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Gamma-irradiation induced direct fabrication of SERS-active Ag nanoparticles on glass substrates

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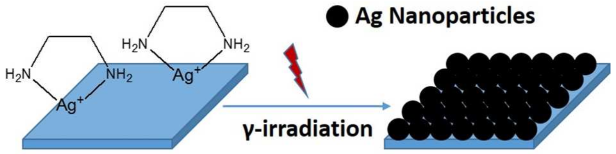
We have demonstrated here a facile Gamma-irradiation induced direct fabrication of Ag nanoparticles on glass substrates for SERS applications. It has been found that complex agents to the Ag^+ ions play the dominant role in enabling Ag growth directly on the glass substrates, where using bare $AgNO_3$ solution only produced Ag particles in the solution, but not on the glass substrate. Moreover, complex agent also decides the size and morphology of the Ag nanoparticles, where using ammonia leads to much larger Ag particles than using ethylenediamine. γ-ray dose can also influence the size of the Ag nanoparticles, and higher dose usually results in larger Ag nanoparticles. The SERS performances of the as-fabricated Ag nanoparticles supported on glass substrates have been compared. The uniform Ag nanoparticles with smaller sizes prepared from using ethylenediamine as the complex agent typically present superior SERS sensitivities. We believe this facile and cost-effective Gamma-irradiation induced fabrication of Ag nanoparticles will be of interest in SERS studies.

Introduction

Gamma-irradiation technique has been widely used in the synthesis of inorganic particles, taking advantage of the strong reductive nature of the produced hydrated electrons (e_{aq}^-).[1-3] Submicrometer to microsized single-crystalline Cu_2O particles has been prepared by γ-irradiation under ambient conditions, with cetyltrimethyl ammonium bromide (CTAB) as a capping material or template.[4] Copper oxide nanowires and cuprous oxide crystals had been synthesized through gamma-irradiating aqueous $CuCl_2$-NaOH-sodium dodecyl sulfate (SDS)-isopropyl alcohol solutions under ambient conditions.[5] Ag nanocrystals with controlled morphologies can be facilely synthesized via gamma-irradiation on aqueous solutions containing $AgNO_3$ salt and poly(vinyl pyrrolidone)(PVP) by adjusting the adsorption dose.[6] Torreggiani, et al fabricated Ag nanoparticles through the γ-irradiation for detection of fungicides based on surface enhanced Raman spectroscopy (SERS).[7] In the past few years, we have also managed to prepare morphology-controlled magnetic metal nanostructures through the gamma-irradiation technique, which showed improved microwave absorption properties.[8-10]

Among all metals, Ag has been regarded as the most promising material to be used in SERS, which typically provides the highest enhancement factor (EF) of the adsorbed analytes.[11-14] However, scatted Ag nanoparticles usually offer very limited enhancement of the Raman signals of a target molecules, as SERS "hot spots" often reside in structures with sharp edges, intersections, and bifurcations.[15-18] Therefore, various techniques have been developed to fabricate patterned SERS substrates with ordered nanostructures so as to reach higher EF.[18-21] In our previous works, we have managed to grow well-defined assembled Ag nanostructures on conducting polymer surfaces, which can be used as highly sensitive and cost-effective SERS substrates for chemical detection.[22, 23]

Herein, we demonstrate a gamma-irradiation induced direct fabrication of Ag nanoparticles on glass substrates (Scheme 1). It has been found that complex agents to the Ag^+ ions play the dominant role in enabling silver growth directly on the glass substrates. The size and morphology of the Ag nanoparticles can be tuned by the dose of gamma irradiation. The as-fabricated Ag nanoparticles supported on glass substrates can be readily used as SERS substrates for chemical detection.



Scheme 1. Schematic illustration of gamma-irradiation induced direct fabrication of Ag nanoparticles on glass substrates.

Experimental

Fabrication of silver nanoparticles. Glass slide was cut into 1 cm×1 cm small pieces. The glass pieces were thoroughly rinsed firstly by base and acid treatment, and then ultrasonication in ethanol for 30 min. In a typical experiment, 50 ml of 0.05 M $AgNO_3$ aqueous solution were complexed with ammonia water or ethylenediamine to form transparent solution. 5 ml of radical scavenger, isopropanol or methanol were then added to the complex solution under magnetic stirring. The solution was then transferred into a plastic bag, and three thoroughly cleaned glass pieces were put into the bag. The solution was then purged with nitrogen gas for 30 min to remove oxygen dissolved in solution. Then, the plastic bag was sealed and placed in the field of a ^{60}Co γ-ray source at a dose rate of 80 Gy/min. After irradiation, the glass pieces were washed with distilled water and anhydrous ethanol for several times respectively and then dried in a vacuum oven for 2 h at 50 °C. For comparison, experiments with bare $AgNO_3$ aqueous solution (without complex agent) were also carried out.

