Nanostructures



Temperature-Induced Stacking to Create Cu₂O Concave Sphere for Light Trapping Capable of Ultrasensitive Single-Particle Surface-Enhanced Raman Scattering

Xiaoxia Li, Yang Shang, Jie Lin, Anran Li, Xiaotian Wang, Bin Li, and Lin Guo*

The fabrication of bowl or concave particles with "asymmetric centers" has drawn considerable attentions, in which multiple scattering occurs inside the particles and the ability of light scattering is distinctly enhanced. However, the limited variety of templates, the uncontrollable dimensions such as the size of concavity and the complex growth process have posed serious limitations to the reproducible construction of concave particles with desired geometries and their light-trapping properties. Herein, a "temperature-induced stacking" strategy is proposed to create controllable concavity Cu₂O spheres for the first time. Different sizes of F68 micelles can be formed through aggregation under different reaction temperatures, which can serve as soft template to tailor concave geometries of Cu₂O spheres. The as-prepared Cu₂O concave sphere (CS) can serve as single-particle (SP) surface-enhanced Raman scattering (SERS) substrate for highly repeatable and consistent Raman spectra. The unique cavity of Cu₂O CS entraps light effectively, which also enhances the scattering length owing to multiple light scattering. Combined with slightly increased surface area and charge-transfer process, Cu₂O CS exhibits remarkable single-particle SERS performance, with an ultralow low detection limit (2×10^{-8} mol L⁻¹) and metal comparable enhancement factor (2.8×10^5) .

X. X. Li, Dr. Y. Shang, J. Lin, Dr. A. R. Li, Prof. X. T. Wang, Prof. L. Guo Beijing Advanced Innovation Center for Biomedical Engineering Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology Ministry of Education School of Chemistry Beihang University Beijing 100191, P. R. China E-mail: guolin@buaa.edu.cn Dr. Y. Shang Key Laboratory of Micro-Nano Measurement-Manipulation and Physics Ministry of Education School of Physics and Nuclear Energy Engineering Beihang University Beijing 100191, China Dr. B. Li College of Chemistry and Molecular Engineering Qingdao University of Science and Technology

Qingdao 266042, Ćhina

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.201801868.

DOI: 10.1002/adfm.201801868

1. Introduction

Over the past decades, fabrication of anisotropic particles, such as misshapen, bowl, concave, patchy, and Janus particles with "asymmetric centers" has drawn considerable attentions.^[1-6] Their reduced morphological symmetries have enabled possibly new or enhanced properties.^[1-6] For bowl-like or concave particles, multiple scattering would occur within the particles, which in turn distinctly enhance the ability of light scattering.^[7-9] Up to now, these structures, especially noble metals and metal oxides, have exhibited a great advantage in optical field, such as surface-enhanced Raman scattering (SERS),^[9–16] liquid crystals,^[17,18] water splitting,^[8,19] and imaging.^[20] Due to the asymmetric geometry of concave particles, a template is often introduced to control their growth. Several groups^[1,7–11,19–22] have reported that the use of monolayer of polystyrene spheres and silica colloids as hard templates for most concave materials fabrication. However, the tedious template-removing process and the

involvement of toxic organic solvent, are two obvious disadvantages for the hard template-assisted concave material fabrication method.

Fortunately, several novel templates have been reported to synthesize concave structures.^[4,11,21,23–25] Lou and co-workers^[4] reported an emulsion-induced interface anisotropic assembly route to create bowl-like polydopamine particles, in which polydopamine seeds were generated on the 1,3,5-trimethylbenzene droplet. Wang and co-workers^[11] fabricated Au nanocups with rough outer surface and faceted inner surface by using PbS nano-octahedra as the sacrificial templates, where Au grew along the PbS nano-octahedra facets. Based on confined-space thermal dewetting, Yin and co-workers^[20] recently reported an original approach for the synthesis of Au nanocups. Although these routes have been proposed, the exploration of new strategies for creating concave structures is still at preliminary stage, especially for tunable concavity, which has significant impact on their light-trapping properties.

