

# Silver-decorated hierarchical cuprous oxide micro/nanospheres as highly effective surface-enhanced Raman scattering substrates

Shih-Yu Fu,<sup>1</sup> Yu-Kuei Hsu,<sup>1,4</sup> Mei-Hsin Chen,<sup>1</sup> Chin-Jung Chuang,<sup>1</sup> Ying-Chu Chen,<sup>2</sup> and Yan-Gu Lin<sup>3,\*</sup>

<sup>1</sup>Department of Opto-Electronic Engineering, National Dong Hwa University, Hualien, 97401, Taiwan  
<sup>2</sup>Karlsruhe Institute of Technology, Institut für Anorganische Chemie, Engesserstraße 15, D-76131 Karlsruhe, Germany

<sup>3</sup>National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan

<sup>4</sup>ykhsu@mail.ndhu.edu.tw  
lin.yg@nsrrc.org.tw

**Abstract:** A facile and simple route to manufacture active surface-enhanced Raman scattering (SERS) substrate based on Ag-decorated Cu<sub>2</sub>O micro/nanospheres on Cu foil was systematically investigated. Hierarchical Cu<sub>2</sub>O micro/nanostructure transfers from CuO nanosheets and Cu(OH)<sub>2</sub> nanowires by means of thermally reducing the oxides from Cu<sup>2+</sup> to Cu<sup>1+</sup> at temperature of 500 °C under nitrogen atmosphere. The subsequent decoration of Ag on Cu<sub>2</sub>O nanostructural substrate was carried out by means of thermal evaporator deposition. Using 4-aminothiophenol (4-ATP) as probing molecules, the SERS experiments showed that the Ag-decorated Cu<sub>2</sub>O micro/nanospheres exhibit excellent detecting performance, which could be used as effective SERS substrate for ultrasensitive detection. Additionally, these novel hierarchical SERS substrates showed good reproducibility and a linear dependence between analyte concentrations and intensities, revealing the advantage of this method for easily scale-up production.

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**OCIS codes:** (290.5860) Scattering, Raman; (300.6450) Spectroscopy, Raman; (160.6000) Semiconductor materials.

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## 1. Introduction

Surface enhanced Raman scattering (SERS) has drawn considerable interest since its discovery and highlighted in the area of biomedicine, physics, environmental monitoring, analytical chemistry, etc. This is due to the highly enhanced vibrational signals, low detection requirements, and good selectivity for adsorbates [1–3]. In the early days, SERS-active substrates were restricted primarily to noble metals (Ag, Au, and Cu) and the transition metals (Pt, Pd, Ru, Rh, Fe, Co, and Ni) rough surfaces with the enhancement factor of 10<sup>6</sup>–10<sup>11</sup> [4–6]. The reason is mainly attributed to the electromagnetic mechanism (EM), which involves the surface plasmon resonance on the metal surface under the excitation of an incident laser, and then leads to a local electromagnetic field enhancement resulting in the enhancement of Raman signal of the adsorbed analytes. In addition to the EM there is also a sample dependent "chemical" enhancement mechanism that may arise due to charge transfer (CT) interactions with the metal. Recently, it has been further found that various semiconductor nanoparticles such as NiO, ZnO, TiO<sub>2</sub>, and Cu<sub>2</sub>O can also directly generate weak SERS activity with typical prominent enhancement factors ranging from 10<sup>1</sup> to 10<sup>4</sup> [7–10]. The enhancement originated from those nanostructures is proposed to be associated with the CT processes between the adsorbed analytes and the substrate. Although the semiconductor nanomaterials exhibit low enhanced Raman signal of the adsorbed analytes, the incorporation of noble metal into semiconductor nanomaterials is highly expected to produce an active and low-cost SERS substrate in comparison with noble metal substrates. Unfortunately, the study on this synergetic contribution from incorporated noble metal and semiconductor in hybrid nanocomposites for SERS is still relatively rare.

