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Facile and rapid fabrication of large-scale silver nanoparticles arrays with high SERS performance†

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A simple and fast self-assembly method (within 1 hour) for fabrication of large-scale silver nanoparticles arrays by using ascorbic acid (Vc) as an active reagent was reported. The effect of Vc and deposition time on the performance of these arrays as the SERS-active substrates were systematically studied and the highest enhancement factor (EF) for rhodamine 6G (R6G) was as large as 3.65×10^8 under 532 nm excitation.

Surface-enhanced Raman scattering (SERS), due to the effect of localized surface plasmon resonances (LSPR) originating from the intensified electric fields in noble metal nanostructures,¹ has been widely used as a powerful analysis tool for a variety of research fields ranging from catalysis,²⁻⁴ sensing,² single-molecule detection,^{3,4} and trace analysis⁵ to DNA detection.^{6,7} The shape, size, morphology and their state of aggregation of plasmonic nanostructures are the main parameters to affect their SERS performance.⁸ Molecules adsorbed in these gaps between the nanostructures (usually called electromagnetic hot spots) exhibit several orders of magnitude of SERS intensities than those absorbed on the surface of isolated nanoparticles.⁹ Therefore, in order to obtain excellent SERS performance, decreasing the distance of the gaps between plasmonic nanostructures is very important.

Numerous available approaches for the preparation of SERS substrates have been proposed, such as electron beam lithography (EBL),¹⁰ nanosphere lithography,^{11,12} chemical vapor deposition (CVD)¹³ and so on. Although the precisely shape- and size-controlled nanostructures could be obtained by means of these methods, it usually needs sophisticated devices, thus it is actually expensive for practical applications. Recently, based on the weak interactions such as van der

Waals' force, electrostatic interaction and dipolar interaction, the self-assembly of mono-disperse metal nanoparticles (e.g. nanospheres, nanowires, nanocubes, nanoplates and nanorods) on substrates of glass, ITO or Si has been widely used as substrates for SERS.¹⁴⁻²³ But it is worth noting that self-assembly method usually needs complex preparation processes and specific substrate surface modifications.^{24,25} Therefore, it still remains a great challenge to develop a simple and rapid method of directly self-assembly of large-scale metal nanoparticles into 2D arrays on no-special surface-modified substrates.

Here, we report a facile self-assembly strategy for fabricating silver nanoparticles (AgNPs) arrays on the no-modified surface of silicon wafers with ascorbic acid (Vc) as an active reagent within one hour. The effect of Vc is to facilitate AgNPs to self-assemble on all the surface of silicon wafers.

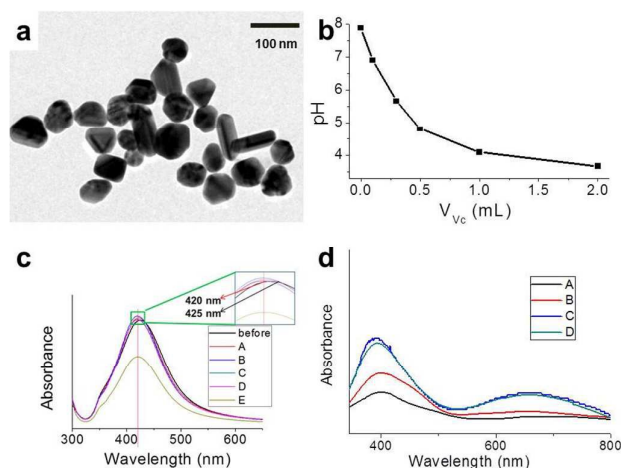


Fig. 1 (a) TEM image of silver nanoparticles reduced by trisodium citrate. (b) The curve graph of the dependence of pH with 0.1 M of Vc's volume in 20 mL silver solution. (c) Absorption spectra of silver colloid under activation with different volume of 0.1 M of Vc added into 20 mL of silver colloid. (before, no Vc; A, 0.1 mL; B, 0.3 mL; C, 0.5 mL; D, 1.0 mL; E, 2.0 mL). (d) Absorption spectrum of AgNPs self-assembled on the glass substrates under activation with different volume of 0.1 M of Vc (A, 0.1 mL; B, 0.3 mL; C, 0.5 mL; D, 1.0 mL).

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An enhancement factor as large as approximately 3.65×10^8 can be obtained with our best as-prepared substrate.

