Ag nanoparticles modified Cu/Cu(OH)₂ film enables sensitive SERS detection via Coffee ring effect

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Abstract

In this work, based on the coffee ring effect, silver nanoparticles (AgNPs) were deposited on a superhydrophobic Cu/Cu(OH)₂ substrate with nanorod structure prepared by solution-immersion and stearic acid modification, and its surface-enhanced Raman scattering (SERS) performance for the detection of trace organic dye was studied. The results show that the superhydrophobic substrate has a better enhancement efficiency. The hybrid hierarchical structure of the AgNPs/Cu/Cu(OH)₂ composite film shows a positive effect on the enhanced coupling electromagnetic field. This method provides a simple alternative for monitoring organic chemical pollutants with multi-step fabrication processes and expensive templates.

1. Introduction

Surface-enhanced Raman spectroscopy (SERS) is a potential and sensitive molecular vibrational bond recognition and analysis technology [1]. It has become prevalent for tracing and sensing various chemical and biological analytes at the molecular level utilizing its characteristic vibration characteristics [2–4]. It can be applied in many fields like medical diagnosis [5–7], environmental monitoring [8], food safety [9], and drug monitoring [10, 11], etc. However, trace analyte sensitivity, and selectivity significantly increases the SERS substrate fabrication and detection complexity, making it more expensive to conduct the trace analyte via the SERS method. It is urgent to develop a simple and effective strategy that can carry out the self-assembly of SERS substrate and the preconcentration of trace analytes simultaneously.

In recent decades, the coffee ring effect has become a powerful tool for the self-assembly of nanomaterials [12]. After evaporation of the droplet on the solid substrate, the dissolved molecules are highly concentrated at the edge, thus forming ring-shaped, which is suitable for enriching molecules and improving detection sensitivity. The shape and size of sediments rely on the substrate’s surface properties, especially the wettability. It is important to note that the substrate’s wettability also plays a critical role in sensitive SERS-based sensors [13]. A superhydrophobic surface can decrease the coffee ring’s diameter than the hydrophilic one [14, 15].

Superhydrophobic surfaces have been synthesized by multi-step chemical means with time-consuming steps [16–18] and high cost [19, 20].

There are many methods available currently to prepare superhydrophobic SERS platforms, such as chemical deposition [21], laser-etching [22], electrochemical deposition [23], thermal evaporation [24], and nano transfer printing [25]. Most of them require expensive noble metal nanoparticles, special reaction conditions, are often long fabricating processes. Copper is one of the most used metal materials for preparing superhydrophobic surfaces because of its low cost and excellent anti-corrosion property [26]. Through the synthetic process, a variety of micro-/nano structures can be created on the copper surface. They are expected to become reliable substrates and were explored for their potential application in SERS detection [27–29].

Here, we proposed a time-saving and inexpensive method to prepare stable AgNPs/Cu/Cu(OH)₂ film with a relatively strictly ordered hybrid micro-/nano hierarchical structure. The superhydrophobic Cu/Cu(OH)₂ film was first synthesized by solution–immersion process and on the clean copper sheet, then deposited silver
nanoparticles composite films by coffee ring effect. The AgNPs/Cu/Cu(OH)₂ composite film is shown to have a rods-like microstructure, which benefits the orderly distribution of hot spots. This strategy is suitable for preparing noble metal decorated small-size ordered substrate, providing a powerful field enhancement for SERS performance.

2. Experimental section

2.1. Materials
Sodium citrate (C₆H₅Na₃O₇, 98.0%), Silver nitrate (AgNO₃, 99.8%), Ammonium persulfate ((NH₄)₂S₂O₈, 98.0%), Sodium hydroxide (NaOH, 96.0%), Stearic acid (C₁₈H₃₆O₂), Hydrochloric acid (HCl, 38.0%), Anhydrous ethanol (C₂H₅OH, 99.8%), Acetone (C₃H₆O), Rhodamine6G (Rh6G), Crystal violet (CV), the above reagents were purchased from Sinopharm Chemical Reagent Co., Ltd and used directly without further purification. Copper foil (T2, 99.9%) was purchased from Shanghai BLING Factory. The experimental water was deionized (DI water).