Characterization. Scanning electron microscope (SEM) measurements were carried out on the FEI Inspect scanning microscope to study the morphology of the samples. The characteristics of the crystallite structure of the prepared samples were determined using an XRD-6000 X-ray diffractometer (Shimadzu) with a Cu Kα radiation source (λ = 1.5481 Å, 40.0 kV, 30.0 mA). The Ag nanoparticles supported on glass substrates were optically characterized by using UV-visible transmission absorption spectroscopy (Varian Cary 300) over 340–800 nm. The SERS spectra were recorded on a Renishaw In Via micro-Raman spectroscopy system, using the TE air-cooled CCD array in a confocal Raman system (wavelength: 633 nm). The incident laser power was kept at 0.1mW, and a total accumulation time of 10 s was employed.

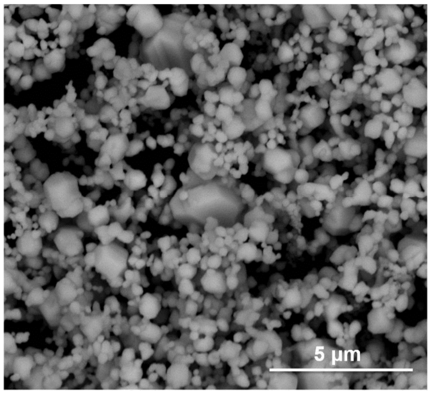


Fig. 1 SEM image of Ag particles collected from the solution when bare $AgNO_3$ aqueous solution was used.

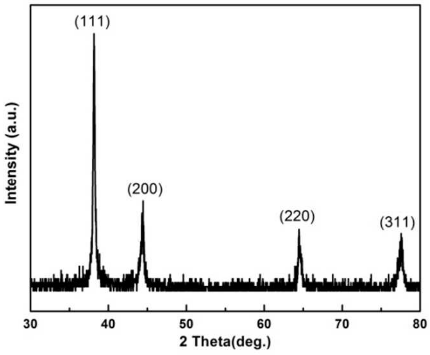


Fig. 2 XRD pattern of the Ag particles collected from the solution when bare $AgNO_3$ aqueous solution was used.

Results and discussion

As have known,[24] γ-irradiation of water leads to short-lived reducing species, hydrated electron (e_{aq}^-) and hydrogen atoms (·H), strong oxidizing species hydroxyl radical (·OH), and other molecular species (Eq. 1). e_{aq}^-, with a reduction potential of -2.77 eV, can theoretically reduce all metal ions except for alkali metal ions and alkaline earth metal ions (Eq. 2). However, in order to avoid metal ion oxidation by ·OH, some alcohol (methanol, isopropanol, *t*-butanol, etc) is usually added as ·OH radical scavenger (Eq. 3). Also, inert gas (nitrogen, argon) should be purged into the solution to remove the dissolved oxygen so as to avoid the reaction of e_{aq}^- with O_2.

$$H_2O \rightsquigarrow \cdot H,\ e_{aq}^-,\ \cdot OH,\ \ldots \quad (1)$$

$$n\, e_{aq}^- + M^{n+} \rightarrow M^0 \quad (2)$$

$$CH_3OH + \cdot OH \rightarrow \cdot CH_2OH + H_2O \quad (3)$$

We found the solutions in all recipes turned black after γ-irradiation, indicating the production of Ag particles. However, when bare $AgNO_3$ aqueous solution was used, no Ag growth was witnessed on the glass pieces. Fig. 1 shows the SEM image of the Ag particles collected from the solution where bare $AgNO_3$ aqueous solution was used. It can be seen that these Ag particles are very broad in size distribution. There are Ag bulks that are 1-3 μm in size, and Ag particles with sizes ranging from 100 -500 nm. The diffraction peaks in the XRD pattern in Fig. 2 shows that these particles are face-centered-cubic (fcc) Ag structure, rather than other Ag salts or impurities. Though Ag particles can be produced in the solution, it is disappointing that no Ag was found on the glass pieces. One possible reason is that when bare $AgNO_3$ aqueous solution was used, the nucleation and growth of Ag particles in the solution overwhelmed that on the glass surface. Therefore, our immediate thought was to control the growth rate of Ag particles under the γ-irradiation and the affinity of solution to the glass substrates.