For triblock copolymer (TCP), especially [poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide); PEO_x – PPO_y – PEO_x], TCP micelles with external hydrophilic PEO





Temperature

Figure 1. Scheme illustration of the aggregation of F68 micelles with the increasing of temperature from 15 to 45 $^\circ\text{C}.$

and internal hydrophobic PPO will form initially in aqueous solution.^[26-30] By increasing the temperature of TCP solution, the hydrogen bond between PEO and water can be broken, inducing the aggregation and segregation of TCP micelles in water.^[26-30] This phase segregation is a very common phenomenon for TCP.^[26-30] Take F68 (PEO₇₈-PPO₃₀-PEO₇₈, at 80.0 g L⁻¹) as an example (Figure S1, Supporting Information), dynamic light scattering (DLS) has verified that monomer F68 spherical micelles with a diameter of ≈4.5 nm are formed at 15 °C (Figure S1a, Supporting Information). It is interesting to note that, by increasing the temperature, monomer F68 micelles would aggregate to be spherical-like structures with diameters of 350, 650, and 1100 nm at 25, 35, and 45 °C, respectively (Figure 1 and Figure S1b-d, Supporting Information). Thus far, studies of TCP have been restricted to produce mesoporous materials by using monomer micelles.^[31-35] So, if those "bigger" micelles are used, could "bigger" pores be produced?

Based on this interesting phenomenon of F68, we propose a strategy to create controllable concavity Cu₂O spheres. Different sizes of F68 micelles could be formed through aggregation under different reaction temperatures (RT), which can serve as soft template to tune the size of concavity of Cu₂O spheres. We define the aggregation of F68 micelles with the increased temperature as temperature-induced stacking (TIS). This is the first time that the concept of TIS has been applied. We further exhibit the use of the as-prepared Cu₂O concave sphere (CS) as single-particle (SP) SERS substrate. Cu₂O concave sphere shows an ultralow limit of detection (LOD) ($2 \times 10^{-8} \text{ mol L}^{-1}$) and metal comparable enhancement factor (EF) (2.8×10^{5}), which is amongst the better performing semiconductor SERS substrate, rivalled even that of the noble metal substrate without "hot spot."

2. Results and Discussion

In our case, an initial solution (IS) was first prepared by mixing $Cu(NH_3)_4^{2+}$ with F68 (80.0 g L⁻¹) aqueous solution. At that

Step 1 Increasing Temperature Initial Solution F68 $G_{F68} - S$ $G_{F68} - S$ $G_{F68} - S$ $G_{F68} - S$ G_{Cu_2O-F68} G_{Cu_2O-F68} G_{Cu_2O-F68} G_{Cu_2O-F68} G_{Cu_2O-F68}

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Figure 2. Scheme illustration of the TIS process for the formation of Cu_2O CSs.

moment, the pH of IS was 9.77 derived from the excess NH₃. With the increased temperature from 15 to 45 °C, the gradually turbid IS (inset of Figure S3, Supporting Information) suggested that F68 micelles aggregated and segregated in water. DLS (Figures S2 and S3, Supporting Information) verified that the size of F68 micelles was slightly increased compared to that of pure F68 aqueous solution (Figure S1, Supporting Information). By increasing the temperature of IS to be 35 °C (step 1 in Figure 2), the dissociation of the hydrogen bond between PEO and water would induce F68 micelles to gradually dehydrate and aggregated into a compact structure, namely, TIS (step 2 in Figure 2).^[36] The corresponding DLS (Figure S2, Supporting Information) demonstrated that the diameter of F68 was 730 nm at the moment. With ascorbic acid (AA) solution instilled to the IS, the deep blue solution (Cu(NH₃) $_{4}^{2+}$) quickly turned into limpid (Cu(NH₃)₂⁺) [Equation (1)]. Cu(NH₃)₂⁺ instantaneously transformed into yellow precipitates (Cu2O) [Equations (2) and (3)]. When the reaction finished, the pH decreased to 7.20. Those processes can be described by the following equations^[37]

$$2Cu(NH_3)_4^{2+} + C_6H_8O_6 = C_6H_6O_6 + 2NH_3 + 2Cu(NH_3)_2^{+} + 2NH_4^{+}$$

$$Cu(NH_3)_2^+ + OH^- \rightleftharpoons CuOH + 2NH_3$$
⁽²⁾

$$2CuOH = Cu_2O + H_2O$$
(3)