Cuprous oxide (Cu<sub>2</sub>O), which has a direct bandgap of 2.1 eV, exhibits great potential for solar energy conversion catalysis, batteries, magnetic storage media, gas sensing, and field emission [11–13]. The SERS capability of Cu<sub>2</sub>O was first proposed by Dolata and associates [14]. Historically one of the main objectives for improving SERS activity has been to fabricate a nanostructural substrate that can provide numerous sites of strong field enhancement, so called hot spots. Hence, various morphologies of Cu<sub>2</sub>O such as nanowires, nanospheres, nanodendrites, and microcrystals were intensively investigated for SERS [15–18]. However, in fact, the novel Cu<sub>2</sub>O micro/nanospheres with dense hot spots are the one of the best candidate for enhancing the SERS activity, but there is no report on this hierarchical nanoarchitecture. Especially, study of the synergetic effect from incorporated Ag in Cu<sub>2</sub>O micro/nanospheres as active SERS substrate is still lacking. In this study, a facile and simple route to produce the hierarchical Cu<sub>2</sub>O micro/nanospheres with the decoration of silver was

proposed as highly effective SERS substrate. Moreover, our results provide a new opportunity to use SERS to explore the molecule-metal-semiconductor interaction, a fundamental but essential question for designing novel devices.

## 2. Experimental

Cu<sub>2</sub>O nanostructural films on copper foil were fabricated via the thermal transformation of lotus-like CuO/Cu(OH)<sub>2</sub> nanosheets/nanowires templates, which were synthesized through a chemical oxidation process shown in Fig. 1. First, the flower-like CuO and Cu(OH)<sub>2</sub> nanowire arrays on copper foil were prepared, 50 mL aqueous solution of 2.5 M NaOH and 0.125 M (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was prepared in a 100 mL glass bottle. A piece of copper foil, which had been ultrasonically cleaned in acetone and subsequently in de-ionized water, was immersed in the solution. A few minutes later, a faint blue color appeared on surface of the copper foil, and the initially colorless solution became increasingly blue. In 10 min., a light-blue film covered the foil. After 30 min., when the color of the film had become dark blue, the copper foil was extracted from the solution, rinsed with water and ethanol, and dried in air. Afterward, the samples were thermally treated at 500 °C in a nitrogen atmosphere for 4 h. The deposition of silver at 100 nm on the annealed samples was carried out by thermal evaporation. The deposition rate was kept at 0.1 nm/s throughout the deposition process. Following the evaporation process, all the samples were respectively immersed in various concentrations of 4-aminothiophenol (4-ATP) solution for adsorption. After at least 3 hours, the samples were removed from the solution and rinsed with distilled water five times.

The morphology of hierarchical Cu<sub>2</sub>O nanostructural films were examined by scanning electron microscopy (SEM, JEM-4000EX), and the structure of the samples were analyzed using X-ray diffractometer (XRD, Bruker D8 Advance diffractometer) with Cu K<sub>α</sub> radiation ( $\lambda = 0.1506$  nm). Raman spectra were measured using a LabRAM HR 550 system equipped with a thermoelectric-cooled CCD multi-channel detector with accuracy better than 1 cm<sup>-1</sup> and a 50x objective. The He-Ne laser emitting at a wavelength of 632.8 nm and a power of 5 mW was used as the source of excitation. Data were acquired with only 5 s accumulation for 4-ATP on the bare Cu<sub>2</sub>O film and the Cu<sub>2</sub>O thin films covered with a 100 nm layer of Ag.

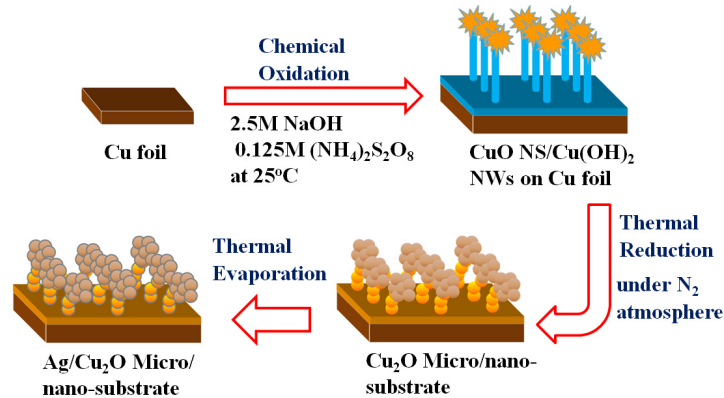


Fig. 1. Schematic illustration of synthesis for Ag-decorated Cu<sub>2</sub>O micro/nanospheres film on Cu foil.