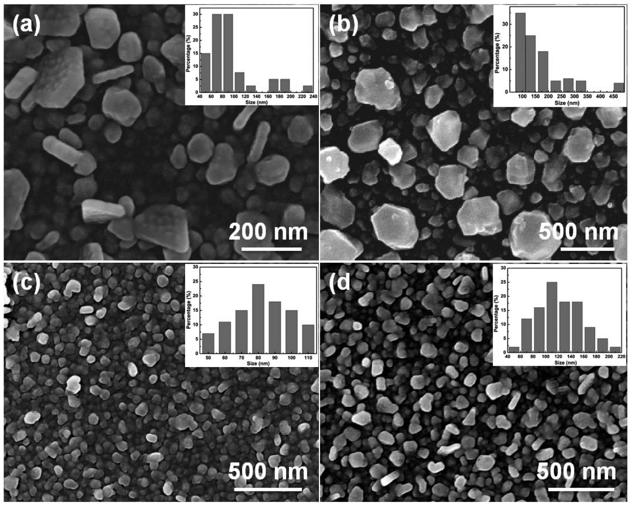


Fig. 3 SEM images of Ag nanoparticles on glass pieces using methanol as the radical scavenger from different complex agents to the Ag^+ ions.(a) ammonia, γ-ray dose: 5 kGy; (b) ammonia, γ-ray dose: 20 kGy;(c) ethylenediamine, γ-ray dose: 5 kGy;(d) ethylenediamine, γ-ray dose: 20 kGy. Insets show the size histograms of the Ag nanoparticles.

In order to reduce the growth rate of Ag particles, we tried to use ammonia or ethylenediamine to form Ag^+ ion complexes before the solution was put under the γ-irradiation. After γ-irradiation, one could still see that the solution color became dark, but the color was much lighter than that using bare $AgNO_3$ aqueous solution. Of note is that by using Ag^+ ion complex solution, we found all three glass pieces were covered by a dense layer of Ag particles. Fig. 3 shows the SEM images of the Ag particles on glass pieces using methanol as the radical scavenger from different complex agents to the Ag^+ ions. As can be seen in Fig. 3(a), when ammonia was used as the complex agent, low dose of γ-ray led to Ag nanoparticles with sizes of 50-100 nm, and Ag nanosheets of about 100-300 nm in size. With an increased γ-ray dose of 20 kGy, one can get Ag particles with larger size, as shown in Fig. 3(b). Besides Ag nanoparticles that are about 100 nm in size, one can also see big particles of about 200-500 nm. It is interesting to find that complex agent can dramatically change the size of the Ag nanoparticles on the glass substrates. When ethylenediamine was used as the complex agent, Ag particles with very narrow size distribution could be obtained, as can be seen in Fig. 3 (c) and (d). A low γ-ray dose of 5 kGy resulted in Ag nanoparticles with 80-100 nm in size, while a higher dose (20 kGy) led to Ag nanoparticles that are 100-150 nm in size. The above results indicate that there is a complex agent effect on the final size and morphology of the Ag particles, which we believe is due to the wettability of the Ag^+ ion complexes to the glass substrate and the reduction rate of the Ag^+ ion complexes by the γ-ray irradiation. Meanwhile, γ-ray dose impacts the size of the Ag nanoparticles in a way that larger sizes will be produced with higher dose.[4,5]

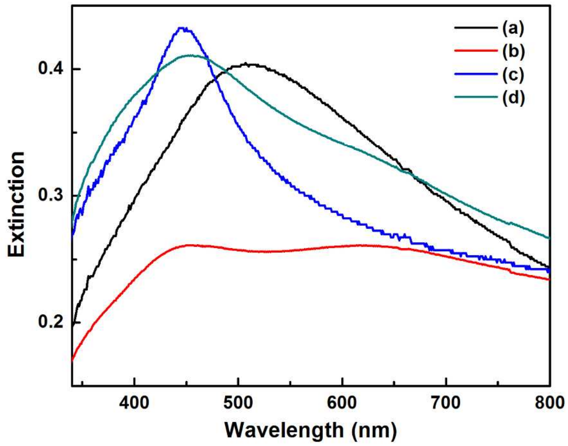


Fig. 4 Solid-state UV-Vis spectra of the as-fabricated Ag particles on glass substrates. Spectra (a)-(d) are collected on the Ag particles as shown in Fig. 3 (a)-(d), respectively.

