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SERS-active silver nanoparticle assemblies on branched Cu_2O crystals through controlled galvanic replacement

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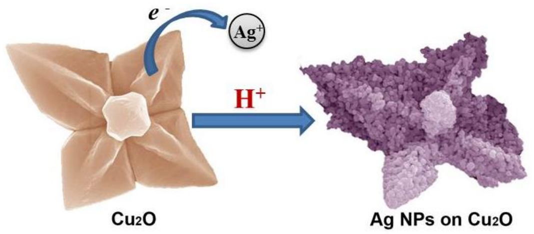
We here demonstrate the fabrication of Ag nanoparticle (NP) assemblies on branched Cu_2O crystals through a galvanic replacement reaction process, where the branched Cu_2O morphology can be well maintained by controlling the reaction environment (acid introduced to initiate the reaction). Cu_2O was transferred into soluble Cu^{2+} species, which renders a clean surface of Ag NPs. The as-fabricated Ag NP assemblies can be used as promising SERS-active substrates for molecule detection, with a detection sensitivity of 10^{-9} mol/L towards both target molecules, MB and RhB. We believe galvanic replacement using Cu_2O as sacrificing template can also be applied to synthesize noble metal (Au, Pt, Pd) NPs or NP assemblies for various applications.

Galvanic replacement reactions involve a corrosion process that is driven by the difference of electrochemical potentials between two metallic species. Preparation of noble metal nanoparticles (MNPs) through the reduction of metal ions by metal oxide (*via* a galvanic replacement process) with an intermediate oxidation state renders a clean surface of the as-prepared MNPs, which has become a facile and novel method in MNP synthesis for various applications.[1] For instance, Lee, et al.[2] reported an electroless Pt deposition on Mn_3O_4 NPs through reaction between Mn_3O_4 and $PtCl_4^{2-}$ complexes, and the obtained Pt/Mn_3O_4 showed enhanced electrocatalytic performance for oxygen reduction. Cuprous oxide (Cu_2O), with a high optical absorption coefficient and a bulk band gap of 2.2 eV, has been recognized as an excellent candidate for applications in photovoltaics,[3, 4] photocatalysis,[5-8] and even electrode materials.[9-11] Recently, Liu, et al.[12] reported an *in situ* growth of Au NPs on the surfaces of Cu_2O nanocubes, which involves a galvanic replacement reaction between Au^{3+} ions and Cu_2O. In our previous work,[13] we reported the synthesis of self-supported Pt nanoclusters consisting of 2-3 nm NPs *via* a galvanic replacement method from Cu_2O, where Cu_2O was transformed into Cu^{2+} ions and surface-clean Pt electrocatalysts can be easily achieved. Ag nanosheet assemblies could be prepared *via* reaction between Ag^+ ions and Cu_2O, which can be used as promising surface-enhanced Raman scattering (SERS) substrates.[14] Of note is that, during the galvanic replacement between metal oxides (Mn_3O_4, Cu_2O, etc.) and metal ions (Pt^{2+}, Au^{3+}, etc.), H^+ ions are essential to initiate such reactions.[2, 13, 14] As we found,[15] different acids introduced into the reaction system in preparing MNPs *via* solution chemistry route could greatly alter the assembly of MNPs into complex structures with various morphologies. Therefore, there might be a facile way to control the MNP morphology during the galvanic replacement process by proper selection of the acid category.

Herein, we report the fabrication of Ag NP assemblies through the galvanic replacement reaction between Ag^+ ions and Cu_2O (Scheme 1). By careful choosing the acid introduced into the reaction system and modulating the reaction process, the Ag NPs can grow on the branched Cu_2O crystals, while the Cu_2O morphology will not be destroyed. The as-fabricated Ag NP assemblies on branched Cu_2O crystals can be applied as highly sensitive SERS substrates for molecule detection.



Scheme 1 Schematic illustration of preparing Ag nanoparticle assemblies on branched Cu_2O crystals through a galvanic replacement process, where "H^+" is highlighted in red to indicate that H^+ is essential to initiate this reaction.

Branched Cu_2O crystals were electrodeposited on indium tin oxide (ITO) substrates through an electrostatic deposition technique (see Experimental Section in ESI† for detail).[16] By controlling the proper applied potential, Cu_2O crystals with branched structure and brown color can fully cover the ITO substrate (Fig. 1a). From the magnified image in Fig. 1b, one can see that these Cu_2O crystals are about 4~5 μm in size, which have four petals and a polyhedral crystal in the center. The evolution of such branched structure has been well explained by overpotential deposition.[16] The ITO substrates with deposited Cu_2O were then immersed in $AgNO_3$ aqueous solution for Ag growth. Without introducing acid into the $AgNO_3$ solution, no reaction was witnessed as the brown color of Cu_2O kept unchanged. As shown in Scheme 1, H^+ ions are essential to initiate the galvanic replacement reaction between Ag^+ ions and Cu_2O (eq. 1).

