



Gold nanoparticle substrates for recyclable surface-enhanced Raman detection of Rhodamine 6G and Sudan I

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ABSTRACT

Excellent and recyclable surface-enhanced Raman scattering substrates were fabricated via a one-step route: reducing gold ions to Au nanoparticles with silicon–hydrogen bond and assembling them in-situ on the Si wafer. Gold nanoparticles with the average size of 22 nm were epitaxially grown and uniformly assembled. The substrate exhibited excellent surface-enhanced Raman effect in the low concentration detection (1×10^{-10} M) of Rhodamine 6G with relative standard deviation of <20%, and sustained stable enhancement efficiency in the recycle usage. The substrates were also employed to detect Sudan I dye with distinguished sensitivity and uniformity. More significantly, these substrates kept Au nanoparticles from growing larger during the Raman detection, compared with the conventional substrates, indicating it was a meaningful possibility for the practical applications.

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1. Introduction

Surface-enhanced Raman scattering (SERS) was first discovered in the late 1970s [1], which showed an enhanced Raman signal of molecules near roughened noble metal surface. In many cases, the SERS substrates are composed of a layer of noble metal particles, Au, Ag, Cu, which are the basis of enhancement [2].

Noble metal nanoparticles (NPs), together with their strong plasmon resonance, are expected to lead to self-assembly with a range of practical applications. The assembly has been of tremendous interest to material fields because it provides effective building blocks for various applications [3–6].

In the assembly, highly ordered arrangement generally induces an excellent enhancement through localized surface plasmon resonance and is distinctly different from those of the corresponding isolated NPs [7–9], which are necessary for SERS experiments [10]. This is because neighboring NPs can affect the resonance frequency in a distance-dependent manner, allowing electromagnetic energy to propagate along arrays [11,12].

During the past few years, various methods have been developed for the assembly of noble metal NPs into SERS substrates, such as, electron beam lithography [10,13], Langmuir–Blodgett ways [14,15], electrostatic actions [16], chelating agent assistance [17], anodic aluminum oxide template [18], DNA functionalized techniques [19,20], polymer-

mediated methods [21–23], capillary-assisted route [24,25], organic-monolayer assisted way [26], and colloidal monolayer routes [27], which have been used as sensitive SERS substrates.

The high enhancement factors associated with assembly was explained with the simulations. Simulations showed that the enhancement was closely associated with particle size, shape, interparticle separation [28], and the fractal structure [29].

In the fabrication of the practical SERS substrates, various difficulties have been encountered: (1) the sensitivity, uniformity, reproducibility, and stability of the substrates were often unsatisfactory; (2) the fabrication was usually time-consuming and needed two or more steps [30]; (3) some substances, such as surfactants, organic compounds, polymers, or biomaterials, were added and remained on the substrates, which is harmful to the SERS [31]; (4) the substrates with large effective area were hard to prepare [24]; (5) most of the substrates were disposable and not reusable [31]; and (6) the noble metal nanoparticles on conventional substrates were apt to agglomerate and grow large under strong laser irradiation during the SERS detection.

In this work, a fast one-step route to the Au NP assembly without any templates or surfactant was reported. The method was conducted at room temperature within a few seconds. The average size of Au NPs was easily controllable below 30 nm. These substrates exhibited satisfactory sensitivity, uniformity and stability in the SERS detection of Rhodamine 6G (R6G) and Sudan I dye (SDI). Also, they were capable of being re-used without obvious SERS enhancement decline. All the above-mentioned points indicated that these substrates were suitable for practical detection.

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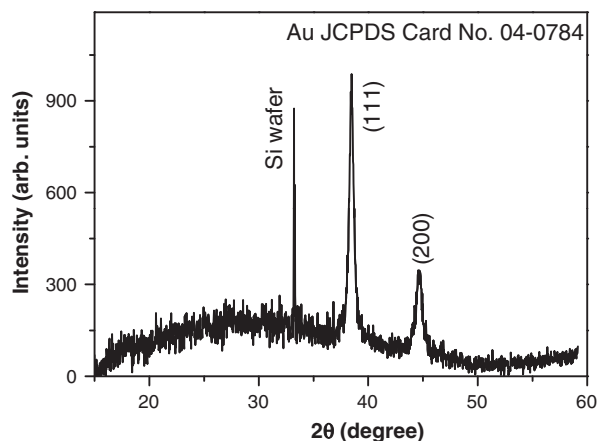


Fig. 1. XRD pattern of Au NPs on Si wafer.