The solid-state UV-Vis spectra of these Ag nanoparticles on glass substrates can be well matched to their size characteristics (Fig. 4). With ammonia as the complex agent, a mixture of 50-100 nm Ag nanoparticles and 100-300 nm Ag nanosheets (see Fig. 3a) produced from low dose of γ-ray presents a broad extinction peak centered at 510 nm (Fig. 4a); larger Ag particles from a higher γ-ray dose display an even broader absorption feature (Fig. 4b). With ethylenediamine as the complex agent, Ag nanoparticles with 80-100 nm in size from a γ-ray dose of 5 kGy shows a sharp extinction peak at 445 nm (Fig. 4c), while broader absorption feature with a peak at 455 nm can be seen for the Ag nanoparticles that are 100-150 nm in size from a higher dose (Fig. 4d).

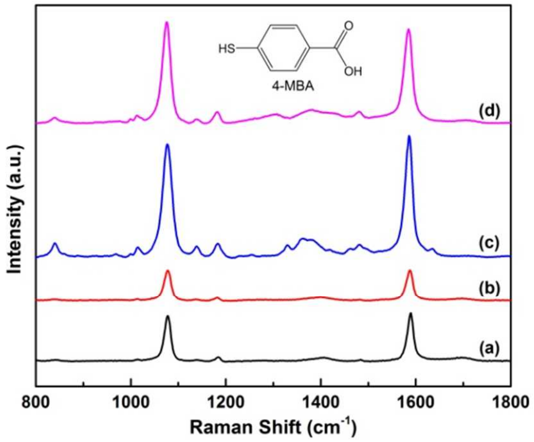


Fig. 5 SERS spectra of 4-mercaptobenzoic acid (4-MBA) on the as-fabricated Ag particles. Spectra (a)-(d) are collected on the Ag particles as shown in Fig. 3 (a)-(d), respectively.

In order to test the SERS behaviors of the as-fabricated Ag nanoparticles, we immersed the glass substrates in a 10^{-6} M 4-mercaptobenozic acid (4-MBA) ethanol solution for 10 min, and then rinsed the substrates in ethanol for several times to remove surface residuals. The Raman spectrum of 4-MBA is dominated by the ν_{8a} (~1590 cm^{-1}) and ν_{12} (~1080 cm^{-1}) aromatic ring vibrations; other weak bands at ~1150 and ~1180 cm^{-1} are attributed to the C-H deformation modes [25]. As can be seen from Fig. 5, SERS performances are quite dependent on the size and morphology of the Ag particles. The Ag nanoparticles prepared using ethylenediamine as the complex agent typically present much enhanced Raman signals of the 4-MBA molecules than those produced using ammonia as the complex agent. It has been demonstrated that the gap between two closely adjacent metal nanoparticles usually has much stronger electromagnetic field and can be SERS "hot spots" for enhancing the Raman signal of a target analyte.[26] Here, the Ag particles with sub-micrometer sizes prepared using ammonia as the complex agent can only provide very limited SERS "hot spots". Moreover, the surface area of these larger Ag particles should also be much smaller than that of the uniform Ag nanoparticles, and thus less 4-MBA molecules can be adsorbed on the surface of the sub-micrometer Ag particles. Therefore, we only see SERS signals that are about 5 times less stronger on the sub-micrometer Ag particles.

Since ethylenediamine is a better complex agent for direct fabrication of Ag nanoparticles on glass substrates, we used another radical scavenger, isopropanol, in the γ-ray irradiation induced preparation of Ag nanoparticles directly on glass substrates. It is found that all three glass substrates are covered by dense Ag layers, and Fig. 6 shows the SEM images of the Ag nanoparticles from different *γ*-ray dose. As can be seen in Fig. 6a, a low dose of 5 kGy led to Ag nanoparticles with very narrow size distribution (60-80 nm). An increased dose of 20 kGy resulted in 100-150 nm Ag nanoparticles that are embedded in the Ag layer consisting of 60-80 nm Ag nanoparticles. This result again verifies that ethylenediamine can be an efficient complex agent to directly prepare uniform Ag nanoparticles on glass substrates and, larger dose of *γ*-ray will typically increase the size of the as-prepared Ag particles.