## 3. Results and discussion

Figure 2(a) shows the hierarchical structures of CuO and Cu(OH)<sub>2</sub> formed by chemical oxidation on a copper substrate. The flower-like microspheres of CuO have a uniform diameter of 2-5 μm, and the thickness of the flower petals are approximately 50-100 nm. Arrays of Cu(OH)<sub>2</sub> nanowires of approximately 100 nm in diameter are seemingly formed under the microflowers; in other words, the microflowers are standing on the nanowire arrays, in a configuration similar to a lotus leaf. The morphological change of the sample after

thermal treatment at 500 °C in a nitrogen atmosphere is displayed in Fig. 2(b). At an annealing temperature of 500 °C for 4 h, the top portion of nanowires merge with the microflowers, transforming the shape into aggregated microspheres with a diameter of around 2 μm; the bottom of the nanowires turn into nanospheres with a diameter of around 300 nm on the copper foil, supporting the clustered microspheres. This morphological evolution could be ascribed to the deoxidization process of CuO. Thus, the conversion of lotus-like nanostructures into hierarchical micro- and nanospheres was obtained by thermal reduction route. Finally, the silver deposited Cu<sub>2</sub>O micro/nanospheres film by thermal evaporation process is shown in Fig. 2(c). Obviously, the surface of Cu<sub>2</sub>O nanostructure becomes rough after silver deposition. The EDS spectra (Fig. 2(d)) clearly showed that the hierarchical composite arrays were composed of micro/nanospherical Cu<sub>2</sub>O and Ag. The elemental composition ratios of Cu to O approximated 2 that can confirm the formation of Cu<sub>2</sub>O by thermal reduction process. Furthermore, the detection of Ag signal with the Cu/Ag elemental composition ratio of around 3 indicates that the decoration of Ag on the Cu<sub>2</sub>O surface was carried out.

The crystal phases of the samples after chemical oxidation, subsequent thermal reduction, and then silver deposition were determined using powder XRD, as shown in Fig. 3. The XRD pattern of the copper foil is also displayed for comparison. After chemical oxidation, the XRD pattern of the lotus-like microflowers/nanowire sample shows diffraction peaks indexed to the monoclinic-phase of CuO (JCPDS card No. 80-0076, marked with squares) along with peaks from the copper substrate (marked with asterisks) and the orthorhombic phase of Cu(OH)<sub>2</sub> (JCPDS card No. 72-0140, marked with circles). At the annealing temperature of 500 °C for 4 h, no CuO and Cu(OH)<sub>2</sub> phases detected; meanwhile, the strong diffraction peaks indexed to cubic-phase Cu<sub>2</sub>O (JCPDS card No. 78-2076, marked with triangles) appear along with those of the copper substrate, marked with asterisks. This reveals the transformation of wire-like Cu(OH)<sub>2</sub> and CuO microflowers to sphere-like Cu<sub>2</sub>O through dehydration and deoxidization in the nitrogen atmosphere. In the Ag-decorated Cu<sub>2</sub>O sample, Ag peaks were indexed to Face-centered Cubic structure (JCPDS card No. 65-2871, marked with inverted triangles). Besides, by comparing the Cu<sub>2</sub>O peaks which showed no changes in the Ag-decorated Cu<sub>2</sub>O sample, we could further confirm the existence of Ag on the surface of Cu<sub>2</sub>O, which is consistent with the SEM findings.

