

# **Synthesis of monodisperse silver nanoparticles and application of its film for surface-enhanced Raman scattering**

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**Abstract:** Two-dimensional (2D) arrays of metal nanoparticles on substrates are of increasing interest for use in catalysis, sensors, information storage, optics, biological technologies, electrical properties and other areas. It is well known that silver nanoparticle film is one of the best candidates for application of surface-enhanced Raman scattering (SERS) substrates. And it is crucial to develop a convenient process to construct a 2D Ag nanoparticle film with excellent SERS enhanced ability and reproducibility. We presented a simple method involving “seeding growth” to prepare monodisperse Ag nanoparticles with controllable size and morphology. The size, structure and composition of the Ag nanoparticles were characterized by UV-vis spectra, transmission electron microscopy and X-ray diffraction. The as-prepared Ag nanoparticles were used to fabricate nanostructured films by the self-assembly procedure, and the resulting nanostructured film showed excellent SERS enhanced ability and reproducibility. The current research will provide new opportunities for the potential applications of such film in the extension of novel SERS.



## Statement of Originality

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## **1. Introduction**

Recently, two-dimensional (2D) arrays of metal nanoparticles on substrates are of increasing interest in catalysis, sensors, information storage, optics, biological technologies, electronics and other areas [1-5]. For example, it is known that silver nanoparticle film is one of the best candidates for application of surface-enhanced Raman scattering (SERS) substrates [6-8]. Due to its unique spectroscopic fingerprint, high sensitivity, and nondestructive data acquisition, SERS has been intensely explored as a powerful and extremely sensitive analytical technique with wide potential applications in biochemistry, chemical synthesis, environmental monitoring, and food safety [9-11]. To obtain a high-performance SERS substrate, monodisperse Ag nanoparticles with controllable size and morphology are required since the functional properties of nanostructured film are largely determined by the size, morphology, and surface properties of the nanoparticles within the thin film [12-14]. Consequently, the development of a new method to prepare nanoparticles with tailored properties will be central to the exploitation of a nanostructured film [15]. Up to now, a great deal of effort has been put into perfecting methods of preparing monodisperse silver nanoparticles. However, previous procedure resulted in silver nanoparticles with a wide range of size and morphology. The synthesis of monodisperse Ag nanoparticles with controllable size and morphology is still a significant challenge.

In this report, we present a simple method involving “seeding growth” to prepare monodisperse Ag nanoparticles with controllable size and morphology [16,17]. Its 2D films are fabricated using a self-assembly technique to deposit nano-scale Ag particles on a chemically modified glass substrate [18]. It has been found that a well-defined and uniform nanometer-scale architecture of Ag nanoparticle film is

formed. The Ag nanoparticle film is employed as a SERS-active substrate, which exhibits good performance in terms of high sensitivity and good reproducibility.

## 2. Experimental section

### 2.1 Chemicals

(3-Aminopropyl) trimethoxysilane (APTMS), AgNO<sub>3</sub>, poly (vinyl pyrrolidone) (PVP, average molecular weight 55,000), and ascorbic acid were purchased from Aldrich. NaBH<sub>4</sub> and sodium citrate were obtained from Sigma. H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub> (30%), and absolute ethanol were purchased from Beijing Chemical Reagents Industry. All chemicals were supplied and used without further purification. Doubly distilled water was used throughout the experiment.

### 2.2 Synthesis of Ag nanoparticles and construction of its 2D film

Silver seeds (4 nm) were prepared according to the method of NaBH<sub>4</sub> reduction [19]. At room temperature, 0.2 g PVP and 0.05 g AgNO<sub>3</sub> were completely dissolved into 100 ml water. Next, 2 ml Ag seed solution was added. And then an excess amount of ascorbic acid (100 mM, 5.0 ml) was added to the solution while stirring. The color of the solution changed to a gray-green color of silver colloids, suggesting the formation of silver nanoparticles. The silver nanoparticles were purified by centrifugation at 4000 rpm for 10 min and washed with deionized water and ethanol several times. The size of the resulting Ag nanoparticles can be controlled by a proper combination of the seeds and initial reaction solution.

The glass substrate was cleaned in a bath of 3 parts H<sub>2</sub>SO<sub>4</sub> to 1 part 30% H<sub>2</sub>O<sub>2</sub> at 70 °C (Piranha solution). It was then rinsed with water and absolute ethanol, and subsequently placed into a dilute solution of 3-aminopropyltrimethoxysilane (APTMS: 0.3 ml APTMS in 3 ml C<sub>2</sub>H<sub>5</sub>OH) for 1 hour, again rinsed with water and ethanol. After being dried with N<sub>2</sub>, the APTMS-coated substrate was then immersed in 10 ml of dilute silver colloids for 6 hours. Prior to use, the glass with Ag nanoparticle film was thoroughly rinsed with water.