The fact that Cu_2O CSs rapidly formed in duration of 5 min suggested that the "bigger" F68 micelles acted as the soft template. Meanwhile, due to surface tension, the anisotropic epitaxial growth that the Cu_2O nucleated on the large F68 micelles resulted in the formation of cavity geometries, which have been widely explained for Janus structures.^[38–40] In solvent, the



surface energy of F68 ($\sigma_{F68-solvent}$) was larger than the surface energy of Cu₂O nuclei ($\sigma_{Cu2O-solvent}$). When Cu₂O nucleated on the surfaces of F68 micelles (the surface of F68 micelles could be deemed as plane in a small area), the interfacial energy between Cu_2O and F68 ($\sigma_{Cu2O-F68}$) is very low due to the bond of Cu in Cu₂O and O in PEO group atoms.^[37] It is difficult for Cu₂O nuclei to spread on the surface of F68 due to the negative total surface energy variation^[6,41,42] ($\Delta \sigma = \sigma_{Cu2O-solvent} + \sigma_{Cu2O-F68} - \sigma_{Cu2O-F68}$ $\sigma_{\rm F68-solvent}$ < 0). This in turn leads to the anisotropic growth of Cu₂O nuclei on the surface of F68 (step 3 in Figure 2). Consequentially, the energy barrier of the growth of Cu₂O in the heterogeneous direction was much higher than that in the homogeneous directions, which further led to the anisotropic growth of the initial F68 micelles. Thus, the Janus nanocomposites had been created by Cu₂O nuclei anisotropic growth on the F68 micelles (step 4 in Figure 2 and Figure S4, Supporting Information). Finally, the cavity geometry was formed after F68 removal through ethanol washing for several times (step 5 in Figure 2).

A proper concentration of F68 (80.0 g L⁻¹) was necessary for the formation of cavity with the ideal size. In the absence of F68, only Cu₂O complete spheres were obtained (Figure S5a, Supporting Information). When the concentration of F68 was halved (40.0 g L⁻¹), some Cu₂O spheres with small cavity appeared in the Cu₂O complete spheres (Figure S5b, Supporting Information). Insufficient F68 micelles would result in smaller diameter of cavities and nonuniform cavities on Cu₂O spheres. If increasing the concentration of F68 by twice (160.0 g L⁻¹), Cu₂O hemispheres would appear due to the larger size of F68 micelles (Figure S5c, Supporting Information).

Furthermore, a key for the construction of concave structure was choosing the surfactant that could results in the commencement of TIS process. By replacing the F68 with P123 (a TCP could TIS, PEO_{20} – PPO_{70} – PEO_{20}), we can obtain Cu₂O spheres with cavity. However, the different chain length and stacking mode of P123 would have resulted in a different diameter and cavity depth (Figure S6a, Supporting Information). However, when F68 was replaced with polyvinylpyrrolidone (a surfactant that dissolve in H₂O), only Cu₂O complete spheres were produced (Figure S6b, Supporting Information) due to the disappeared TIS process.

Overview scanning electron microscopy (SEM) (**Figure 3**a) revealed that the sizes of the Cu₂O CSs typically range from 1.4 to 1.6 µm. Magnified SEM image (Figure 3b) clearly showed that the Cu₂O CSs possessed relatively smooth surface and an eccentric cavity with a diameter of \approx 700 ± 50 nm. Figure 3c exhibited the depth of cavity (*h*) is \approx 300 ± 30 nm, and the fact that no channels or pores were found in transmission electron microscopy (TEM) image demonstrated the F68 did not serve as pore-forming agent during the rapid reduction process.^[37] The measured lattice spacing in the high-resolution (HR) TEM image (Figure 3d) was \approx 0.24 nm, fitting well with the (111) crystal plane of the cubic Cu₂O. The selected area electron diffraction (SAED) pattern (inset in Figure 3d) of the Cu₂O CS exhibited discontinuous bright diffraction rings, revealing polycrystalline structure nature.^[37]

Due to the increased size of F68 micelles (4.5, 400, 730, and 1300 nm at 15, 25, 35, and 45 °C, respectively, Figure S2, Supporting Information), different concavity of Cu_2O spheres could be obtained from complete spheres, to multiconcave