To examine the SERS property, the measurement of Raman spectrometer under laser wavelength of 632.8 nm as excitation source through the 50x object lens and exposure of 5 s was utilized. Figure 4(a) displays the comparison of Raman signal from 1 mM 4-ATP solution and 1 mM 4-ATP adsorbed on Cu<sub>2</sub>O surface. Raman peaks of 1081, 1145, 1189, 1384, 1435, and 1587 cm<sup>-1</sup> are characteristic SERS signals of the 4-ATP molecule on the Cu<sub>2</sub>O substrates. Meanwhile, those particular modes can be divided into two groups. The one belongs to *a<sub>1</sub>* mode and these bands at about 1587, 1189, 1081 cm<sup>-1</sup> have been assigned to the modes of *v<sub>CC</sub>*, 8a (*a<sub>1</sub>*), *δ<sub>CH</sub>*, 9a (*a<sub>1</sub>*), *v<sub>CS</sub>*, 7a (*a<sub>1</sub>*) and *v<sub>CC</sub>*, 7a (*a<sub>1</sub>*), respectively [19]. The other is attributed to *b<sub>2</sub>* mode and the peaks at 1435, 1384 and 1145 cm<sup>-1</sup> corresponding to 19*b<sub>2</sub>*, 3*b<sub>2</sub>*, and 9*b<sub>2</sub>* modes of 4-ATP are apparently enhanced while those are found inconspicuous in normal Raman spectra [19]. It could clearly make sure that this hierarchical Cu<sub>2</sub>O micro/nanospheres have the ability to enhance Raman signal. The results are consistent with the literatures reported for 4-ATP adsorbed onto Cu<sub>2</sub>O nanocrystals as well as TiO<sub>2</sub>, which has been attributed to the dominant contribution of the Cu<sub>2</sub>O-to-molecule mechanism and EM [15,17]. In order to probe the detection limit of Cu<sub>2</sub>O micro/nanospheres, the samples were immersed into the different concentration of 4-ATP solutions. Figure 4(b) shows the Raman spectra from the hierarchical Cu<sub>2</sub>O films with 4-ATP concentrations varied from 1 × 10<sup>-3</sup> to 10 × 10<sup>-6</sup> M. Obviously the signals gradually decrease with decreasing the 4-ATP concentration. We could clearly observe 4-ATP Raman signals when a solution with a concentration as low as 10 μM was used.

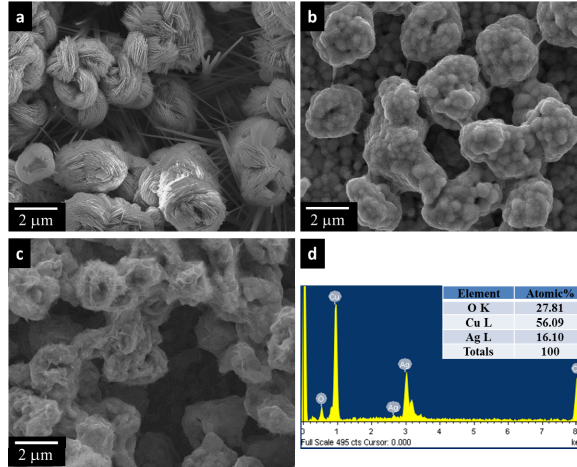


Fig. 2. (a) FESEM image of flower-like CuO standing on Cu(OH)<sub>2</sub> nanowires. FESEM image of (b) bare and (c) Ag-decorated Cu<sub>2</sub>O micro/nanospheres film. (d) EDS of Ag-decorated Cu<sub>2</sub>O micro/nano-spheres film.

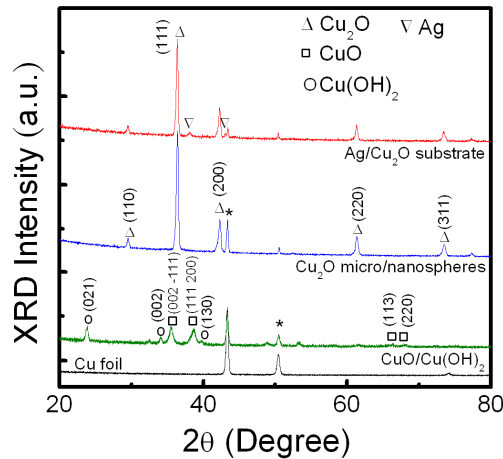


Fig. 3. X-ray diffraction patterns of bare and Ag-decorated Cu<sub>2</sub>O micro/nanospheres film.

