ESI (Electronic Supporting Information)

A new route for the synthesis of Ag nanopore-inlay-nanogap structure:

integrated Ag-core@graphene-shell@Ag-jacket nanoparticles for

high-efficiency SERS detection

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1. Experimental Section

Synthesis of Cu@G-NPs: The synthesis process of Cu@G-NPs can be divided into three stages according to the different morphology in the continuous reaction (Fig. S1a). First, a Cu nanofilm with 100 nm in thickness was deposited on an ultra-flat SiO₂/Si substrate using the magnetron sputtering equipment (JCPS-500) with deposition rate of 0.3-0.5 Å·s⁻¹. Second, the dual temperature zone of the tube furnace heated to: temperature (t) of 900 °C in low temperature zone and t of 1100 °C in high temperature zone, with flowing gas mixture of argon in 80 sccm and H₂ in 80 sccm for 20 min. In this stage, the as-prepared Cu nanofilm on the SiO₂/Si substrate would split into Cu-NPs. Third, argon would be replaced by the carbon source gas of CH₄ in 80 sccm and, accordingly, CH₄ molecule would be decomposed into C atom and H₂ in high temperature zone (t of 1100 °C). When a large number of drifting C atoms spreading into the low temperature zone (t of 900 °C) with gas-flow, they would be doped into surface of Cu-NPs due to the soluble-carbon characteristic of metallic copper. Finally, after the completion of the growth process and the cooling process of the quartz tube, G-shells can be gradually formed outside the Cu-NPs through the precipitation of C atoms.

Synthesis of AgC@G@AgJ-NPs: Before the start of the reaction, the pretreatment process for Cu@G-NPs in FeCl₃ aqueous solution is meaningful, and this assistant process can separate Cu-cores and G-shell from a certain distance as the space for the subsequent replacement reaction. The nanocasting processes in both inside-G-shell replacement reaction and outside-G-shell redox reaction were proceeding with moderate stirring (Fig. S1f). First, the ultra-flat SiO₂/Si substrate with Cu@G-NPs distribution was immersed into 1 mM AgNO₃ solution for 3 h, and the color on the ultra-flat SiO₂/Si substrate would change into deep-brown color as the reaction progress. Then, 10 mM ascorbic acid ($_L$ -AA) solution was dropwise added into AgNO₃ reaction solution and, accordingly, the color on the ultra-flat SiO₂/Si substrate would change into nearly black color. The whole reaction process were proceeded in the vacuum glove box (Etelux Lab 2000).

SERS detection of R6G: Rhodamine 6G (R6G) was detected at ultralow concentrations to evaluate the SERS sensitivity of the AgC@G@AgJ-NPs. In the SERS experiments, the prepared R6G solution with same volume (10 μ L, concentration of 10⁻¹⁰ M) were respectively

dropwise added on five separate SiO₂/Si substrates with different nanoparticles distribution (respectively are nanoparticles of sample 1, 2, 3, 4, and 5), washed with deionized water and dried for SERS detection. All the SERS spectra were collected under the same conditions (include integration time, laser power, focus, etc.) using a HR Evolution-800 Raman microscope system (HORIBA) at an excitation wavelength of 632.8 nm. Herein, we collected SERS spectra from 20 randomly selected points on each substrate, and the displayed SERS spectra are the average spectra. The slight red (or blue) shift of the obtained Raman spectra can be attributed to the various possible interactions between R6G molecules and metal-NPs, including the charge transfer between R6G molecules and metal-NPs, etc.

Reagents: The silver nitrate (AgNO₃), ascorbic acid (_L-AA), and rhodamine 6G (R6G) were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification. All solutions were prepared using purified water (Milli-Q, Millipore system).

Characterizations: Surface morphology of all the synthesized samples were observed using field emission scanning electron microscopy (FESEM, FEI Quatan FEG 250), information of the microstructures were obtained with field-emission transmission electron microscope (TEM, JEOL JEM-2100), and X-ray diffraction (XRD) patterns were characterized using a D/max-2400 diffraction spectrometer (Rigaku, Japan). The SERS experiments were performed on a HR Evolution-800 Raman microscope system (HORIBA), and the instrument is equipped with a standard 632.8 nm laser (laser spot ~0.8 μ m).

2. Supporting images and table



Fig. S1. (a) Schematic of the synthetic process of Cu@G-NPs. FESEM image (b), sizedistribution (c), TEM image (d), and HRTEM image (e) of the Cu@G-NPs. (f) Schematic of the synthetic process of AgC@G@AgJ-NPs. Using the statistics on all of the Cu@G-NPs in the FESEM image, the majority of the as-synthesized Cu@G-NPs are within the size range of 40–120 nm, with an interparticle distance of 50-150 nm (Fig. S1c).