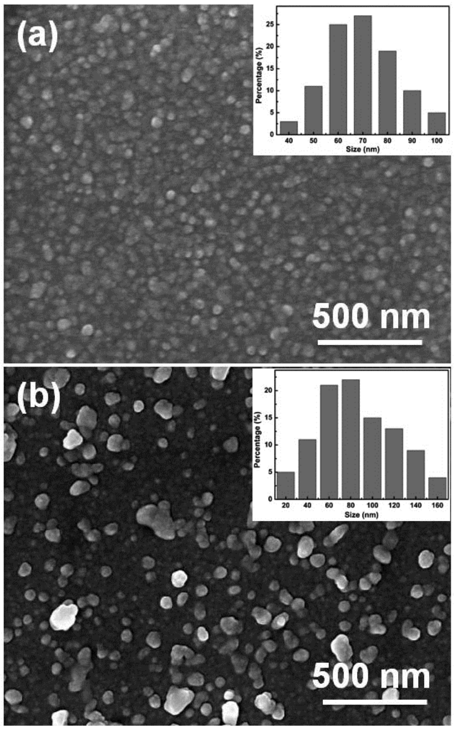


Fig. 6 SEM images of Ag nanoparticles on glass pieces using isopropanol as the radical scavenger and ethylenediamine as the complex agent to the Ag^+ ions.(a) *γ*-ray dose: 5 kGy;(b) *γ*-ray dose: 20 kGy. Insets show the size histograms of the Ag nanoparticles.

The SERS performance of the Ag nanoparticles prepared from using isopropanol as the radical scavenger were compared with that of Ag nanoparticles with methanol as the radical scavenger, as shown in Fig. 7. It can be seen that with same radical scavenger isopropanol, SERS sensitivity of the larger Ag nanoparticles prepared from a dose of 20 kGy is about half of that on the uniform 60-80 nm nanoparticles. While, the Ag nanoparticles prepared with methanol as the radical scavenger, as shown in Fig. 3c, provide the best SERS performance. We think it can be rationalized by the fact that though the Ag nanoparticles prepared with methanol as the radical scavenger are slightly larger in size than those shown in Fig. 6a, they are somehow stacked into 3-dimentional structures, where edges and intersections of these nanoparticles may create more SERS “hot spots” for enhancing the Raman signal of the 4-MBA molecules.[15] Nevertheless, these Ag nanoparticles (shown in Fig. 3c, d and Fig. 6a) fabricated on glass substrates are actually feasible for practical application in chemical detection based on SERS technique.

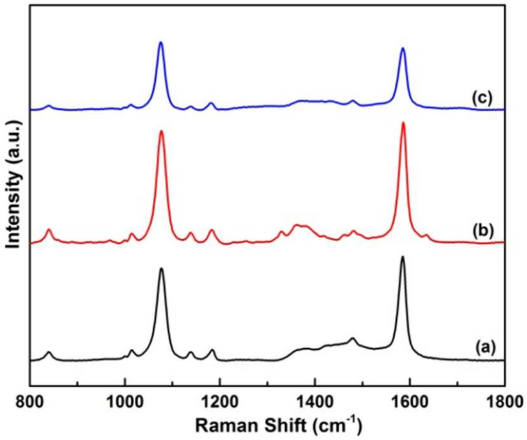


Fig. 7 SERS spectra of 4-mercaptobenzoic acid (4-MBA) on the as-fabricated Ag particles. Spectra (a)-(c) are collected on the Ag particles as shown in Fig. 6(a), Fig. 3(c), and Fig. 6(b), respectively.

Conclusions

In summary, we have demonstrated a Gamma-irradiation induced direct fabrication of Ag nanoparticles on glass substrates for chemical detection based on SERS technique. It is found that using bare $AgNO_3$ solution only produces Ag particles in the solution, but not on the glass substrates. When ammonia or ethylenediamine is used to form Ag^+ ion complexes, a layer of Ag nanoparticles can be deposited on the glass substrates, and ethylenediamine is more efficient in producing uniform Ag nanoparticles with smaller sizes. Dose of *γ*-ray can also impact the size of the Ag nanoparticles, where higher dosage typically leads to larger particles. These Ag nanoparticles fabricated on glass substrates can be well used in chemical detection by SERS technique. We believe these as-fabricated efficient and cost-effective SERS substrates are practically feasible in sensing applications.

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Notes and references

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1. N. J. Withers, K. Sankar, B. A. Akins, T. A. Memon, T. Y. Gu, J. J. Gu, G. A. Smolyakov, M. R. Greenberg, T. J. Boyle and M. Osinski, *Appl Phys Lett*, 2008, **93**.

