



Facile Interface Self-Assembly of Gold Nanoparticles as Surface-Enhanced Raman Scattering Substrate for Monitoring the Reduction of *p*-Nitrophenol

ZHAOSHUN ZHANG, CHUNYE WEN, FAN LIAO*, LILI ZHU and MINGWANG SHAO*

Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-based Functional Materials and Devices & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215123, P.R. China

*Corresponding authors: Fax: +86 512 65882846; Tel: +86 512 65880953; E-mail: fliao@suda.edu.cn; mwshao@suda.edu.cn

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A facile interface self-assembly method was proposed to fabricate the gold monolayer film without any specific molecular cross-linkers. The film was served as a surface-enhanced Raman scattering substrate, which exhibited high enhancement and reproducibility to the 1×10^{-9} M rhodamine 6G aqueous solution. Based on the substrate, the *in situ* and real-time monitoring for the reduction of *p*-nitrophenol to *p*-aminophenol was demonstrated successfully.

Keywords: Nanoparticles, Interfaces, Self-assembly, Surface-enhanced Raman scattering.

INTRODUCTION

Although infrared¹, UV-visible² and X-ray absorption spectroscopies^{1,3} are techniques for *in situ* monitoring catalytic reactions, the limitations in solvent, chemical information and phase state restrict their applications in various fields. As a powerful analytical technology, the surface-enhanced Raman scattering (SERS) not only eliminates those limitations, but also fulfils all the criteria for monitoring molecular transformations in heterogeneous catalysis due to its remarkable chemical specificity, high sensitivity and excellent surface selectivity⁴.

High sensitivity and reproducibility SERS signals could be achieved by improving the electromagnetic (EM) resonance effect of noble metal nanoparticles (NPs) in the visible and/or near-IR ranges. In order to harvest the SERS substrates with even higher sensitivity and reproducibility, the key point is to induce long range ordering of noble metal nanoparticle nanostructures with clear surface. Therefore, various methods, such as lithography⁵, molecular imprinting⁶, vacuum evaporation⁷, epitaxial growth⁸ and template-based method⁹, have been used to fabricate periodic noble metal nanostructures. Beyond these methods, self-assembly is a simple and effective method to fabricate SERS substrates with two-dimensional structure¹⁰.

At present, the *in situ* and real-time monitoring based on these noble metals SERS substrates has been applied primarily in biology field^{11,12}. Although there are some applications in chemical reactions¹³⁻¹⁵, it is still a challenge to obtain facile

and efficient SERS substrate for monitoring different chemical reactions.

The catalytic reduction of *p*-nitrophenol to *p*-aminophenol is an important industrial reaction¹⁶⁻¹⁸. In this reaction, *p*-nitrophenol, as an environmental pollutant, has potential risks in humans from its carcinogenic and mutagenic properties. Therefore, monitoring this reduction process is crucial both for the synthesis of *p*-aminophenol in industry and the dispose of pollutant in environmental protection¹⁹.

Herein, a simple interface self-assembly method was proposed to fabricate Au monolayer film, which served as SERS substrate with size of 5 mm × 5 mm. The excellent reproducibility of the substrate was demonstrated in the detection of 1×10^{-9} M rhodamine 6G (R6G) aqueous solution. More importantly, it served as a SERS platform to *in situ* and real-time monitoring the reduction of *p*-nitrophenol successfully.

EXPERIMENTAL

All reagents, including sodium borohydride (NaBH₄, 96 %), cetyltrimethyl ammonium bromide (CTAB), *p*-nitrophenol, *n*-hexane and ethanol, were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification.

The size and morphology of the product were examined by transmission electron microscope (TEM, Tecnai G2 F20). The AFM measurement was conducted on a Multimode V system (Veeco, Bruker). Raman spectra were collected on an

HR 800 Raman spectroscope (J Y, France) equipped with a synapse CCD detector and a confocal Olympus microscope. The spectrograph uses 600 g mm^{-1} gratings and a 633 nm He-Ne laser. SERS spectra were collected at $50\times$ objective (Olympus) with a numerical aperture of 0.90 and the accumulation time of 1 s. SERS experiments were conducted in the line-mapping mode and $1 \mu\text{m}$ increment using $1 \times 10^{-9} \text{ M}$ R6G aqueous solution as model molecules.