We synthesized silver colloid with trisodium citrate as a reduced reagent according to the chemical synthetic method previously reported (see ESI).²⁶ It is easy to find that most of the nanoparticles in our experimental system are spherical or torispherical with rather narrow size distribution but few are rodlike, which are mixed structures of nanoparticles (Fig. 1a) with an average size of ~ 60 nm.²⁷ The typical process of preparing large scale AgNPs arrays is in the aqueous solution, 0.5 mL of 0.1 M of Vc was added into 20 mL of as-prepared silver colloid under strongly stirring, then silicon wafers were immersed into the Vc-modified silver colloid for 1 h (see ESI†). We find that Vc is the key ingredient (see Fig. S1) for the self-assembly production of large-scale silver nanoparticle arrays because it can modify the surface activity of AgNPs through adjusting the colloidal stability by changing the pH of silver colloid and regulating the electrostatic repulsion potential and the van der Waals attraction potential of AgNPs.²⁸ The activity of silver colloid increases with the volume of Vc, and this promotes the self-assembly of AgNPs on Si/glass substrates. However, if the volume of Vc added are excess too much, the silver colloid can become unstable, which causes AgNPs themselves agglomeration. So appropriate amount of Vc to activate is of great importance to get a better self-assembly AgNPs arrays. Fig. 1b shows the effect of Vc on the pH of silver colloid. At first, the pH of silver colloid decreases fast with increasing the volume of 0.1 M of Vc (0~0.5 mL), then it becomes slowly (0.5~2 mL). After adding 1 mL of Vc, the agglomeration and sedimentation of AgNPs occur (see Fig. S2). This phenomenon indicates that AgNPs are activated by Vc. The UV-vis absorption spectrums in Fig. 1c shows that the λ_{SPR} of AgNPs in solution is 425 nm, and changes a little bit after adding Vc (only from 425 to 420 nm), which means Vc does not alter the optical property.

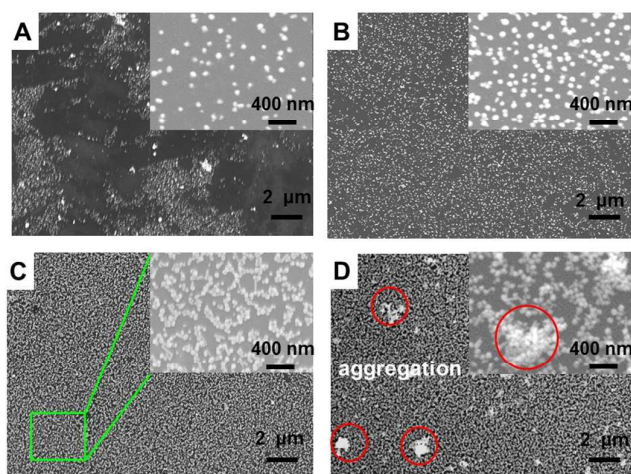


Fig. 2 SEM images of as-prepared AgNPs arrays under activation with different volume of 0.1 M of Vc (A, 0.1 mL; B, 0.3 mL; C, 0.5 mL; D, 1.0 mL; and the inserts: their corresponding high resolution SEM images.).

The influence of Vc on the self-assembly behavior of AgNPs was studied. Four self-assembly substrates were fabricated by immersing silicon wafers into the bottles containing 20 mL of silver colloid activated by adding different amount of Vc for 1 h, which are denoted as A, B, C and D, respectively (A: 0.1 mL, B: 0.3 mL, C: 0.5 mL, D: 1.0 mL). As shown in Fig. 2, AgNPs can easily self-assemble onto the surface of silicon wafers after activation of Vc. The density and uniformity of self-assembly substrate increase correspondingly with the volume of 0.1 M of Vc added into silver colloid (Fig. 2A cf. B cf. C), indicating the increasing activity of silver colloid.²⁸ Besides this, the micro-morphology of AgNPs arrays also varies with the volume of Vc. A few AgNPs link together closely to form nanochain structures on substrate C (Fig. 2C), which are the mainly origin of “hot spots”. That is because chain growth in this case makes the system more stable.²⁸ However, when further increasing the volume of Vc, submicron-sized silver aggregates can be found on substrate D (Fig. 2D) due to the instability of silver colloid. These aggregates possibly reduce the numbers of “hot spots” and make the substrate nonuniform, which are not good for a SERS substrate and reduce the reproducibility of substrate. All these data demonstrate that the self-assembly behavior can be turned conveniently by Vc and appropriate amount of Vc (~ 0.5 mL) can be used to obtain a better self-assembly substrate. It is worth noting that nanochain structures usually show some novel optical properties, such as the local surface plasmonic resonance (LSPR) coupling and more enhanced electromagnetic field. In order to study the effect of the nanochain structures on the optical property of AgNPs arrays, absorption spectrums of substrates A to D assembled on the glass were obtained. As shown in Fig. 1d, substrate A and B exhibit relatively weaker LSPR coupling peak and single peak at about ~ 400 nm, which is different from λ_{SPR} at 425 nm in solution due to the change of surrounding environment refractive index.²⁹ The peak intensity of substrate B is larger than that of A, corresponding with the SEM results (Fig. 2A cf. B). Substrate C and D both exhibit two absorbance bands. One is near 400 nm and the other absorbance band red-shifted to ~ 660 nm. According to the SEM images of C and D (Fig. 2C and 2D), the peak at ~ 660 nm is attributed to the LSPR coupling effect along the axis of the nanochain structures between adjacent AgNPs.³⁰ Should the peak at 400 nm be attributed to two contributions: one is the SPR effect of the individual AgNPs and the other is the LSPR coupling effect perpendicular to the axis of the nanochain structures.³⁰ So the peak intensities at 400 nm of substrates C and D are larger than those of A and B. But the submicron-sized silver aggregates on substrate D (Fig. 2D) seem not to change the LSPR coupling property (Fig. 1, plot C cf. plot D).