spheres, concave spheres, and finally to hemispheres, respectively (Figure 4). SEM revealed the quite uniform sizes of the Cu₂O particles with the diameter of \approx 1.4 ± 0.2 µm and relatively smooth surface (Figure S7, Supporting Information). At 15 °C, the individual F68 micelles did nothing useful during the formation of Cu₂O, resulting in its sphere structure (Figure 4a). When increasing the temperature to 25 °C and the small-scale F68 micelles would decorate Cu₂O spheres in different directions. Finally, multiconcave spheres with an average of four cavities were generated. Those cavities had smaller diameter $(500 \pm 150 \text{ nm})$ and shallower depth $(100 \pm 50 \text{ nm})$ (Figure 4b). Only one cavity was created on most Cu2O spheres at 35 °C (Figure 4c). When further increasing the temperature to 45 °C, the larger F68 micelles would result in larger cavities, even hemispheres can be obtained (Figure 4d). Also, the cubic Cu₂O phase (JCPDS No. 05-0667, information from CD-ROM) of those four samples was verified by X-ray Diffraction (XRD) characterization (Figure S8, Supporting Information).

Because of their similar diameter ($d_2 = 1.4 \pm 0.2 \,\mu$ m) to laser spot size ($d_1 = 1.58 \,\mu$ m), the four Cu₂O spheres (in Figure 4) can serve as SP-SERS for highly repeatable and consistent Raman spectra (**Figure 5**a and Figures S10–S15 and details in the Supporting Information, "Single-particle SERS performance of Cu₂O spheres"). When Cu₂O materials were acted as SERS substrates, chemical enhancement (CE) effect was always taken into consideration.^[43,44] CE induced by charge transfer (CT) played the crucial role at the semiconductor–molecule interface, where amplification of the molecular polarization tensor occurs^[45–48] and thus enhanced the Raman scattering of molecules. Herein we used crystal violet (CV) as probe molecule. The a[°] vibration mode (1615 cm⁻¹) of CV was more enhanced than other vibration modes, which was a nontotally symmetric mode and only came from the CT process.^[49–51] The



Figure 3. a,b) SEM and c) TEM images of Cu_2O CSs. d) HRTEM image of the framed area in (c). The inset of (d) illustrates the corresponding SAED patterns.





Figure 4. Scheme illustration and the corresponding SEM images of Cu_2O spheres with controllable concavity obtained under different reaction temperatures: a) 15, b) 25, c) 35, and d) 45 °C, scale bar = 1 μ m.

classical CE was derived from resonant Raman scattering effect between the excitation wavelength and charge-transfer complex (semiconductor and probe molecule).^[49–51] To verify the interaction between Cu₂O CSs and CV, ultraviolet-visible absorption



Figure 5. a) Schematic diagram of the light trapping by using single Cu₂O CS particle as SERS substrate. b) Calculated electric field ($|E|/|E_0|$) distributions of a single CS. c) A comparison of the Raman intensities of CV molecule (2×10^{-5} M) at peak of 1615 cm⁻¹ adsorbed on single complete sphere, multi-CS, CS, and hemisphere (the left columns), and the corresponding downward particles (the right columns).

spectra of CV adsorbed on Cu₂O CSs were collected to compare with pristine Cu₂O CSs and CV (Figure S10, Supporting Information). A new band from 650 to 725 nm appeared, suggesting that a CT process happened between Cu₂O CSs and CV molecules.

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A concentration of 2×10^{-5} M CV was used to prevent the supersaturated adsorption (Figure S11, Supporting Information). SP-SERS spectra of 2×10^{-5} M CV adsorbed on the four Cu₂O spheres placed on marked silicon (Figure S12, Supporting Information) were measured from 20 different regions (Figure S13, Supporting Information). The strongest vibration peak at 1615 cm⁻¹ of CV was used as reference for the spectra normalization, and the signal intensity was averaged for final analysis. From the view of the opposite of the cavity (the opposite side of the sphere) (Figure S12e-h, Supporting Information), SEM images showed consistent, perfect spherical morphology for all Cu₂O spheres. With light directly irradiated onto the opposite side of the spheres of all samples, all the irradiation areas were not different due to the similar morphology of all samples. It also meant that the number of CV molecules adsorbed on the irradiation area was almost identical (details in the Supporting Information, "Surface areas of the four spheres"). Thus, it is understandable that the peak intensities of CV on the opposite side of the other spheres were very close to complete sphere (Figure 5c and Figure S13a2-d2, Supporting Information). Therefore, Raman scattering enhancement contributed by CE should be almost identical for all samples.

Interestingly, the intensities of the Raman peak differed significantly if light directly shined onto the cavity of multiconcave-, concave-, and hemispheres (Figure 5c and Figures S12b–d and S13b2–d2, Supporting Information). For multiconcave sphere, the peak intensity was enhanced 40% compare to the complete sphere. For hemisphere, the peak intensity was doubled compare to the complete sphere. For the CS, the peak intensity was sixfold as compare to the complete sphere.