2.2. Synthesis of AgNPs
AgNPs were synthesized through the method described by Lee Meisel et al [30] AgNO₃ (36 mg) was dissolved in deionized water (200 ml) and added into a three-port flask, heated to boiling through an oil bath with continuous stirring using a magnetic stirring apparatus. Then, 4 ml of 1% sodium citrate aqueous solution was rapidly added under intense stirring and heated for 1.5 h under the condition of micro boiling. The reactants were naturally cooled to room temperature after the reaction stopped.

2.3. Fabrication of superhydrophobic substrate
Firstly, the copper foils with a 5 mm × 5 mm size were ultrasonically cleaned in acetone, ethanol, and 2M hydrochloric acid in order at room temperature for 30 min to remove organic pollutants and surface oxides. The copper foil was thoroughly washed with deionized water and dried at 60 °C. Cu/Cu(OH)₂ nanorod arrays were prepared by the alkali-assisted surface oxidation method [31]. The copper sheet was immersed in a mixture of 2.8 M sodium hydroxide solution and 0.16 M ammonium persulfate solution with a ratio of 1:1 at room temperature for 25 min. In the soaking process, the copper sheet’s surface gradually changed from aquamarine to sea-green color. Finally, the copper foil was taken out and washed with deionized water, then immersed in an ethanol solution of 0.005 M stearic acid for 25 min. The hydrophobic substrate was obtained after washing with ethanol, drying at 60 °C.

2.4. Modification of the surface wettability and the formation of coffee rings
In figure 1, a nitrogen plasma machine (RT-ZS-MHz, China) was used to treat the surface of the copper sheet for 0 s, 20 s, 25 s, 30 s, and 50 s at 50 mW. The wettability of the film was changed, and it was investigated by measuring the contact angles (CAs) as a function of plasma processing time [32, 33]. 5 μl 1 × 10⁻³ mol l⁻¹ Rh6G solution was dropped onto the treated surface of the substrate, and the influence of the water droplet’s gravity
can be ignored when measuring the contact angle. Figure 1(a) shows that the Rh6G solution’s water droplet can form a coffee ring on the substrate after natural drying [34]. Furthermore, in figure 1(b), the AgNPs colloid’s coffee ring was deposited the same way, and then the molecular probe solution was added to be naturally dried again.

2.5. Characterizations
The scanning electron microscope (Hitachi s4800, Japan) was used to measure the morphology of the Cu/Cu(OH)$_2$ film, and the composition elements of the substrate were analyzed by energy dispersive spectroscopy (EDS). The SERS measurements were performed on Raman spectroscopy. The Raman measurement instrument was equipped with a 785 nm laser (Laser785-5HS, China). The laser power was 30 mW, the exposure time was 0.5 s, and integrated once every time. Randomly selected four points in the coffee ring’s outer ring, and SERS detections were performed with the spectrometer under the condition of constant parameters. The mean value was taken to be the analytes’ SERS intensity. The static contact angle was measured on the copper sheet at room temperature using the sessile drop method using an optical contact angle meter (SL200C, USA). The droplet size is about 5 μl so that its gravity effect can be ignored.

3. Results and discussion

3.1. Morphologies and Microstructures of the substrate
The scanning electron microscope (SEM) images of the Cu/Cu(OH)$_2$ film sample are shown in figure 2(a). As one can see, the surface was covered with dense nanorod arrays. Figure 2(b) shows that the film’s microstructure is mainly microporous and columnar at low magnification, and some cavities can be observed. From the higher magnification SEM image shown in figure 2(c), it is observed that the nanorods are about 150–400 nm in diameter. Figure 2(d) shows the XRD pattern of Cu(OH)$_2$ nanorod arrays. The diffraction peaks marked with an asterisk (*) at 2θ = 43.3° and 50.3° are from the copper substrate. All the other diffraction peaks are indexed to orthorhombic Cu(OH)$_2$ (JCPDS Card File 13–0420) [35]. Therefore, it can be concluded that the nanorod arrays and the hierarchical structure are mainly composed of Cu(OH)$_2$.