Preparation of Au and Pt colloid: Gold and platinum colloids were prepared as previous work²⁰. Briefly, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.2 mL, 0.03 M) and CTAB (2 mL, 0.03 M) were diluted with 40 mL deionized water. Then the freshly prepared NaBH_4 solution (0.1 mL, 0.1 M) was added dropwisely and a suspension of Au colloid was obtained after 2 min.

Platinum colloid was prepared similar to Au colloid. $\text{HPtCl}_4 \cdot 3\text{H}_2\text{O}$ (0.4 mL, 0.02 M) and CTAB (4 mL, 0.01 M) were diluted with 40 mL deionized water. With the addition of fresh NaBH_4 solution (0.4 mL, 0.1 M), a suspension of Pt colloid was obtained.

Preparation of the Au monolayer film: The as-prepared Au colloid was added into a 50 mL beaker and then hexane (5 mL) was added in to produce a hexane/water interface. When ethanol (1 mL) was added to the interface slowly, the Au colloidal spheres were immediately trapped at the interface. After most of the hexane at the top of the vessel was carefully removed by syringe, the densely packed film was transferred to a Si wafer and then dried at room temperature to obtain an Au monolayer film. The Au monolayer film was calcined in Mufe furnace at $400 \text{ }^\circ\text{C}$ for 20 min to remove the surfactant.

In situ monitoring process: The *in situ* monitoring the reduction of *p*-nitrophenol included the following steps: Firstly, Pt colloid (0.1 mL), *p*-nitrophenol (0.2 mL, 10^{-3} M) and distilled water (0.7 mL) were mixed well to obtain aqueous solution. Then, the Au monolayer film on Si wafer was put into a groove containing the above mixed solution. After the NaBH_4 aqueous solution (0.08 mL, 0.01 M) was added into the above system, the SERS signals were collected per minute interval.

RESULTS AND DISCUSSION

As observed from the TEM image in Fig. 1, Au NPs are quite small with diameter in the range of 5-10 nm.

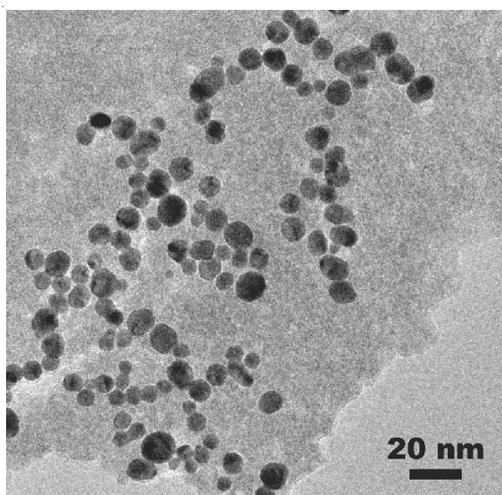


Fig. 1. TEM image of Au colloid prepared freshly

The assembly of Au colloids to film at the oil-water interface was illustrated in Fig. 2. Gold colloids are trapped at the oil-water interface by using ethanol as an inducer at first. An appropriate quantity of ethanol was beneficial to the formation of a perfect film for it could decrease the surface charge of the nanoparticles²⁰. In this process, the Au NPs moved to the interface and were incompactly trapped there. With the evaporation of hexane, the contact area between hexane and water decreased. The surface pressure from interfacial tension at the hexane/water interface compressed the interfacial colloid into a close-packed structure, which was the driving force to ordered monolayer film.