Brunauer-Emmett-Teller (BET) N2 adsorption-desorption profiles (Figure S9 and details in the Supporting Information, "Surface areas of the four spheres") showed that the specific surface areas (SSA) of complete-, multiconcave, concave-, and hemispheres were 7.23, 8.51, 9.63, and 15.22 m² g⁻¹, respectively. The SSA was calculated by dividing the surface area (SA) by mass (M), where M was the product of density (ρ) and volume (V). ρ was identical since that the four Cu₂O spheres were obtained through same system. V could be easily derived from the SEM images (Figure 4). Thus, under light directly irradiated to the cavity, irradiation areas of complete-, multiconcave-, concave-, and hemispheres were 3.08, 3.74, 4.61, and 3.40×10^6 nm², respectively. For the multiconcave sphere, the increased loading of the CV molecules due to the increased irradiation area may dominate the enhancement of peak intensity. For the CS and hemisphere, although the loading of the CV molecules was enhanced caused by the increased irradiation areas, it was not enough to enhance the peak intensities for sixfold and twofold. Thus, it inferred that the markedly enhanced Raman performances mainly attributed to unique concave geometries.

It is well documented that concave-like structure possessed strong light scattering ability, thereby greatly improving light trapping.^[7–9,52–54] 3D finite-difference time domain (3D-FDTD) simulation (Figure 5b and Figure S15, Supporting Information) was conducted to investigate the electric field ($|E|/|E_0|$) distributions around the four Cu₂O spheres, which is essential to understand the mechanism of the light trapping as well



as the different SERS performances.[55,56] The observation of distribution $|E|/|E_0|$ of CS and hemisphere inside the cavity demonstrates that light trapping occurs within the cavity.^[55] Especially, the distribution of $|E|/|E_0|$ of CS is found in the cavity enclosed by walls, suggesting a considerable improvement of light trapping ability inside the cavity of CS. The cavity enhances the scattering length owing to multiple light scattering inside the unique concave structures.^[7–9] Furthermore, for the CS, the effective enhancement sites partly coincide with the molecular adsorption sites. For the hemisphere, although the light trapping occurs on the cavity, the most effective SERS enhancement area concentrates at the top of the molecular adsorption sites. The maximum intensity $|E|/|E_0|$ of CS is 1.8, while that of hemisphere is 1.2. As the SERS signals were roughly proportional to $(|E|/|E_0|)^4$, CS obviously has stronger SERS enhancement than hemisphere. Therefore, combined with the increased SA, the Raman scattering signal is enhanced to around sixfold for CS. For hemisphere, the weaker light trapping with slightly increased SA coenhances the Raman scattering signal to around twofold. In contrast, for the multiconcave sphere, the maximum intensity of $|E|/|E_0|$ appeared over where the cavity forms. The shallow and small cavity cannot effectively entrap light; and the enhanced Raman intensity is attributed to their increased surface area.

The excellent light-trapping properties endowed Cu₂O CS with outstanding SERS performances. As a result, an ultralow LOD for 2×10^{-8} M of CV and Rhodamine 6G (R6G) could be reached by using Cu₂O CS as substrates (**Figure 6**a,c and



Figure 6. a,c) Raman spectra collected for single Cu₂O CS at four different concentrations (2×10^{-5} , 2×10^{-6} , 2×10^{-7} , and 2×10^{-8} M) of CV and R6G molecule, respectively. b,d) The statistical Raman intensities of CV and R6G molecule at peak of 1615 and 610 cm⁻¹, acquired by recording spectra at 20 stochastic spots at different locations across from two substrates.