Fig. S2. Raman spectra of the Cu@G-NPs.



Fig. S3. Typical XRD pattern of the Cu@G-NPs.



Fig. S4. FESEM images of the samples in different stage, respectively are sample after the pretreatment process (a), samples with reaction time of 50min (b), 3h (c), and sample after the secondary nucleation and growth process (d). Herein, we collected FESEM images in same area of sample 1 and prodromic Cu@G-NPs, and the particle-distribution of these two samples is almost the same in this area. From the large-scale FESEM images of sample 4 and 5, one can see that the particle-distribution is very uniform. Generally speaking, the high-magnification Raman objective with a laser beam diameter of around 0.8 mm usually contains one relatively large nanoparticle with a diameter of around 300 nm and three relatively small nanoparticles with a diameter of around 70 nm, or four medium sized nanoparticles with a diameter of between 100-200 nm.



Fig. S5. Typical XRD patterns of the primary AgC@G@AgJ-NPs (sample 4) and the AgC@G@AgJ-NPs (sample 5). The XRD patterns demonstrate that the as-synthesized Ag-NPs are in f-cc phase in sample 4 and 5.



Fig. S6. EDS pattern of the primary AgC@G@AgJ-NPs (sample 4). The peaks of C element are difficult to distinguished, which is due to the ultralow content of C element. This EDS pattern shows that there are no residual Cu atoms in sample 4.



Fig. S7. (a) and (b) are magnified images of Fig. 3b and 3c, respectively.



Fig. S8. Raman signals in one period SERS detection of 1200s. In this experiment, we continuously collected Raman signals from one selected point. The collection time of each spectra is 30s, and the time interval also is 30s. The very little fluctuation in Raman signals indicates that this AgC@G@AgJ-NPs have good stability for long-term detection.



Fig. S9. Raman intensity at 615 and 1366 cm⁻¹ peaks respectively collected from the Raman mapping along with the black arrow line (a), and points marked with number 1-10 (b).



Fig. S10. SERS detection of thiabendazole (TBZ) with different concentrations from 0.02ppm to 5 ppm on AgC@G@AgJ-NPs substrate. TBZ always used for chemical fungicide and parasiticide, and the recognizable Raman signals of TBZ at 0.02 ppm indicate the good SERS activity of the AgC@G@AgJ-NPs for non-polar molecules.

Peaks	615cm ⁻¹		1366cm ⁻¹	
	0.04659		0.03659	
	0.06751		0.01630	
	0.14326		0.16553	
	0.07200		0.12322	
Standard-	0.02025	average D:	0.15379	average D:
deviation (D)	0.00379	0.05839	0.01956	0.07514
	0.01866		0.01478	
	0.04659		0.03253	
	0.02033		0.07911	
	0.14489		0.10995	

Table 1. Standard-deviation (*D*) of the Raman intensity at 615 and 1366 cm⁻¹ peaks of the selected 10 Raman spectra in Fig. 3f (number 1-10).





Fig. S11. (a) LaMer curve of the Ag atom concentration vs time, including the generation of atoms, selfnucleation, primary growth, secondary nucleation and growth. (b) Schematics of the Ag clusters or nanostructures in different stages.

In this experiment, our strategy to fabricate the integrated AgC@G@AgJ-NPs contain nanopores/nanogaps with sub-10 nm scale is based on the twice nucleation and growth process using Cu@G-NPs as the sacrificial templates. In the metal nanocrystal synthesis according to