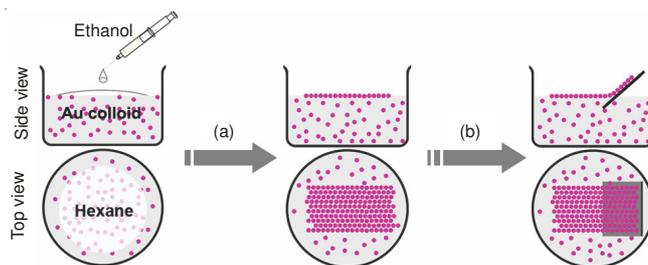


Fig. 2. Schematic representation of the fabrication of well-arranged Au monolayer film: (a) nanoparticles assemble into a monolayer film after most of hexane and ethanol have evaporated, and (b) the assembled Au monolayer film was easily transferred onto Si wafer

The surfactant was indispensable in regulating the morphology and size of the Au NPs. Yet, it had a negative effect on the SERS detection. Therefore, thermal treatment was introduced to remove the surfactant and obtain bare Au NPs film.

The temperature of thermal treatment was critical for the strong and uniform SERS signal, which was determined by two factors. First, CTAB should be removed completely at this temperature to obtain clean surface of Au NPs. The second was to lower the mobility of Au NPs on Si substrate. According to the eutectic point ($360 \text{ }^\circ\text{C}$) of Au-Si system²¹, Au-Si alloy layer can form on the interface of two phases at the temperature of $400 \text{ }^\circ\text{C}$ ²². The formed Au-Si alloy layer made the Au NPs fixed firmly on the surface of Si wafer, preventing the aggregation and growth of Au NPs during the SERS testing. When the temperature was above $430 \text{ }^\circ\text{C}$, the covalently bonded Au-Si alloy would form. The surface electrons oscillation was restricted, which hindered the EM field coupling on the surface of Au NPs and decreased the SERS signals.

Fig. 3 shows the AFM images of Au monolayer film after $400 \text{ }^\circ\text{C}$ annealing treatment, revealing a large-scale assembly of uniform, well-arranged and closely-packed Au NPs.

The annealed Au monolayer film was served as SERS substrate, employing R6G as the probe molecule, owing to its well-established vibrational characteristics. The substrate was first immersed in a $1 \times 10^{-9} \text{ M}$ R6G aqueous solution for 5 h and taken out. After dried, the substrate was used for SERS detection.

The Au monolayer film yielded high SERS activity as shown in the upper part of Fig. 4. The Raman spectrum shows the intense peaks of R6G's main vibrational features of carbon skeleton stretching modes at 1366 , 1512 , 1580 and 1653 cm^{-1} , which are similar to those of the normal Raman spectrum²³. It

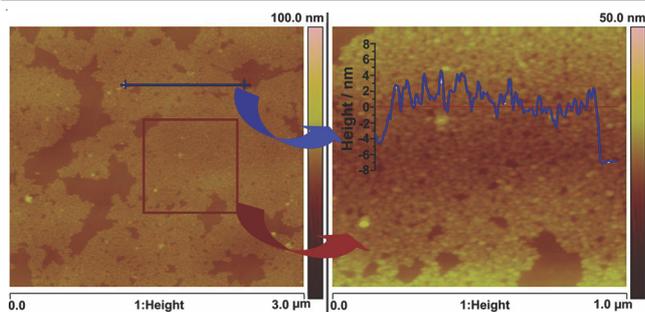


Fig. 3. AFM images with different magnifications of the Au monolayer film after calcination showing the large-scale and uniform Au assembly: (a) in a low magnification, and (b) in a large magnification

is worth noting that there was also a band centered at 1130 cm^{-1} , which was barely observed in the normal Raman spectrum. The appearance of this band proved the enhancement effect of the substrate⁸. The lower part of Fig. 4 is a contour map of the SERS signals conducting under line scanning mode at intervals of $1\text{ }\mu\text{m}$. In all 90 points, each point exhibited a favourable enhancement of the Raman signal, demonstrating the high reproducibility of the SERS signals on the Au monolayer film substrate.