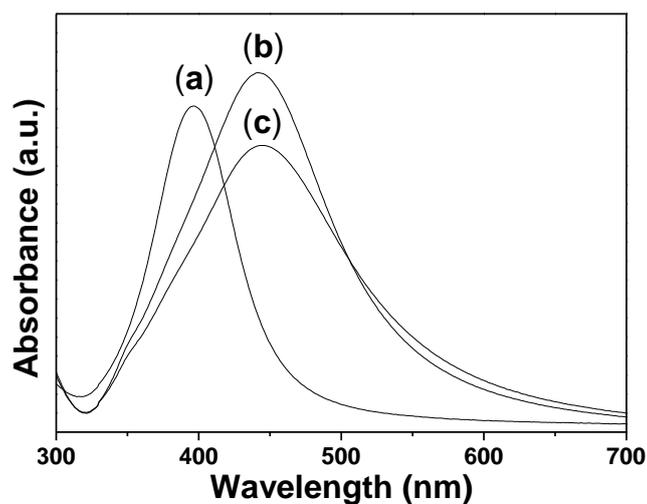
### 2.3 Characterization

The UV-vis absorption spectra were measured using a Perkin Elmer spectrophotometer (Lambda 7). The crystal structure of the Ag nanoparticles was investigated by powder X-ray diffraction (XRD, D/max 2000, Rigaku, CuK $\alpha$  radiation). The sample for XRD was prepared by adding the condensed colloid to glass substrates and being left to air-dry. The size distribution of nanoparticles was characterized by TEM on a JEOL 2000-FX transmission electron microscopy at 200 KV. The sample for TEM was prepared by placing a drop of the solution onto a carbon-coated copper grid and evaporating it in the air at room temperature. The morphology of the film was measured on an atomic force microscope (AFM, Mader 2000) with the tapping mode.

20  $\mu$ l of solution containing 1  $\mu$ M Rhodamine 6G (R6G) was drop-coated onto the surface of the glass substrate with a Ag film. After 25 min, the substrate was dried under a stream of nitrogen. For comparison, 2 ml of colloidal Ag solution were placed in a 1 cm path length quartz cuvette and the solution of R6G was added, resulting in a final R6G concentration of 1  $\mu$ M. Raman spectra were measured with a Renishaw 1000 model confocal microscopy Raman spectrometer and the radiation wavelength is 514.5 nm in ambient air.

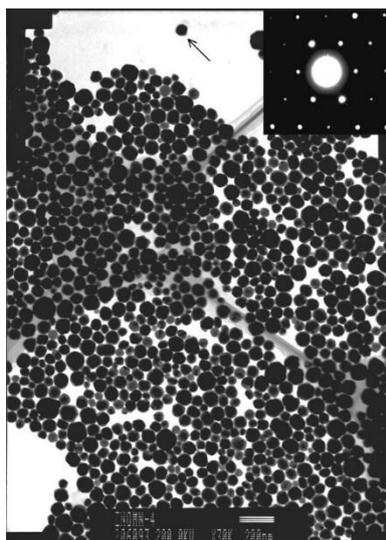
### 3. Results and discussion

Silver colloid with an average diameter of 4 nm was prepared by the NaBH<sub>4</sub> reduction [19], and then these small silver nanoparticles were used as seeds to prepare large Ag nanoparticles [20]. The as-prepared samples were characterized by UV-vis absorption spectroscopy, X-ray powder diffraction and transmission electron microscopy.



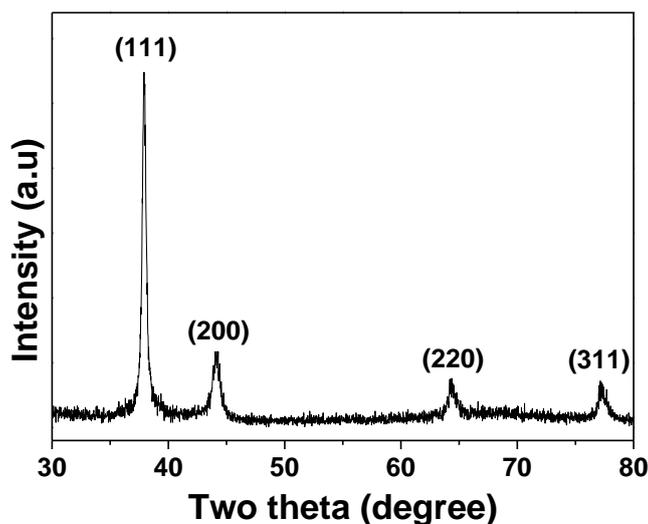
**Figure 1.** UV-vis absorption spectra of (a) 4 nm Ag seed, (b) Ag nanoparticles, and (c) Ag nanoparticle film.