the mechanism of LaMer and Dinegar (Fig. S11a),¹ at the initial reaction stage (replacement reaction between Ag ions and Cu atoms), the concentration of Ag atoms steadily increases with time as the precursor (AgNO₃) is reduced (stage I in Fig. S11b, herein the Cu atoms are not shown in these schematics). Herein, the breakages in G-shell act as the immobilized interexchange channels and reactive sites for Ag ions and Cu atoms, which can prevent the reaction from preforming in all directions, and further leads to a non-hollow and multi-cores structure. The replacement reaction between Ag ions and Cu atoms continues until the inexistence Cu atoms are completely consumed, and thereupon the generation of Ag atoms process has completed. Then, in the nucleation process, i.e., when the concentration arrives the supersaturation point (C_{Min}), the Ag atoms begin to aggregate into small clusters (namely the nuclei) via homogeneous-nucleation around the breakages (stage II in Fig. S11b). In this process, a part of Ag clusters may leak out of the G-shell due to the atomic thickness of graphene, which can further act as the "seeds" for the outside-G-shell crystal growth. A large amount of Ag nuclei once formed, they can rapidly grow up into Ag nanocrystals in both inside and outside the G-shell by virtue of the increscent size (stage III in Fig. S11b) and, concurrently, the number of Ag atoms decreases. In this stage, the activation energy for structural fluctuation will become so high along with an Ag cluster grown into a certain critical size, which can lead to the Ag cluster eventually be trapped in a well-defined structure as a "seed". These so-called "seeds" further grow into final nanocrystal through the addition of Ag atoms until the concentration decreases to the solubility (Cs). The discontinuous and independent breakages in G-shell divide the total reaction sites into several parts for independently conducting in each part. Thus, there will emerge multiple independent "seeds" outside the G-shell surface to support the outside-G-shell crystal growth. In fact, it has been demonstrated that the abundant small clusters are the building units for the formation of Ag nanocrystal, and preferentially induce crystal growth in cluster-aggregative nucleation pathway rather than the atom-mediated classical crystallization.²⁻⁴ Moreover, the free energies of various facets of an Ag polyhedron increase in the order of $\gamma_{(111)} < \gamma_{(100)} < \gamma_{(110)}$,⁵ and the clusters prefer to attach on the facets owning the highest surface energy to reduce the overall energy to a minimum and, therefore, the (111) facets is more stable for crystal growth without any capping agent. On this occasion, the outside

particle growth process via coalescence and aggregation of the small Ag clusters, resulting in a single larger Ag nanocrystal at growth stage in (111) facets. As time goes on, the nanorod-like Ag nanostructures will be emerged on the G-shell due to the orientated attachment mechanism in particle-mediated aggregation process by virtue of multi-region graphene as the growth templets. Finally in the primary growth, an equilibrium state will be reached due to the consequent sharp reduction of Ag atoms concentration, which is determined by the chemical potential of the Ag atoms in the solution and the chemical potential of the surface atoms of nanocrystals.⁶ The outside-G-shell nano-frameworks can provide the support for the fabrication of Ag nanoporous structure. An atomic concentration fluctuation in the reaction solution can be created when we dropwise added the L-AA solution, which can result in the secondary nucleation and growth process (stage IV in Fig. S11b). Abundant free-suspended Ag clusters can be formed through the reductant of L-AA for AgNO₃ precursor, and attached on the nanorod-like Ag nanostructures in the secondary growth process until the overall system reached the second equilibrium state. As described above, we systematacially investigated the growth mechanism of the as-synthetized AgC@G@AgJ-NPs according to the mechanism of LaMer and Dinegar using FESEM, TEM and HRTEM images, and this may provide a new way for the design and fabrication of noble-metal nanoporous structures in the micro reaction cavity in various plasmonic applications.

The multiple roles of an individual G-shell in our experiment include that: i) a micro reaction cavity for the inside-G-shell replacement reaction between Ag ions and Cu atoms; ii) a growth template for the outside-G-shell redox reaction between Ag ions and _L-AA; iii) an additional enhancer for Raman signal based on the CM. Moreover, in the detection, graphene may act as an enrichment layer for probe molecules in nanogaps through the expansive " π " bond. There is a relatively obvious boundary between the Ag-core and G-shell, and this is different with Cu@G-NPs (the boundary is obscure between Cu-core and G-shell), which is due to the generation of G-shell is derived from the precipitation of C atoms in Cu surface.



4. Calculation of the average enhancement factor (EF) of the AgC@G@AgJ-NPs.

Fig. S12. (a) Raman spectra collected from the R6G aqueous solution with concentration of 10⁻⁴ M, and the corresponding Raman spectra after subtracting a baseline. (b) Size-distribution of the AgC@G@AgJ-NPs.

The SERS spectra reveal the characteristic vibrational peaks of R6G, for instance, at 610, 769, 1125, 1183, 1313, 1360, 1504, 1566 and 1647 cm⁻¹, and these peaks are in accordance with the Raman spectra of R6G molecule in the solid state or in aqueous solution in published papers.⁷ The average EF of the AgC@G@AgJ-NPs can be estimated using the following computational formula:

$$EF = \left(\frac{I_{A-Surface}}{N_{surface}}\right) / \left(\frac{I_{Solution}}{N_{Solution}}\right) = \frac{I_{A-Surface}}{N_{Surface}} \times \frac{N_{Solution}}{I_{Solution}}$$

In this formula, $I_{A-Surface}$ and $N_{surface}$ are respectively the average Raman intensity collected from the AgC@G@AgJ-NPs and number of R6G molecules on the AgC@G@AgJ-NPs within the laser spot, and $I_{solution}$ and $N_{solution}$ are respectively the Raman intensity and the number of R6G molecules in R6G aqueous solution within the laser spot. The Raman intensity of R6G molecules in R6G aqueous solution with concentration of 10⁻⁴ M is shown in Fig. S12a. Herein, in order to obtain the accurate Raman intensity, we have performed a subtraction of baseline treatment for Raman spectra.