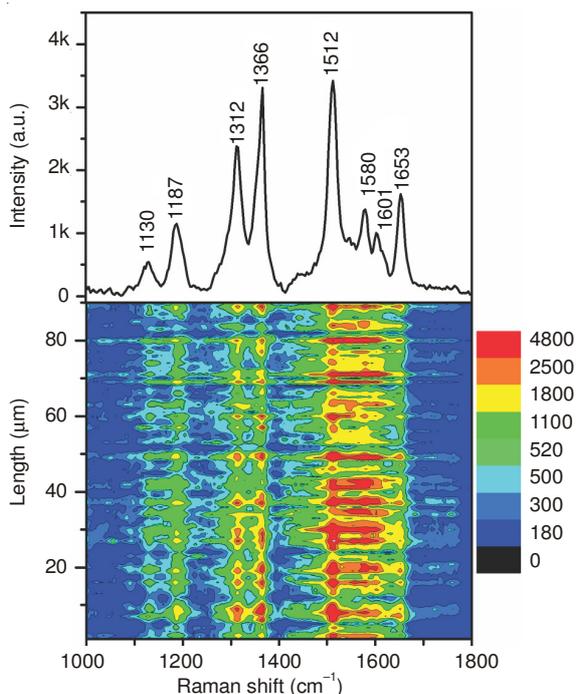


Fig. 4. Raman spectra of R6G aqueous solution ($1 \times 10^{-9}\text{ M}$) on the Au monolayer film substrate (upper part) and the SERS contour (lower part)

According to the excellent SERS behaviour, the Au monolayer film was taken as SERS substrate to monitor the reduction process of *p*-nitrophenol. For starting the catalytic reaction, $80\text{ }\mu\text{L}$ 0.01 M aqueous NaBH_4 solutions were added to the suspension containing Pt NPs and *p*-nitrophenol. The corresponding SERS spectra were recorded immediately. The spectra were collected per minute interval, as shown in Fig. 5. The nitril C-N stretching vibration band at 1330 cm^{-1} was monitored during the reaction^{24,25}. With increasing reaction time (Fig. 5), the intensity of the band at 1330 cm^{-1} lowered

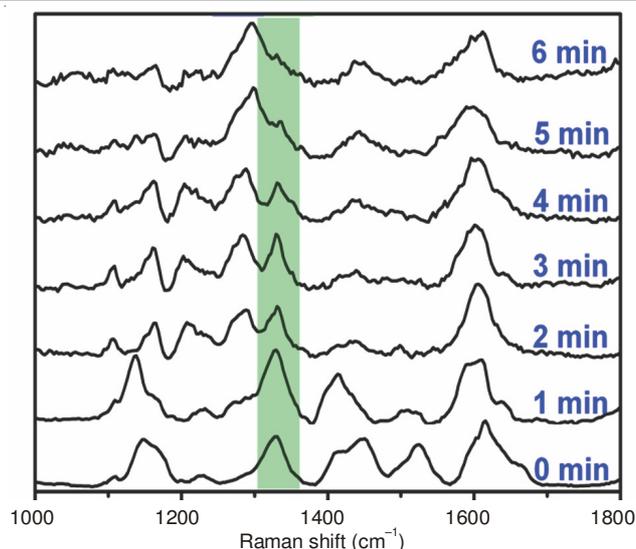


Fig. 5. Raman spectra of reduction of *p*-nitrophenol monitored in real time

gradually and almost disappeared after 6 min, indicating the complete reduction of *p*-nitrophenol. The obtained results confirmed that the SERS substrates might be employed to monitor other chemical reactions.

Conclusion

In summary, Au monolayer films were fabricated using simple interface self-assembly method without specific molecular cross-linkers. The films served as SERS substrates in the detection of $1 \times 10^{-9}\text{ M}$ R6G, which exhibited large Raman enhancement and high reproducibility. Taking the SERS substrate as a detection platform, the *in situ* and real-time monitoring for reduction process of *p*-nitrophenol was achieved, indicating the high sensitivity and practicability of the Au monolayer film substrate.

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