In order to further improve the SERS signal, the decoration of Ag layer on Cu<sub>2</sub>O micro/nanospheres film was accomplished by thermal evaporation process. Figure 5(a) shows the comparison of bare and Ag-decorated Cu<sub>2</sub>O micro/nanosphere films in the 1 mM 4-ATP. It can be noticed that in comparison with the bare Cu<sub>2</sub>O nanostructural film, the Ag-decorated Cu<sub>2</sub>O micro/nanosphere film exhibits a significantly higher ratio of signal/noise; this suggests a more intense SERS enhancement. The possible SERS enhancement mechanism could be ascribed to EM. Since the EM enhancement is due to a large increase of the electric field caused by surface plasmon resonances induced by the laser light in Ag layer on the surface of Cu<sub>2</sub>O. The Cu<sub>2</sub>O micro/nanosphere film is covered by Ag layer and may cause charge transfer from Ag layer and Cu<sub>2</sub>O nanoparticles to absorber. In addition, the novel and hierarchical Cu<sub>2</sub>O micro/nanospheres significantly offer large surface area with dense hot spots for immobilizing the 4-ATP molecules. Hence, the adsorbed 4-ATP molecules on the Ag surface are located in an enhanced electromagnetic field and consequently exhibit a stronger Raman signal. The SERS spectra of 4-ATP at different concentrations were further measured by using the Ag-decorated Cu<sub>2</sub>O micro/nanospheres film as SERS substrate. As shown in Fig. 5(b), the spectral intensities were decreased by diluting the concentrations of the target

molecule. Many bands were distinctly observed from the Fig. 5(b) even when the 4-ATP concentration was reduced down to  $1 \times 10^{-7}$  M, demonstrating the high sensitivity of the Ag-decorated  $\text{Cu}_2\text{O}$  micro/nanospheres film. These results confirmed that this novel Ag- $\text{Cu}_2\text{O}$  hierarchical film could achieve ultra-trace detection of analyte.

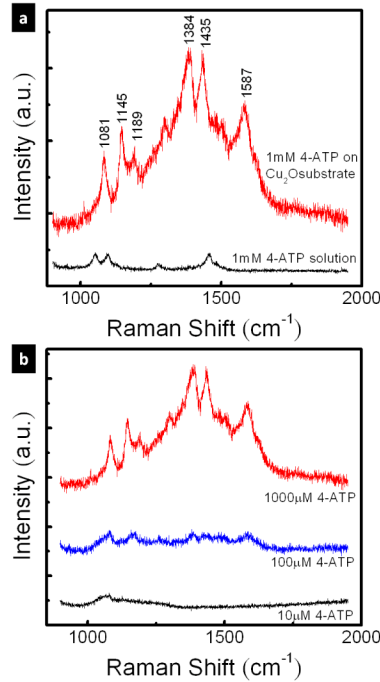


Fig. 4. (a) Raman spectra of 4-ATP adsorbed on the  $\text{Cu}_2\text{O}$  micro/nanospheres film (top) and the 1 mM 4-ATP solution (bottom). (b) Raman spectra of 4-ATP with variable concentration adsorbed on the  $\text{Cu}_2\text{O}$  micro/nanospheres film.

By taking 4-ATP as the test molecule, the enhancement factor (EF) of the Ag-decorated  $\text{Cu}_2\text{O}$  micro/nanospheres film as SERS substrate was estimated by the following Eq. (1) [15]:

$$EF = \left( \frac{I_{\text{SERS}}}{I_{\text{bulk}}} \right) \left( \frac{N_{\text{bulk}}}{N_{\text{ads}}} \right) \quad (1)$$

where  $I_{\text{SERS}}$  and  $I_{\text{bulk}}$  are the Raman signals at a typical vibration (1145  $\text{cm}^{-1}$  were chosen in our study) of the 4-ATP molecules adsorbed on a substrate with the SERS effect and 4-ATP molecules in solution.  $N_{\text{ads}}$  and  $N_{\text{bulk}}$  are the numbers of the adsorbed molecules on Ag- $\text{Cu}_2\text{O}$  micro/nanospheres film and the 4-ATP molecules in solution within the laser spot, respectively. In detail, for determination of  $N_{\text{bulk}}$  and  $N_{\text{ads}}$ , the sampling volume was obtained by the radius of the laser spot ( $\sim 5 \mu\text{m}$ ) and the penetration depth of the focused laser ( $\sim 15 \mu\text{m}$ ). The  $N_{\text{bulk}}$  was determined by multiplying the volume of the illuminated focus spot size and number density of 4-ATP molecules in solution. The  $N_{\text{ads}}$  could be estimated by multiplying the area of the illuminated focus spot size, the bounding density of the adsorbed molecules on the nanospheres surfaces, and the number density of nanospheres [15]. Therefore, we can know the ratio  $N_{\text{bulk}}/N_{\text{ads}}$  was about  $\sim 10^4$  within the same area of laser spot. Then the above two samples were tested by Raman spectroscopy under same condition, and thus the ratio  $I_{\text{SERS}}/I_{\text{bulk}}$  could be calculated to be about  $\sim 10^2$  from the intensity of the corresponding peaks. Finally, the EF value was calculated to be about  $10^6$ . The enhancement factor as high as  $1 \times 10^6$  revealed the Ag-decorated  $\text{Cu}_2\text{O}$  micro/nanospheres film could be used as effective SERS substrate in trace detection.