Figure 1 showed the UV-vis absorption spectra of silver nanoparticles (As-Prepared Sample), silver nanoparticle film, and the seed solution itself. Generally, silver nanoparticles with diameters below 5 nm have a high-absorption band with a maximum at about 400 nm [21]. In this case, the absorption band located at 396 nm can be exclusively attributed to plasmon resonance of silver seed particles (Figure 1a). With the increase of particle size, the plasmon band will be broadened and red-shifted to higher wavelength (Figure 1b) [22]. As seen from Figure 1c, the plasmon band became even broader and a little red-shifted after silver nanoparticles were fabricated into a 2D film.



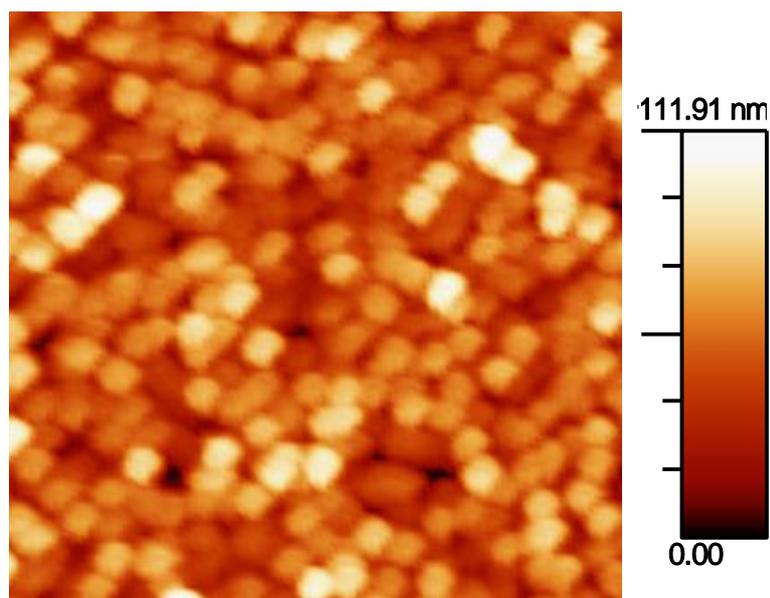
**Figure 2.** TEM image of the Ag nanoparticles. The inset shows the diffraction pattern recorded by aligning the electron beam perpendicular to an individual silver nanoparticle (as indicated by an arrow).

The formation of silver nanoparticles was further confirmed by TEM. Figure 2 gives a typical TEM image of the Ag nanoparticles. This image indicates that the Ag nanoparticles are nearly monodispersed. The particles are clearly spherical in morphology and the majority of them are faceted “multiple twinned particles” [23,24]. The inset shows the electron diffraction pattern of the single silver nanoparticles (as indicated by an arrow in Figure 2). An analysis of a large number of Ag nanoparticles yielded an average diameter of 80 nm.



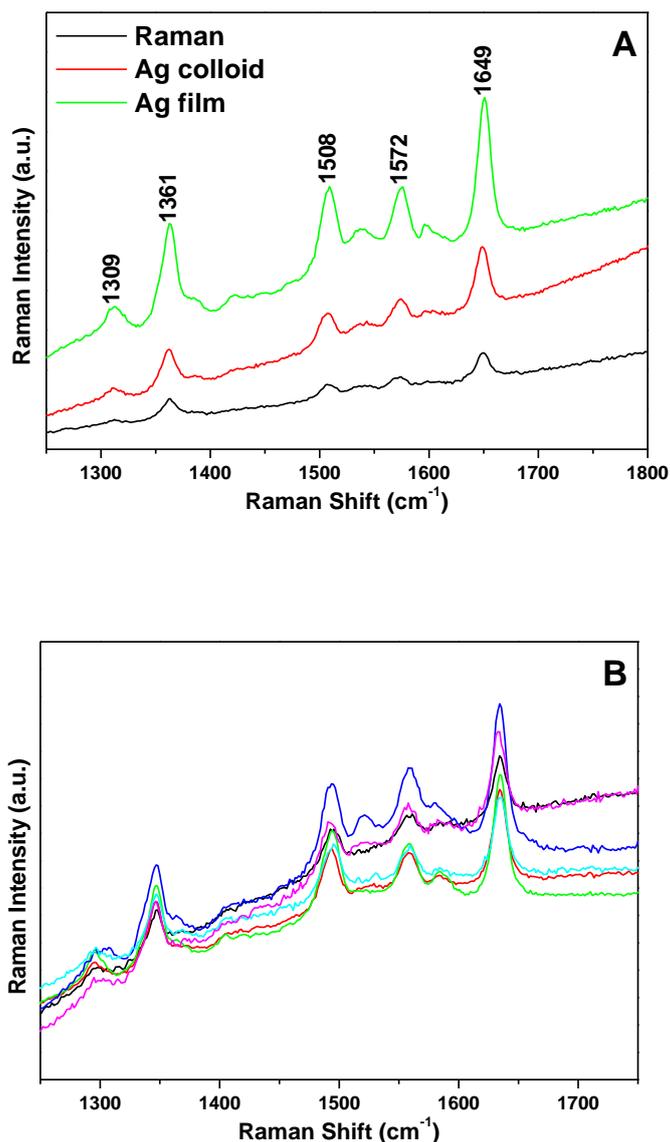
**Figure 3.** A typical XRD pattern of Ag nanoparticles.