Raman spectrum is not only a strongly analytical tool but also an effective testing tool to verify the performance of our self-assembly substrates. R6G, a typical organic molecule as a probe molecule, which was extensively studied in previous literatures,^{31, 32} is chosen to investigate the SERS activities of substrates (experimental details see ESI). Lasers with excitation wavelength of 532 nm and 638 nm³³ were used in our experimental system. There are nine Raman peaks of R6G

with strong scattering intensities at 613, 773, 1128, 1183, 1312, 1365, 1511, 1577 and 1653 cm^{-1} , respectively (Fig. 3).³¹ Peaks at 613, 773 and 1128 cm^{-1} are assigned to the vibrational modes of plane bend of the C-C ring, out-of-plane and in-plane bend of the C-H respectively.³³ The band at 1183 cm^{-1} is due to the C-C stretching vibrations mode.³⁰ While Peaks at 1312, 1365, 1511, 1577 and 1653 cm^{-1} are correspond with aromatic C-C stretching vibrations modes.³² The intensities of R6G at 1365 cm^{-1} were calculated based on peak area through measuring 5 points randomly and averaging them (Fig. 3b and 3d). The intensities of R6G on substrate A to D are strong even under 532 nm excitation with very low power (0.025 mW), mainly because of the Surface-Enhance Resonance Raman scattering (SERRS) effect of R6G.³⁴ The intensity of R6G on C is a little larger than that of A and B due to the contribution of "hot spots" originating from the LSPR coupling in silver nanochain structures of C between the neighboring nanoparticles.³⁰ While the intensity of D is less than C, A likely

reason is that the submicron-sized silver aggregates of D decreases the number of "hot spots", thus weaken the intensity. However, when the excitation source with a wavelength of 638 nm, which is closer to the LSPR coupling peak of nanochain structure (660 nm) compared with that of 532 nm, is used to test R6G, the intensities of C and D are much higher than those of A and B (Fig. 4d), indicating that LSPR coupling enhancement effect of AgNPs plays the main role on the contribution of SERS intensity. The SERS performance analysis of substrates are completely consistent with their SEM result.

To investigate relationship between the self-assembly time of substrates and their SERS performance, the substrates with self-assembly time of 0, 15, 30, 60 min were prepared (see Fig. S4). The density of substrate increases fast with time (see Fig. S5), and the SERS intensity of R6G also increases (see Fig. S6). It is noting that when the self-assembly time of AgNPs is over 1 h, the SERS intensity of R6G almost remains the same even increasing self-assembly time (Fig. 4), indicating that AgNPs could not assemble onto the substrate surface because of the electrostatic repulsion between AgNPs. The result shows that the activation of Vc makes the self-assembly of AgNPs on silicon wafer fast (within 1 h), which greatly shorten the self-assembly time compared with the previous literature (~ several days).²⁵ The proposed self-assembly strategy has advantages of easy preparation, low cost, simpleness, fast and large-scale self-assembly area. It has great potential in realizing industrial application.

Our as-prepared SERS substrate C has a high sensitivity which can detect R6G solution down to 10^{-8} M (see Fig. S7). To further demonstrate the performance of the SERS substrate, the enhancement factor (EF) of the substrate C was calculated by using the method reported by Van Duyne.³⁵ The formula of EF is defined as follows:

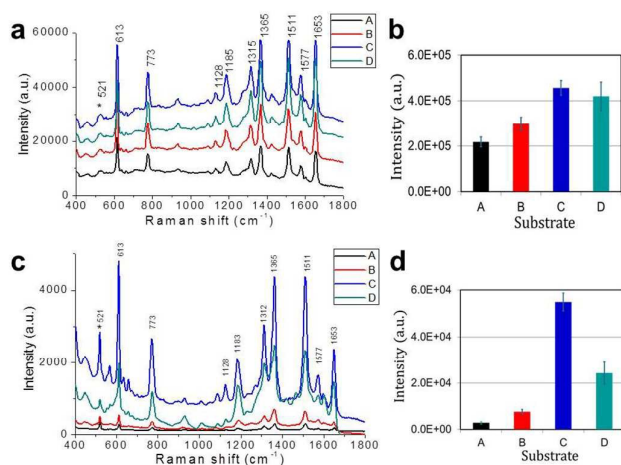


Fig. 3 SERS spectra of 10^{-5} M of R6G absorbed on as-prepared substrates A, B, C and D with excitation wavelength of (a) 532 nm (laser power: 0.025 mW, exposure time: 5s) and (c) 638 nm (laser power: 0.24 mW, exposure time: 1s), symbol "." express the peak of Si. (b) and (d) are intensities of the Raman band of R6G at 1365 cm^{-1} respectively.