$$I_{Solution} = 235.45 \ (counts)$$

$$N_{Solution} = 6.02 \times 10^{23} mol^{-1} \times 10^{-4} mol/L \times \left[\pi \left(\frac{d}{2}\right)^2 \times H\right] = 1.21 \times 10^{7}$$

Where d is the diameter of the light spot (about 0.80 μ m), and H is the effective depth of

focus and can be estimated of about 400 $\mu m.$

$$I_{A-Surface} = 22937.88 \ (conuts)$$

$$N_{Surface} = D_{R6G} \times S_{spot}$$

$$S_{spot} = \pi \times \left(\frac{d}{2}\right)^2 = \pi \times 0.4^2 \mu m^2 = 0.50 \mu m^2$$

$$D_{R6G} = \frac{N_{R6G}}{S_{total}} = \frac{N_{R6G}}{S_{Si/SiO_2} + S_{NPs}}$$

Where ${}^{D}_{R6G}$ is the density of R6G molecule on the AgC@G@AgJ-NPs, ${}^{S}_{spot}$ is the irradiated area of laser spot, ${}^{S}_{total}$ is the total effective area of the distribution of dropped solution which incorporate the area of Si/SiO₂ substrate (${}^{S}_{Si/SiO_2}$) and the effective surface of all the AgC@G@AgJ-NPs (${}^{S}_{NPs}$), and ${}^{N}_{R6G}$ is the number of R6G molecules we used. Herein, in order to obtain the number of molecules on AgC@G@AgJ-NPs, we directly dropped 10 µL R6G solution (10⁻¹⁰ M) on this substrate and rinsed using deionized water. The binding force between AgC@G@AgJ-NPs and R6G molecules is strong, and most of R6G molecules can be stayed on the substrate after rinse. The stain area of the distribution of dropped R6G solution is about 3.14×10^6 µm² (diameter of about 2mm). So the ${}^{N}_{R6G}$ can be calculated as:

$$N_{R6G} = 6.02 \times 10^{23} \times 10 \times 10^{-6} L \times 10^{-10} mol/L = 6.02 \times 10^{8}$$

Herein, we build a simplified model for the AgC@G@AgJ-NPs, i.e., an individual AgC@G@AgJ-NPs can be perceived as a hemispheres. We can calculate the fraction of coverage of AgC@G@AgJ-NPs according to Fig. S12b (size-distribution in a selected area in Fig. S4d, about 3.34×10^6 nm²), and approximately to be 22.38%. So the effective surface (S_{total}) in Fig. S12b can be calculated as:

$$S_{total} = \left\{ \frac{1}{2} \times 4 \times \pi \times \left[\left(\frac{d_1}{2} \right)^2 + \left(\frac{d_2}{2} \right)^2 + \dots + \left(\frac{d_n}{2} \right)^2 \right] + 3.34 \times 10^6 \times (1 - 22) \times 10^6 nm^2 \right\}$$

So the S_{total} in the stain area of $3.14 \times 10^6 \mu m^2$ can be approximately estimated as:

$$S_{total} = \frac{3.14 \times 10^6 \mu m^2}{3.34 \times 10^6 n m^2} \times 4.08 \times 10^6 n m^2 = 3.84 \times 10^6 \mu m^2$$

Based on the above results, D_{R6G} and $N_{Surface}$ can be calculated as:

$$D_{R6G} = \frac{N_{R6G}}{S_{total}} = \frac{6.02 \times 10^8}{3.84 \times 10^6 \mu m^2} = 156.8 \mu m^{-2}$$

 $N_{Surface} = D_{R6G} \times S_{spot} = 78.4$

From the above, the EF can be calculated as:

$$EF = \frac{I_{Surface}}{N_{Surface}} \times \frac{N_{Solution}}{I_{Solution}} = \frac{22937.88}{78.4} \times \frac{1.21 \times 10^7}{235.45} = 1.51 \times 10^7$$

The AgC@G@AgJ-NPs display high density of hot spots owing to the intraparticle nanopores and nanogaps, showing an excellent SERS activity with an average EF up to 10^7 in magnitude under 632.8 nm excitation wavelength.

Note:

The calculation of D_{R6G} is based on the assumption of uniform distribution of R6G molecules. However, in fact, most of R6G molecules will be distributed to boundary region, therefore the distribution density of R6G molecules in central region where we collected Raman signals is lower than the average value. So the actual value of EF is reasonably higher than the calculated value.

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