$$Cu_2O + 2Ag^+ + 2H^+ \rightarrow 2Cu^{2+} + 2Ag + H_2O \qquad (1)$$

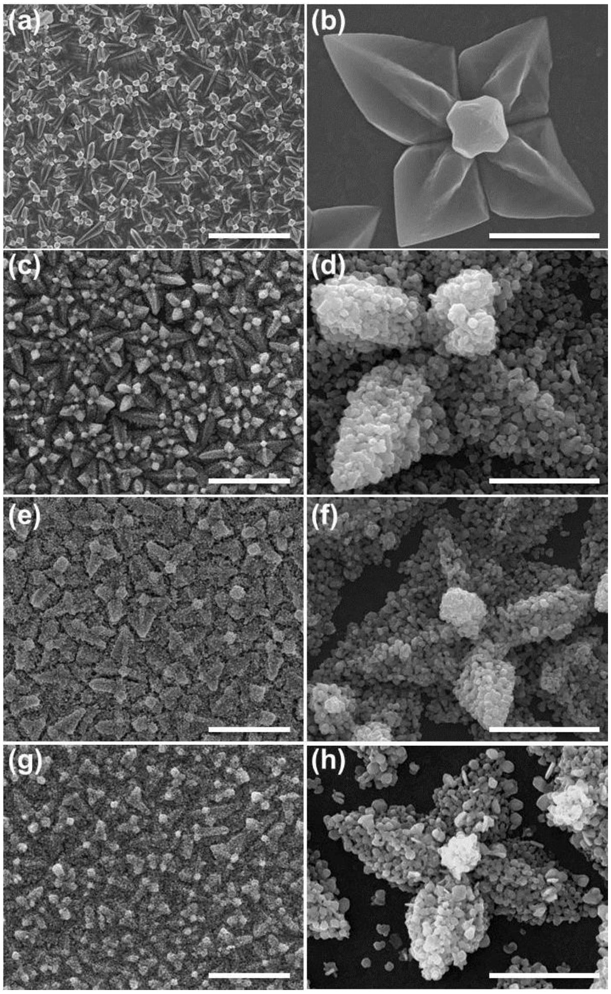


Fig. 1 SEM images of (a, b) electrodeposited Cu_2O crystals on ITO substrate, and Ag nanoparticle assemblies obtained from galvanic replacement for (c, d) 10 s, (e, f) 30 s, and (g, h) 1 min. During the galvanic replacement process, 5-sulfosalicylic acid was used as the additive acid. Scale bars in (a, c, e, g) are 5 μm; in (b, d, f, h) are 2 μm.

Moreover, Cu_2O will be transferred into soluble Cu^{2+} species, without forming any precipitates. Here, we have tested the Ag growth by using various acids, and we have found that the acid category can greatly change the Ag growth behavior. Interestingly, with 5-sulfosalicylic acid as the H^+ source, Ag NPs can readily grow on the surface of Cu_2O crystals by careful controlling the reaction time period, without destroying the branched structures (Fig. 1c-h). When H^+ ions are introduced, galvanic replacement reaction between Ag^+ ions and Cu_2O follows a very rapid process, where the brown color will be changed to grey almost immediately. Just in 10 s (Fig. 1c), the smooth Cu_2O surfaces are decorated with uniform dots, which are Ag NPs. From Fig. 1d, one can see that the petals and center of the Cu_2O crystals are fully decorated with Ag NPs that are about 50-100 nm in size. After 30 s, the dotted morphology on the Cu_2O crystals becomes more obvious (Fig. 1e), and the magnified image indicates that more Ag NPs have been deposited on the Cu_2O surfaces (Fig. 1f). At 1 min, one can see that Ag NPs grow into small nanosheets, and some Ag nanosheets fall scattered onto the ITO substrates (Fig. 1g, h). Moreover, at this stage, the Ag nanosheets become loosely packed, with a tendency of structure collapse. The structure evolution from NPs into nanosheets can be well explained by the acid effect, as we have found in our previous work that organic acid introduced during the Ag growth tend to direct the formation of sheet-like structures.[17] However, with even prolonged reaction period, the branched Cu_2O structures can be destroyed, and more scattered Ag NPs will be found on the ITO substrates (see Fig. S1 in ESI†). This may be rationalized by the fact that when more and more Cu_2O is "eaten" by Ag^+ ions, the subsequent Ag NPs added onto the branched crystals will lead to a structure collapse at a critical point. Notably, when other acids (camphorsulfonic acid, citric acid, and lactic acid) were introduced into the reaction system, we did not see Ag growth perfectly along the Cu_2O surfaces. Instead, Ag particles that are assembled by Ag NPs grown out of the Cu_2O surfaces are obtained (see Fig. S2 in ESI†), and the applied acid can change the assembly manner as we found in the acid-directed synthesis of Ag particles with complex structures.[15] We think the unique role of 5-sulfosalicylic acid in this process might be due to its better affinity to both the Cu_2O surfaces and Ag nuclei, and thus the Ag NPs can grow on the Cu_2O surfaces, with branched structures maintained undestroyed.