Figures S16 and S17, Supporting Information). The relationship between the Raman intensities and concentrations for CV and R6G molecule fitted relatively well with the linear curve fitting model (Figure 6b,d). EF was calculated based on the magnification of Raman intensity compared with that on bare substrate (details in the Supporting Information, Calculation of EF). The conservative EF was calculated to be around 2.8×10^5 for CV (peak at 1615 cm⁻¹) and 2.5×10^5 for R6G (peak at 610 cm⁻¹) adsorbed on single Cu₂O CS, which is amongst the better performing SERS substrate as reported (Table S1, Supporting Information), rivalled even that of the noble metal substrate without "hot spot."^[12,57,58]

3. Conclusions

In conclusion, Cu₂O spheres with controllable concavity can be obtained through a TIS process. Different sizes of F68 micelles could be formed through aggregation under different reaction temperatures, which can serve as soft template to tune the concave geometries of Cu₂O spheres. The FDTD simulation exhibits the high distribution $|E|/|E_0|$ of CS inside the cavity. Additionally, the highest intensity of $|E|/|E_0|$ was found in the cavity enclosed by walls, suggesting that the unique cavity of Cu₂O CS entraps light effectively, which also enhances the scattering length owing to multiple light scattering. This light trapping and slightly increased SA coenhances the Raman scattering signal to around sixfold. Combined with charge-transfer process, Cu₂O CS shows a remarkable SP-SERS performance with ultralow LOD (2×10^{-8} mol L⁻¹) and a metal comparable EF (2.8×10^5). As a novel approach for designing new functional materials, this synthetic strategy, is not just limited in the synthesis of concave structures, it would inspire more researches on the fabrication of a new generation of SERS substrate.

4. Experimental Section

Synthesis of Cu₂O Concave Spheres: All of the chemical reagents used in this experiment were of analytical grade without further purification. Cu (NH₃)₄²⁺ aqueous solution was first prepared by adding ammonia solution (NH₃·H₂O, 14.0 M) into copper chloride (CuCl₂, 0.20 M) aqueous solution to keep molar ratio of NH₃ to Cu²⁺ at 10: 1. An IS was prepared by mixing Cu(NH₃)₄²⁺ solution (2.25 mL) and 14.0 mL triblock copolymer Pluronic F68 (PEO₇₈–PPO₃₀–PEO₇₈, MW 8400, 80.0 g L⁻¹) together into a 100 mL glass flask. Then kept IS under stirring for 1 h in water bath at 35 °C (calibrated by Lauda Ecoline staredition RE 106). Subsequently, 3.4 mL AA (0.60 M) was added dropwise into the above mixture. A yellow turbid formed instantly. The mixture was aged for 5 min under constant stirring. The resulted orange-yellow precipitate was collected by centrifuging and washed with ethanol for several times to remove the F68 and finally dried under vacuum at 60 °C for 4 h.

Synthesis of Cu_2O Complete, Multiconcave Sphere, Hemisphere and Spheres: The reaction temperature was changed to 15, 25, and 45 °C while keeping other conditions identical.

Characterization: The powder XRD of the samples was characterized by the Rigaku Rotaflex Dmax2200 diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54056$ Å). The morphologies of the samples were observed using Hitachi S-4800 SEM with an accelerating voltage of 10 kV. TEM and high-resolution transmission electron microscopy (HRTEM) images were recorded by JEOL JEM-2100F, with an accelerating voltage of 200 kV. pH value was measured by pH meter (PHS-3C). Zeta-potential measurement and DLS were measured using Malvern Nano ZS90, UK. Raman spectra were acquired with a Jobin Yvon Raman spectrometer model HR800. Laser 647 and 514.5 nm lines from an Ar–Kr ion laser were used as excitation source. This laser power was density was $\approx 10^9$ W m⁻² (laser power: ≈ 2 mW; laser spot: 1.58 μ m²) to the surface of the sample. Ultraviolet-visible absorption spectra were recorded by UV– vis–NIR spectrophotometer (UV-3600, Shimadzu). Specific surface areas were measured by using at least 0.1 g samples at –196 °C through BET nitrogen adsorption–desorption (NOVA 2200e, Quanthachrome, USA).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

X.L. and Y.S. contributed equally to this work. X.L., Y.S., and L.G. conceived the study and cowrote the paper. X.L. and Y.S. designed and performed the experiments and analyzed the data. J.L. assisted in SERS measurement. A.L. helped in FDTD simulations. X.W. and B.L. discussed the SERS mechanism and F68 aggregation. The authors thank Yew Von Lim and Mei Er Pam for polishing the paper. This project was supported by the National Natural Science Foundation of China (21601009 and 51532001), National Basic Research Program of China (2014CB931802), and the International Postdoctoral Exchange Fellowship Program.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

concave structures, cuprous oxide, F68, light trapping, surface-enhanced raman scattering (SERS)

Received: March 14, 2018 Revised: May 21, 2018 Published online:

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