Preparation of CuO/Ag rough nanostructures as SERS-active substrates

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Abstract. In this paper, CuO nanostructures with nanometer roughness were firstly prepared by electrochemical anodic oxidation method, and then CuO/Ag composite nanostructures were prepared by magnetron sputtering method on the surface of CuO substrate. The successful deposition of Ag films on CuO was confirmed by XRD, UV-Vis and SEM. In addition, the effects of different Ag sputtering time on substrate morphology and SERS properties were studied. Due to the many gaps between the rough CuO/Ag nanomorphology, the substrate has many "hot spots" and adsorption sites, which can effectively improve the SERS performance of the substrate. We selected R6G dye molecule as the probe molecule to evaluate the SERS performance of the substrate. The final experimental results show that the preparation method of CuO/Ag rough nanostructure is simple, and it has significant SERS performance improvement. The substrate's detection limit for R6G can even reach 10^-11M.

1. Introduction

While the development of science and technology brings us a convenient life, it also brings many problems to be discovered and solved in environmental pollution[1], food safety[2], biotechnology[3], etc. With the rapid development of various spectroscopic techniques, these techniques are widely used to detect the presence of harmful substance[4]. Raman spectroscopy is widely used in chemical analysis[5], environmental monitoring[6] and other fields due to its high sensitivity, non-damage to samples and real-time operation. With people's further understanding of SERS enhanced mechanism, noble metal nanostructures such as gold, silver and copper and their nanocomposite materials were considered to be able to achieve substantial SERS effect[7]. Generally speaking, the surface of high-performance SERS substrate should have enough "hot spots", the generation of these "hot spots" is attributed to the Localized Surface Plasmon Resonance (LSPR) of metal nanoparticles, which brings very strong enhancement of the electromagnetic (EM) field, while the cracks and tips on the surface of nanoscale rough materials can produce a large number of hot spots[8]. Therefore, it is of great significance to prepare nano-sized rough morphology by simple method for SERS performance of reinforced materials.

Three-dimensional SERS structure mainly has two advantages: one is to increase specific surface area, the other is to have excellent light capture effect[9]. Among them, the latter can make the incident light reflect multiple times in the Raman substrate, greatly improving the utilization rate of light. It is worth noting that, in addition to the ultra-sensitive detection ability, high-quality SERS active substrate also needs to have good stability, good repeatability, good durability, simple and economical preparation process and many other factors[10]. Therefore, to design a SERS substrate with practical value, this seemingly simple problem is still facing a big challenge today.

In this paper, a simple anodic oxidation method was used to prepare CuO substrates with nanometer roughness from Cu sheets, and then Ag films were deposited on the surface of CuO/Ag nanocomposite
substrates by magnetron sputtering method. The thickness of Ag film on CuO surface was changed by controlling the time of magnetron sputtering, and the Raman enhancement effect of R6G molecule as probe molecule was used to explore more suitable preparation conditions.

2. Experiment

2.1. Materials
Copper foil, sodium hydroxide (AR), acetone (AR), sodium thiosulfate (AR), hydrochloric acid (AR), ethanol (AR) and other chemical reagents were purchased from Gaojing Chemical Reagent Co. Ltd. Rhodamine 6G (R6G) was purchased from Mike Chemical Reagent Co. Ltd. All reagents (analytical grade) can be received without further purification. Deionized water was used throughout the experiment.

2.2. Synthesis of CuO nanostructures
The copper foils were washed with acetone, ethanol and deionized water for 15min. Copper foil was soaked in 0.25M hydrochloric acid for 5min to remove surface oxides, then washed with deionized water and ethanol and dried. A mixture of 50mL 7.5mM Na₂S₂O₃ and 0.102M NaOH was used as the electrolyte, heated to 60°C in a water bath, and reacted for a 10 minutes at a constant current of 1.0mA. After the reaction, the sample was quickly taken out, washed with ethanol and deionized water, and dried.

2.3. Synthesis of CuO/Ag nanostructures
Silver nanoparticles were grown on CuO thin films by DC magnetron sputtering. The diameter of Ag target material used is 60mm and the thickness is 5mm. The sputtering vacuum was 6×10⁻⁴Pa, the instrument pressure was 1.0Pa, the working gas was Ar gas, the substrate temperature was room temperature, the sputtering time was 10s, 60s, denoted as CuO/Ag10s and CuO/Ag60s, respectively.