A typical X-ray diffraction (XRD) pattern of the silver nanoparticles is shown in Figure 3, and the peaks at 37.9 °, 44.2 °, 64.2 °, and 77.3 ° correspond to the diffractions of (111), (200), (220), and (311) crystal planes of the face-centered cubic (fcc) structure of metallic Ag, respectively. It is worth noting that the ratio between the intensities of the (200) and (111) diffraction peaks is much lower than the conventional value (0.23 *versus* 0.4). The ratio between the intensities of the (220) and (111) diffraction peaks is also much lower than the conventional value (0.098 *versus* 0.25). These results show that the face-centered cubic (fcc) structure of silver metal confers its tendency to nucleate and grow into nanoparticles with their surfaces bounded by the lowest-energy (111) facets [25,26]. The lattice constant calculated from the XRD pattern was 4.108, which is close to the reported data ( $a=4.0862$ , JCPDS file, No. 04-0783).



**Figure 4.** AFM image ( $2\ \mu\text{m} \times 2\ \mu\text{m}$ ) of APTMS-derivatized glass with coverage of colloidal Ag.

The morphology of the Ag nanoparticle film was inspected using tapping-mode AFM atomic force microscope (AFM). The AFM image of silver nanoparticle film prepared on an APTMS-coated glass is shown in Figure 4. As evidenced in the image, the silver nanoparticles are immobilized on the APTMS-modified glass surface and formed a densely-packed nanostructured film. The average particle size is approximately 80 nm, a measurement that is consistent with the TEM result.



**Figure 5.** (A) The normal Raman ( $10^{-3}$  M) and SERS spectra of R6G molecules absorbed on a Ag colloid and its nanostructured film. (B) SERS spectra of R6G molecules collected on the randomly-selected 6 places of the Ag nanostructured film.

The application of the Ag nanoparticle film to surface-enhanced Raman scattering (SERS) substrates was investigated using R6G molecules as a probe molecule. Figure 5A compares the normal Raman and SERS signal intensities of the R6G molecule obtained from the Ag colloidal nanoparticles and its nanostructured film. As observed in the figure, Ag colloid and its nanostructured film all exhibited excellent SERS enhanced ability. Moreover, the nanostructured film on the APTMS-coated substrate shows a significantly stronger SERS signal corresponding to the Raman band for the

R6G molecule relative to the colloid silver solution [18]. It is known from both theory and experiment that closely spaced but physically separated particle arrays can be strongly enhancing. The above results indicate that the nanostructured film presented highly efficient SERS active substrates.

For practical SERS applications, signal reproducibility is one of the essential parameters. To test the signal reproducibility of our sample, SERS spectra of R6G molecules from 6 randomly-selected places on the Ag nanostructured film were collected under identical experimental conditions. As shown in Figure 5B, the Raman spectra of R6G are enhanced greatly at each acquisition point, indicative of good SERS activity and reproducibility of the Ag nanostructured film. However, there are still slight fluctuations in the peak intensities, which may be due to the nonuniform adsorption of R6G molecules on the surface of the Ag nanoparticle film.

#### **4. Conclusion**

In summary, relative monodisperse Ag nanoparticles were prepared by the seeding growth method. And then its high-quality film was fabricated by a self-assembly method, and its application as SERS substrates was investigated. Such nanostructured film exhibits strong SERS enhanced ability and good reproducibility, which can be used as prospective SERS substrates. In addition, such nanostructured film will provide new opportunities for chemical and biological sensing applications.

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