Fig. 2 shows the X-ray diffraction (XRD) patterns of the Cu_2O crystals and Ag NP assemblies obtained at different time periods, which reveals the Ag growth process on the Cu_2O crystals. After the typical electrodeposition process, the diffraction peaks at 2θ=~36.5°, 42.4°, 61.8° and 73.8° of the obtained brown particles can be indexed to the (111), (200), (220) and (311) planes of cubic Cu_2O crystals (JCPDF 65-3288). At a reaction time of 10 s, the Cu_2O peaks are greatly decreased, indicating the reaction between Cu_2O and Ag^+ ions, but one can see very limited Ag diffraction peaks owing to the short reaction time. After 30 s, the Cu_2O peaks are almost undistinguishable, and Ag peaks become obvious. After 1 min of reaction, besides the peaks ascribed to ITO substrate, the peaks at 2θ=~38.2°, 44.6°, 64.5° and 77.3° can be well indexed to the (111), (200), (220) and (311) planes of cubic Ag crystals (JCPDF 04-0783). This result indicates that during the galvanic replacement process, Cu_2O is gradually consumed by Ag^+ ions, and Ag NP assembly are formed on the Cu_2O surfaces.

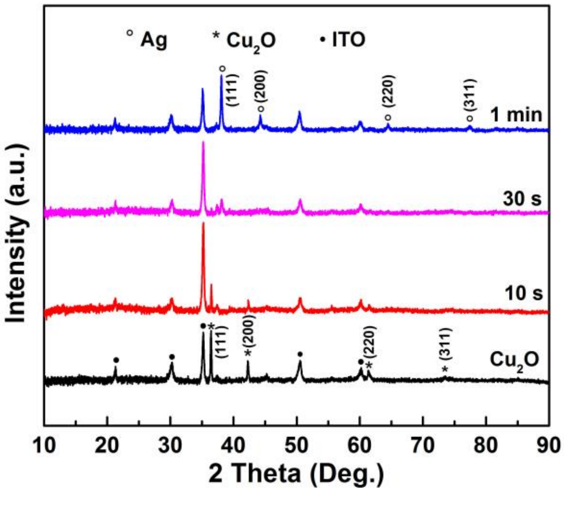


Fig. 2 XRD patterns of Cu_2O crystals on ITO substrate and Ag nanoparticle assemblies obtained from galvanic replacement for different time periods.

As SERS hot spots are usually located at the interstitial sites (intersections, bifurcations, and high radius of curvatures) in nanostructures,[18, 19] we are extremely interested in the SERS responses of these Ag NP assemblies. Firstly, we compared the SERS performances on Ag NP assemblies and Cu_2O crystals, using rhodamine B (RhB) as a target molecule (Fig. 3). Though SERS property of porous Cu_2O nanostructures has been reported,[20] here we found that these branched Cu_2O crystals show very limited SERS activity, mainly due to their large size without obvious nanoscale features. As for the Ag NP assemblies obtained at different reaction stages, it is found that the sample collected at 30 s shows the strongest enhancement towards RhB molecules with the same concentration of 10^{-6} mol/L. We believe this best SERS response can be interpreted by the fact that at this stage, the Ag NP assemblies are well formed with close packed Ag NPs, and the branched structures are maintained to provide 3-dimentional (3D) nanoscale features. Therefore, more SERS hot spots can be formed at the interstitial sites through assembly process of the Ag NPs. Larger Ag size and loose packed structures for Ag NP assemblies at 1 min may typically reduce the surface area and hot spot numbers.

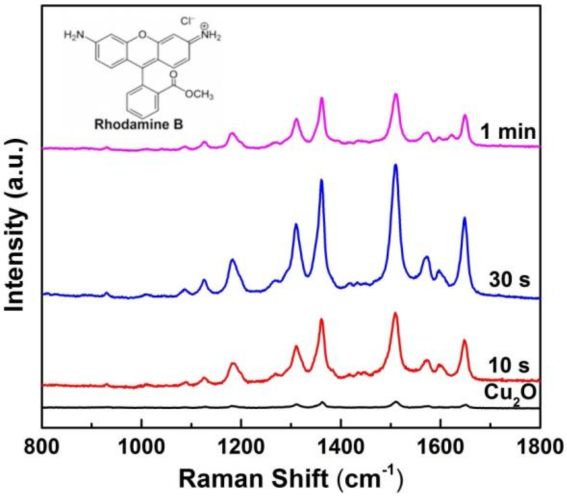


Fig. 3 SERS spectra of rhodamine B (RhB) of 10^{-6} mol/L measured on electrodeposited Cu_2O crystals on ITO substrate, and Ag nanoparticle assemblies obtained from galvanic replacement for 10 s, 30 s, and 1 min.

