNO$_3$ and sodium citrate was used as the electrolyte. First, 0.05g AgNO$_3$ added in 50ml water, 0.05g sodium citrate added in 10ml water as reductant and stabilizer. Then they are stirred and mixed thoroughly. No other chemical components were added to avoid interference of characteristic Raman signal detection. The ITO glasses were washed with acetone, ethanol and deionized water three times in a turn, and soaked with ammonia, hydrogen peroxide and deionized water 1:1:4 for 15min. Then, the ITO (1×4cm) glass was washed by DI water and used as the working electrode, a Graphite (1.5×4cm) was used as the counter electrode. Finally, the Ag micro/nanostructures were fabricated by choosing appropriate deposition current density for 1 hour at room temperature.

2.3. Measurement and instrument
The morphology of the substrates characterized by scanning electron microscopy (FESEM Hitachi S-4800). The phase composition of the measurement of the sample was prepared by X-ray diffraction (XRD, Bruker D8 Discover) using CuKα (λ=1.5406 Å) radiation at 40 kV and 40 mA. The UV-VIS absorption spectra were obtained by the UV-VIS spectrophotometer (Hitachi-U3900).

2.4. Raman spectral measurements
The Ag micro/nanostructures were immersed in 10$^{-6}$ mol/L aqueous solution of R6G for 30 min. Then, washed with deionized water and dried. The Raman spectra were recorded by a confocal microprobe Raman system (Renishaw, inVia) with a laser beam of 785 nm wavelength. 2.5 mW power, and 1 s integral time.

3. Results and discussions

![Figure1](image)

Figure1. The XRD spectra of the ITO substrate (black) and the Ag micro/nanostructures deposited on the ITO substrate.
The Ag micro/nanostructure was synthesized on the ITO substrate by electrodeposition at the current density of 0.2 mA/cm² for 1 hour. The figure 1 showing the details of the crystal direction of silver nanostructures were characterized by XRD. Taken from the Ag films displays four peaks of Ag crystal, which correspond to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) reflections for the fcc structure of metallic silver (JCPDS File No.04-0783), respectively. The {1 1 1} diffraction peaks are significant high intensity and the ratio between the {1 1 1} and {2 0 0} diffraction line was approximately about 0.4 (JCPDF card 0.4) [18], which suggested that the sample exclusively consists of Nano-sheets that were preferentially oriented with their planes.

Figure 2. The different magnification SEM images of the Ag spherical micro/nanostructures at the current density of 0.2 mA/cm². (a) Low-magnification, (b) High-magnification.

The obtained sample was characterized by SEM. The figure 2a presents low-magnification SEM, which indicates that the film morphology comprises of many monodisperse Ag microspheres with an average diameter of approximately 4μm. From the high-magnification SEM image (figure 2b), the single microsphere was consist of many nanosheets with the radial arrangement, approximately 50nm thick and several hundred nanometers long, these nanostructures created many good Raman “hot spots”. Under these experimental conditions, the distribution and shape of silver nanoparticles was uniform.

With the increase of current density, the morphology of the Ag micro/nanostructures become more and more uniform. It can be seen from the image (figure 3a) that the uniformity of the micro/nanostructures at 0.05 mA/cm² is very poor and the sizes are inconformity. Under the current density of 0.1 mA/cm² and 0.15mA/cm² (figure 3b, c), the nanosheets on the silver microspheres became more obvious, longer and with a diameter uniform. Under the density of 0.25mA/cm² (figure 3d), the size of the microspheres increased and filled the entire substrate lead the silver microspheres to cluster together, the nanosheets on the silver microspheres became more obvious, longer and with a diameter uniform.

Figure 3. The SEM images of the Ag spherical micro/nanostructures synthesized at different current density. (a)0.05mA/cm², (b)0.1mA/cm², (c)0.15mA/cm², (d)0.25mA/cm².
Figure 4. The UV-VIS absorption spectra of Ag spherical micro/nanostructures electrodeposited at different current density.

The figure 4 displays the UV-visible absorption spectra of Ag micro/nanostructures deposited at different current density. As the current density increases, the ultraviolet absorption spectrum of silver films first shifts red and then gradually shifts blue, due to the change in the size of nanoparticles[19] and reveals the plasmon absorption band peak at about 314 nm.

Figure 5. Raman spectra of $10^{-6}$ mol/L R6G absorbed on the Ag micro/nanostructures deposited at different current density as shown in Figure 2 and Figure 3. (a)0.05mA/cm$^2$, (b)0.1mA/cm$^2$, (c)0.15mA/cm$^2$, (d)0.20mA/cm$^2$, (e)0.25mA/cm$^2$.

Considering the specific structure of these Ag micro/nanostructures, the SERS performance was investigated by chosen Rhodamine 6G (R6G) as the probe molecule. The SERS spectra of R6G at different current density conditions as shown in figure 5. From the spectra, we can distinctly observe the characteristic Raman peaks of R6G molecules when the R6G concentration was $10^{-6}$mol/L, revealing the prepared Ag spherical micro/nanostructures having a good enhanced effect. In this figure, the characteristic peaks at 613, 774, 1365, and 1507 cm$^{-1}$, which are assigned to C–C–C ring in-plane, and out-of-plane bending, and aromatic C–C stretching vibrations of R6G molecule [20], respectively. The Raman signal becomes better as the current density increases and then deteriorates, which attributed to the size change of the Ag microspheres. Under the condition of 0.2mA/cm$^2$, the gap between nanosheets was reasonable and the morphology of silver nanoparticles was uniform which
created many of Raman hot spots. This shows that the Ag micro/nanostructures prepared by this simple method have good Raman properties.

4. Conclusions
In summary, we proposed a facile galvanostatic deposition strategy and Ag spherical microstructures consisted of many nanosheets are successfully prepared at room temperature. The mixed AgNO₃ and sodium citrate aqueous solution was chosen as the electrolyte. Sodium citrate as a stabilizer and reducing agent plays a key role in the formation of the Ag microsphere. Furthermore, through changing the current density, the process of growth and morphologic evolution were investigated. From the Raman spectra of R6G molecule, we knew such Ag micro/nanostructures having a good enhanced effect due to plentiful gaps between the Ag nanosheets. Therefore, such Ag spherical micro/nanostructures would serve as good SERS-active substrates applied to various SERS-based detection.

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