2.4. Measurement and instrument
The microstructure of the composite substrate was characterized by scanning electron microscopy (FESEM Hitachi S-4800). The phase composition of the material was analyzed by X-ray diffraction (XRD, Bruker D8 Discover) using CuKα (λ=1.5406Å) radiation at 40 kV and 40 mA. UV-Vis absorption spectra were measured by Hitachi U3900 spectrophotometer.

2.5. Raman spectral measurements
The CuO/Ag nanocomposite structure was immersed in 10⁻⁶ mol/L R6G aqueous solution for 30 min, then washed with deionized water and dried. Raman spectra were recorded by a confocal microreflex (Renishaw, Invia Reflex) with a laser wavelength of 532 nm. The laser power is 0.5mW, the integration time is 5s, and the number of integration is once. Substrate adsorption of other concentrations of R6G solution operation is the same as above.
3. Results and discussions

Fig. 1 shows the details of crystal directions of CuO and CuO/Ag nanocomposite structures characterized by XRD. It can be seen from the figure that the diffraction peaks of copper correspond to the (111), (200) and (220) crystal planes of copper respectively. After the anodic oxidation reaction, relatively weak diffraction peaks appear around 35.6° and 38.7°. They correspond to the (002) and (111) crystal faces of CuO (JCPDS File No.89-5899), respectively. Four crystal peaks of silver were obtained from the material after 60 s magnetron sputtering, which correspond to the diffraction peaks of (111), (200), (220) and (311) of the metallic silver FCC structure (JCPDS File No.65-2871). The above XRD characterization indicates that the CuO/Ag composite nanostructures have been successfully prepared.

Fig. 2a shows CuO under low magnification scanning electron microscopy (SEM), indicating that a large number of dense CuO nanoscale structures grow on its surface. According to the high-power scanning electron microscope image (Fig. 2d), the thickness of individual CuO nanosheets is very thin and the edges are flocculent. These nanostructures create many good Raman "hot spots". As can be seen from Fig. 2b and 2e, after 10 seconds of magnetron sputtering, silver adheres to the surface of CuO nanosheets, making the thickness of the lamellar structure significantly increased and the "hot spot" at the tip of the lamellar structure more obvious. As can be seen from Figure 2c and Figure 2f, when the sputtering time increases to 60 seconds, the thickness of the nanosheet further increases and the uniformity is good.
Fig. 3 shows the UV-Vis absorption spectra of CuO/Ag nanostructures prepared at different sputtering times. CuO has an obvious absorption edge at about 560nm. After loading silver for 10 seconds, the substrate has no significant change in the absorption of visible light bands, and there is an obvious absorption peak at 314nm. After loading silver for 60 seconds, the absorption peak strength at 314nm increases significantly. This indicates that the silver nanofilms are successfully recombined with CuO, and the silver loading capacity increases with the increase of sputtering time.

Fig. 4. Raman spectra of 10⁻⁶ mol/L R6G absorbed on the CuO, CuO/Ag10s and CuO/Ag60s.

In this paper, Rhodamine 6G (R6G) was selected as the probe molecule to study the SERS properties of CuO/Ag composite nanomaterials. SERS spectra of the substrates prepared under different reaction conditions adsorbed R6G are shown in Fig. 4. We can clearly observe from the spectrogram that, compared with CuO, CuO/Ag substrate has a more obvious Raman characteristic peak when the concentration of R6G molecule is 10⁻⁶ mol/L, indicating that the prepared CuO/Ag nanostructure has a good enhancement effect. Among them, CuO/Ag60S substrate showed the best SERS performance.
Fig. 5. Raman spectra of R6G with different concentrations absorbed on the CuO/Ag60s.

As shown in Fig. 5, when CuO/Ag60S substrates adsorbed different concentrations of R6G solutions, the spectra and some characteristic peaks of R6G could be clearly identified, even as low as $10^{-11}$ M, showing good Raman enhancement performance.

4. Conclusions
In conclusion, we propose a simple anodic oxidation strategy to successfully prepare rough CuO nanostructures, and then use magnetron sputtering to plate silver films of different thickness on their surfaces to obtain CuO/Ag composite nanomaterials. According to the Raman spectra of R6G molecules, this rough CuO/Ag nanostructure has a good enhancement effect due to the abundant interludes between CuO/Ag nanosheets. The CuO/Ag60s substrate's detection limit for R6G can even reach $10^{-11}$M. Therefore, this rough CuO/Ag nanostructure can be used as a good SERS active substrate for the detection of various dye molecules and pollutants.

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