Therefore, we choose the Ag NP assemblies obtained at 30 s as the typical sample and another target molecule, methylene blue (MB) to measure the SERS sensitivities in molecule detection (see Fig. S3 in ESI†). Raman spectrum of MB is dominated by ν(C-C) ring stretching at 1618 cm^{-1}, α(C-H) in-plane ring deformation at 1398 cm^{-1}.[21] Here, a detection sensitivity of 10^{-9} mol/L can be reached for MB, which is comparable to that on the Ag nanosheets formed on Cu_2O after a reaction time of 30 min.[14] It needs to note that we only need a reaction time of less than 1 min to fabricate such SERS-active Ag NP assemblies. In order to demonstrate the generality of the as-fabricated Ag NP assemblies as promising SERS-active substrates, we also measured the concentration-dependent SERS spectra towards RhB, which shows a similar sensitivity of 10^{-9} mol/L (see Fig. S4 in ESI†). Moreover, it is interesting to see that SERS spectra taken from different sites on the Ag NP assemblies supported on branched Cu_2O crystals show similar enhancement bahaviors (Fig. 4). This result indicates that the Ag NP assemblies fabricated on branched Cu_2O crystals can be readily used as efficient SERS substrates for sensitive molecule detection. Though Ag particles obtained using acids other than 5-sulfosalicylic acid also show some SERS activity of the target molecules, the enhancement is relatively weaker due to the lack of homogeneous surface nanosclae roughness, and the SERS response over the surface is not uniform (see Fig. S5 in ESI†).

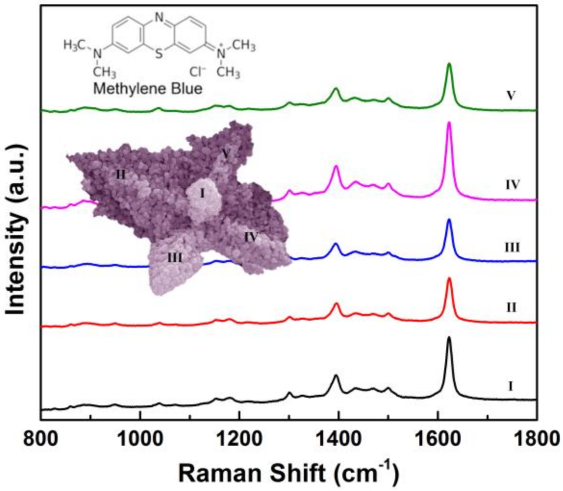


Fig. 4 SERS spectra of methylene blue (MB, 10^{-6} mol/L) taken from different sites on the Ag nanoparticle assemblies supported on branched Cu_2O crystals.

In summary, we have demonstrated a facile fabrication of Ag NP assemblies on branched Cu_2O crystals through a galvanic replacement reaction process between Cu_2O and Ag^+ ions. By controlling the acidic environment and reaction time period, the structure and morphology of Ag NP assemblies can be effectively modulated. Cu_2O will be transferred into soluble Cu^{2+} species, leading to Ag NPs with clean surfaces. Of great interest is that when 5-sulfosalicylic acid was used as the H^+ source, Ag NPs are assembled on Cu_2O crystal surfaces and the branched structures are well maintained. The as-fabricated Ag NP assemblies can be used as promising SERS-active substrates for molecule detection, with a detection sensitivity of 10^{-9} mol/L towards both target molecules, MB and RhB. We believe this galvanic replacement process can also be applied to synthesize noble metal (Au, Pt, Pd) NPs or NP assemblies for various applications.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, Fig. S1-S5. See DOI: 10.1039/c000000x/

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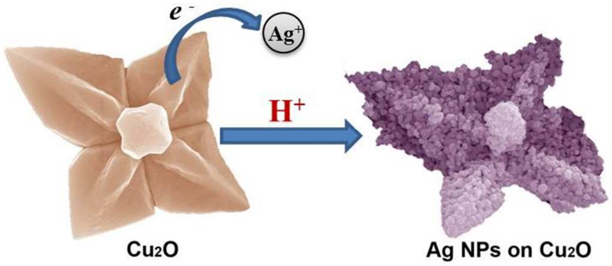
Graphical Abstract



We here demonstrate the fabrication of highly SERS-active Ag nanoparticle assemblies on branched Cu_2O crystals through a galvanic replacement reaction process.