Figure 3(a) shows a SEM image of the coffee ring’s outermost ring deposited by AgNPs on the Cu/Cu(OH)$_2$ film. To confirm that the AgNPs have been successfully embedded into the substrate surface, EDS mapping was performed. Figure 3(b) shows the corresponding EDS elemental mapping of figure 3(a). It is clearly observed that AgNPs abound at the edges of coffee rings. Figures 3(c)–(e) shows that O, Cu, Ag are located on the surface of the substrate, while Ag is uniformly covering the outer ring. Furthermore, based on the EDS spectrum of the AgNPs on the Cu/Cu(OH)$_2$ substrate. Figure 3(f) shows the characteristic peaks of Ag and Cu elements are
distinct. Moreover, the EDS analysis also reveals that the element of Ag rises in the coffee ring area except for the initial Cu and O from the Cu/Cu(OH)$_2$ film, which lays a foundation for generating uniform hot spots.

It is observed from figure 4(a) that the AgNPs present various shapes with wide particle size distribution. The prepared AgNPs consist of not only spherical but also triangular and rod-like particles. According to TEM images of AgNPs, a total number of $N = 100$ nanoparticles were obtained from figure 4(a). The Sturges method was used to obtain the histogram of particle size [36]. Width = $(D_{\text{max}} - D_{\text{min}}) / k$, where $k = 1 + 3.322 \ast \log_{10}(N)$, $D_{\text{max}}$ and $D_{\text{min}}$ represent the maximum and minimum particle size, respectively. Histograms are well modeled with normal distributions in figure 4(b). The average particle size of the prepared nanoparticles is about 70.50 nm.

The combination of textured micro nanorod array and cavities on the surface of Cu/Cu(OH)$_2$ film is beneficial to the deposit of AgNPs to improve SERS sensitivity. Furthermore, in figure 4(c), the hierarchical structures of a layer of AgNPs cover the substrate surface with high density and continuous distribution. It could
encapsulate Cu/Cu(OH)$_2$ nanorods, and the nanogap between them was filled and covered. The SEM image of AgNPs/Cu/Cu(OH)$_2$ composite film indicates that many AgNPs adhere to the Cu/Cu(OH)$_2$ nanorods supporting the clustered microspheres.

### 3.2. SERS measurements of R6G on plasma-treated Cu/Cu(OH)$_2$ film

Figure 5(a) shows that the water droplet’s CA on the stearic acid-modified surface is 152.85°, meaning that the Cu/Cu(OH)$_2$ film has excellent hydrophobic properties. Even if the water droplet (5 µl) suspended on the micro-injector is seriously deformed, it is difficult to stick to the surface and very easy to slide. After 20 s and 25 s of nitrogen plasma bombardment time, the CAs of the surface are 108.38° and 98.22°, respectively. As the surface continues to be bombarded, it becomes hydrophilic. The CA is reduced from 75.66° to 22.89° with the time increased from 30 s to 50 s.

Interestingly, the Raman signal decreases with the reduction of the CA, as shown in figure 5(b). The changing trend of Raman intensity of coffee rings at the peak of 1514 cm$^{-1}$ for different surfaces with different CA is shown in figure 5(c). It can be seen that the substrate with the strongest hydrophobicity has the best Raman enhancement effect. The superhydrophobic surfaces can drive and highly aggregate target molecules of analyte in the evaporated droplet [37]. The density of AgNPs increased on Cu/Cu(OH)$_2$ film, providing plenty of ‘hot spots’, which leads to high sensitivity [38, 39].