The Ag-decorated Cu<sub>2</sub>O micro/nanospheres film was also used as SERS substrate to investigate the relationship between intensities of SERS spectra and 4-ATP concentrations. Five different concentrations were adopted and used to immobilize onto the five samples in the experiment, and the relationship between the intensities and concentrations was drawn in Fig. 6. A linear dependence was found between the logarithmic concentrations of 4-ATP and the intensities of the fingerprint peak (1145 cm<sup>-1</sup>) as shown in Eq. (2) below, where  $I$  is the peak intensity of the SERS spectra of 4-ATP, and  $C$  is the concentration of 4-ATP.

$$\log I = 5.81 + 0.61 \times \log C \quad (2)$$

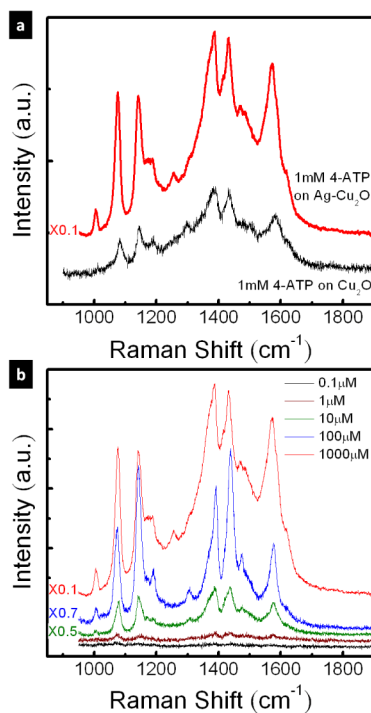


Fig. 5. (a) Raman spectra of 4-ATP adsorbed on the bare and Ag-decorated Cu<sub>2</sub>O micro/nanospheres film. (b) Raman spectra of 4-ATP with variable concentration adsorbed on the Ag-decorated Cu<sub>2</sub>O micro/nanospheres film.

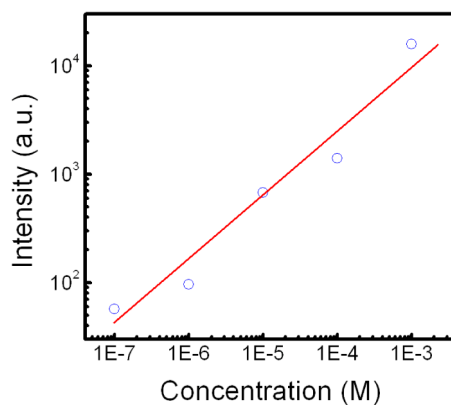


Fig. 6. The linear relationship between the logarithmic intensities at 1145 cm<sup>-1</sup> and concentrations of 4-ATP.

#### 4. Conclusions

In summary, the novel Ag-decorated Cu<sub>2</sub>O micro/nanospheres on Cu foil made by a simple and facile process could be successfully applied to active SERS substrate. Direct-grown Cu<sub>2</sub>O hierarchical films with micro/nanospheres on copper foil were fabricated via a template route through the transformation of lotus-like CuO/Cu(OH)<sub>2</sub> nanosheets/nanowires at annealing temperature of 500 °C for 4 h under a nitrogen atmosphere. The decoration of Ag on hierarchical Cu<sub>2</sub>O nanostructures was further analyzed by SEM, EDS, and XRD. The SERS measurement results indicated that the Ag-decorated Cu<sub>2</sub>O micro/nanospheres with high density of hot spots exhibited excellent performance with EF value of 10<sup>6</sup>. This hierarchical SERS substrate also demonstrated good reproducibility and a linear dependence between concentration and intensity. Therefore, our work has demonstrated a simple way to synthesize Ag-decorated Cu<sub>2</sub>O micro/nanospheres as effective SERS substrate.

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