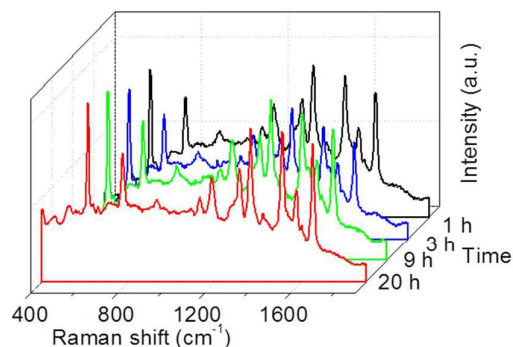


Fig. 4 SERS spectra of R6G with different self-assembly time under 532 nm excitation.

Table 1 Enhancement factor (EF) comparisons of SERS substrates for different fabricating methods.

Materials	Substrates	Fabricating methods	The order of magnitude of EF for R6G	Reference
Ag/SiNW	Si	Nanosphere lithography and chemical etching	10^6	36
AgNPs	Ti foil	Pulsed laser deposition	10^6	37
AgNPs	Glassy carbon	Self-assembly	10^6	38
AuNPs	Glass	Self-assembly	10^6	30
AgNPs	Si	This paper	10^8	

$$EF = \frac{I_{\text{SERS}} \times N_{\text{Raman}}}{N_{\text{SERS}} \times I_{\text{Raman}}} = \frac{I_{\text{SERS}} \times N_{\text{Raman}} \times P_{\text{Raman}} \times T_{\text{Raman}}}{N_{\text{SERS}} \times I_{\text{Raman}} \times P_{\text{SERS}} \times T_{\text{SERS}}}$$

Where N_{Raman} and I_{Raman} are the number of absorbed analyte and peak intensity of the Raman signal for the regular Raman measurement with 10^{-3} M R6G solution on the silicon wafer, respectively; N_{SERS} and I_{SERS} are the number of absorbed analyte, i.e., 10^{-7} M R6G used in this experiment (see Fig. S8) and peak intensity for SERS measurement, respectively; P and T are the corresponding laser power and exposure time respectively. This calculation is based on the fact that the intensity of SERS is proportional to the number of molecules under otherwise equal conditions. Here, we used the concentration take place of the number of R6G absorbed on the substrate approximately by making the experimental condition same. The EF obtained from substrate C is 3.65×10^8 , which is two orders of magnitude larger than other methods reported in the literature (Table 1).^{30, 36-38} Besides the high sensitivity, the reproducibility of SERS substrate is also of great importance. The uniform nanostructure and homogeneous spatial distribution of the electric field of the array can get improved reproducibility.³⁹ To test the reproducibility of the substrate C, SERS spectrums of R6G molecules with a concentration of 10^{-7} M from ten random-selected places on self-assembly AgNPs arrays were collected under identical experimental conditions (see Fig. S9). The relative standard deviation (RSD) of substrate C at 1365 cm^{-1} is about 8%, indicating a good reproducibility. These results declare that our as-prepared self-assembly substrate has excellent SERS performance.

In conclusion, we report a facile and fast self-assembly method to deposit AgNPs on silicon wafer substrate without any modifying and sophisticated surface-pretreatment by using Vc as an active reagent. Self-assembly density and uniformity of AgNPs could be conveniently adjusted by Vc. The nanochain structure of AgNPs arrays exhibits excellent SERS signals, and shows an excellent EF as high as 3.65×10^8 . The whole self-assembly process of AgNPs only need 1 hour, which greatly shorten the fabricating time. This proposed approach provides a rapid, effective, inexpensive, reproducible, and facile method for preparing high-quality SERS substrates. Furthermore, our proposed self-assembly strategy has a tremendous potential for practical applications in organic and inorganic pollutants detection. Our next work will devote ourselves to fabricate more uniform nanoparticles and develop some easily versatile self-assembly strategies by using this idea.

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Facile and rapid fabrication of large-scale silver nanoparticles arrays with high SERS performance

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A facile and rapid self-assembly method for fabricating high performance SERS substrate was reported here by using ascorbic acid as an active reagent.