### 3.3. SERS Sensitivity of the AgNPs/Cu/Cu(OH)$_2$ composite film

Reproducibility studies were conducted to verify the Raman assignments of dye solution with different concentration gradients. The Raman spectra of analytes on the coffee rings’ selected positions are shown in figure 6. The characteristic peaks of Rh6G solutions can be identified, and the relative standard deviation was 7.8%. Thus, the coffee ring’s property of enriching molecules leads to excellent stability on the superhydrophobic substrate. Besides, the SERS response of the CV solution also demonstrates this result, and the relative standard deviation was 4.8%.

The detection abilities of the composite film were tested by Raman spectroscopy using Rh6G and CV as a model. Figure 7(a) shows the SERS spectra of five different concentrations of Rh6G solutions dried on the Cu/Cu(OH)$_2$ film. It is hard to distinguish Rh6G solution’s Raman characteristic peaks at a $10^{-5}$ mol l$^{-1}$ concentration from this figure. While from figure 7(b), the limit of detection value was as low as $10^{-8}$ M, indicating that this composite structure was sensitive enough to the AgNPs/Cu/Cu(OH)$_2$ film. We examined its analytical performance for CV molecules to explore the potential detection diversity of this kind of SERS substrate. The SERS spectra of CV with six concentrations ranging from $10^{-8}$ to $10^{-4}$ M are shown in figure 7(d). It showed that the lowest probed attention for CV was $10^{-7}$ M. The result demonstrated that the synthesized AgNPs/Cu/Cu(OH)$_2$ composite film exhibits a strong Raman signal to reliably quantitatively detect these concentrations of Rh6G and CV due to the hierarchical structure.

Even at a low concentration, the strong SERS signal of Rh6G and CV solution can also be distinguished, which can be ascribed to the contribution of the electromagnetic mechanism introduced by metal nanoparticles [40]. The increased light absorption induced by AgNPs led to the increase of the electric field [41]. The charge transfer between the superhydrophobic substrate and the metal nanoparticles layer, thus causing surface plasmon resonances. This kind of tunable nanoscale resonances can produce high electromagnetic fields near noble metals and enhance its electromagnetic coupling, consequently, excite uniform SERS ‘hot spots’ [41].

The characteristic peak intensity for Rh6G and CV solution at 1514 cm$^{-1}$ and 1625 cm$^{-1}$, respectively, increases linearly with the molecular concentration. As shown in figures 8(a) and (b), a well-defined linear relationship can be obtained with correlation coefficient (R$^2$) values of 0.9429 and 0.9329, directly reflecting
good linearity between concentration and SERS intensity of analytes, which is benefitted from the coffee ring’s ability to concentrate the target molecules and reduce the space between nanoparticles. Several AgNPs adhered to Cu(OH)$_2$ nanorods so that the composite film significantly offered a large surface area with dense hot spots for seizing the dye molecules.

Hence, the adsorbed dye molecules on the substrate are located in an enhanced electromagnetic field and exhibit a stronger Raman signal. The enhancement factors of substrate for CV and Rh6G solution are $5.23 \times 10^4$ and $8.37 \times 10^4$, respectively [42]. Without complex and expensive specialized equipment, the
proposed method can significantly improve the Raman intensity of the target analyte with high reproducibility and meet high-sensitivity SERS detection requirements.

4. Conclusions

In summary, we used superhydrophobic films with nanorod structure on copper and deposited silver nanoparticles and probe molecules on the surface of these films by using the coffee ring effect. This SERS sensor exhibited sensitive detection performance to Rh6G and CV solutions even at the concentration of $10^{-8}$ M and $10^{-7}$ M, attributed to the surface plasmon resonances caused by dense AgNPs adhered to Cu(OH)$_2$ nanorods. This method helps to stimulate the plasmon coupling and improve the substrate’s SERS capability. This study provides a low-cost and straightforward strategy that may exhibit potential superiority in trace analysis of various toxic dye detection.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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