2. S. I. Bin Ahmad, M. S. B. Ahmad and S. Bin Radiman, *Nanoscience and Nanotechnology*, 2009, **1136**, 186-190.
3. N. M. Huang, S. Radiman, H. N. Lim, P. S. Khiew, W. S. Chiu, T. K. Tan, A. Ahmad and H. Idris, *Nanoscience and Nanotechnology*, 2009, **1136**, 191-195.
4. H. R. Liu, W. F. Miao, S. Yang, Z. M. Zhang and J. F. Chen, *Cryst Growth Des*, 2009, **9**, 1733-1740.
5. Z. B. Hai, C. H. Zhu, J. L. Huang, H. R. Liu and J. F. Chen, *Inorg Chem*, 2010, **49**, 7217-7219.
6. Y. B. Zhao, A. H. Chen and S. Liang, *J Cryst Growth*, 2013, **372**, 116-120.
7. A. Torreggiani, Z. Jurasekova, M. D'Angelantonio, M. Tamba, J. V. Garcia-Ramos and S. Sanchez-Cortes, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2009, **339**, 60-67.
8. H. T. Zhao, X. J. Han, L. F. Zhang, G. Y. Wang, C. Wang, X. A. Li and P. Xu, *Radiat Phys Chem*, 2011, **80**, 390-393.
9. H. T. Zhao, B. Zhang, J. S. Zhang, L. F. Zhang, X. J. Han, P. Xu and Y. Zhou, *J Phys Chem C*, 2010, **114**, 21214-21218.
10. H. T. Zhao, X. J. Han, M. F. Han, L. F. Zhang and P. Xu, *Mater Sci Eng B-Adv*, 2010, **167**, 1-5.
11. M. T. Sun, Z. L. Zhang, H. R. Zheng and H. X. Xu, *Sci Rep-Uk*, 2012, **2**, 647.
12. M. Fan and A. G. Brolo, *Phys Chem Chem Phys*, 2009, **11**, 7381-7389.
13. D. He, B. Hu, Q. F. Yao, K. Wang and S. H. Yu, *ACS Nano*, 2009, **3**, 3993-4002.
14. M. T. Sun and H. X. Xu, *Small*, 2012, **8**, 2777-2786.
15. P. Xu, X. Han, B. Zhang, Y. Du and H.-L. Wang, *Chem Soc Rev*, 2014, DOI:10.1039/c1033cs60380f.
16. Y. Y. Xia and H. P. Xiao, *Journal of Raman Spectroscopy*, 2012, **43**, 469-473.
17. P. Xu, S. H. Jeon, N. H. Mack, S. K. Doorn, D. J. Williams, X. J. Han and H. L. Wang, *Nanoscale*, 2010, **2**, 1436-1440.
18. Y. Y. Xia, T. J. Li and J. Chen, *Physical Chemistry Chemical Physics*, 2013, **15**, 11900-11903.
19. C. L. Haynes, A. D. McFarland and R. P. Van Duyne, *Anal Chem*, 2005, **77**, 338a-346a.
20. M. Yang, R. Alvarez-Puebla, H. S. Kim, P. Aldeanueva-Potel, L. M. Liz-Marzan and N. A. Kotov, *Nano Lett*, 2010, **10**, 4013-4019.
21. M. Sun, Z. Zhang, P. Wang, Q. Li, F. Ma and H. Xu, *Light: Science & Applications*, 2013, **2**, e112.
22. P. Xu, B. Zhang, N. H. Mack, S. K. Doorn, X. J. Han and H. L. Wang, *J Mater Chem*, 2010, **20**, 7222-7226.
23. P. Xu, X. Han, B. Zhang, Y. Du and H.-L. Wang, *Chem Soc Rev*, 2014, **43**, 1349-1360.
24. J. L. Marignier, J. Belloni, M. O. Delcourt and J. P. Chevalier, *Nature*, 1985, **317**, 344-345.
25. P. Xu, N. H. Mack, S. H. Jeon, S. K. Doorn, X. J. Han and H. L. Wang, *Langmuir*, 2010, **26**, 8882-8886.
26. W. Y. Li, P. H. C. Camargo, X. M. Lu and Y. N. Xia, *Nano Lett*, 2009, **9**, 485-490.

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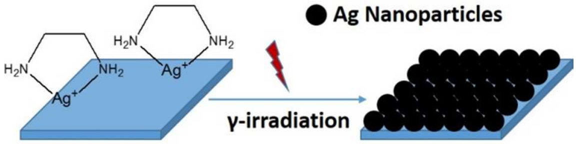

SERS-active Ag nanoparticles are directly fabricated on glass substrates through a Gamma-irradiation induced reduction technique.