2. Experimental section

2.1. Materials and methods

All chemicals were analytical reagent with purity greater than 99.7%. They were purchased from Shanghai Chemical Company and used without further purification. The water used was doubly distilled water. Silicon wafers (p type, $0.01\text{--}0.05\ \Omega\cdot\text{cm}$) were purchased from Hefei Kejing Materials S2 Technology Co., Ltd. (China).

The Si wafer was cut into $1\ \text{cm} \times 1\ \text{cm}$ in size and cleared as follows: the cut Si wafer was cleared sequentially with acetone (5 min), ethanol (5 min), $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (3:1 H_2SO_4 (97%)/ H_2O_2 (30%), 10 min), and water (2–3 times). Then, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.0394 g, 1×10^{-4} mol), 10 mL distilled water and 5 mL 4% HF solutions were mixed in a Teflon beaker at room temperature. The cleared Si wafer was put into the above solution for just 2 s, taken out, rinsed with distilled water, and dried at room temperature. Then a dense and well-ordered Au NP array was grown and assembled on the Si wafer.

2.2. Characterization

The as-prepared products were characterized via X-ray powder diffraction (XRD), which was performed with a Philips X'pert PRO MPD diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15406\ \text{nm}$). A scanning rate of 0.05°s^{-1} was applied to record the pattern in the 2θ range of $10\text{--}60^\circ$. The morphology of the samples was captured by scanning electron microscopy (SEM) with a FEI Quanta 200F SEM spectrometer operating at an accelerating voltage of 30 kV. Atomic force microscope (AFM) measurement was conducted on a Multimode V system (Veeco, Bruker).

Samples were scanned with antimony (n) doped Si tips ($2.75\ \mu\text{m}$, SCM-PIT, Veeco Metrology) with the coating of 20 nm PtIr. The cantilevers have a spring constant (k) of 2.8 N/m, and resonance frequency of 75 kHz. The topological data was recorded under tapping mode, at a driving frequency of 72.2 kHz.

2.3. SERS of the noble metal assembly

Raman spectra were collected with an HR 800 Raman spectroscopy (J Y, France) equipped with a synapse CCD detector and a confocal Olympus microscope. SERS experiments were conducted in the line-mapping mode and $1\ \mu\text{m}$ increment using R6G methanol solution as model molecules. The spectrograph used 600 g/mm gratings. SERS spectra were collected at $100\times$ objective (Olympus) with a numerical aperture of 0.90 and the accumulation time of 1 s. In addition, the filter in the SERS spectra was D0.6. And a 633 nm He–Ne laser was employed in all the Raman detections.

3. Results and discussion

3.1. Characterization of Au, Ag or Cu NP assembly on Si wafer

The XRD pattern of Au NPs in-situ growing on Si wafer is shown in Fig. 1. In addition to the diffraction peak of Si, the other peaks may be indexed as (111) and (200) crystal planes of Au (JCPDS Card No. 04–0784).

Fig. 2a shows its low magnification SEM image, revealing a large scale and uniform assembly of Au NPs. And the large magnification image (Fig. 2b) shows that the Au NPs are well distributed in an orderly manner on the silicon wafer. Also, measured by the AFM images (Fig. 3a), the average diameters of Au NPs are 22 nm with a density of 248 NPs per square micrometer.

The assembly of Au NPs may be explained as follows: Si wafer is covered with an oxide layer, which may be easily removed by HF solution. The wafer was then intensively covered with hydrogen atoms (Si–H bond), which have the ability to reduce noble metal ions [32]. Therefore, gold ions may be reduced, and well-ordered Au NPs were grown in-situ and assembled on the Si wafer.

This Si–H bond assembly may produce uniform array on Si wafer. In addition, it is uncomplicated, low-cost to be operated and controllable with few contaminations. More importantly, the Au NP assembly could be employed as SERS substrate and exhibited excellent behavior.

3.2. SERS of Au NP assembly

To evaluate the SERS of Au NP assembly, Raman spectra were collected using R6G as the probe molecule because of its well-established vibrational features.

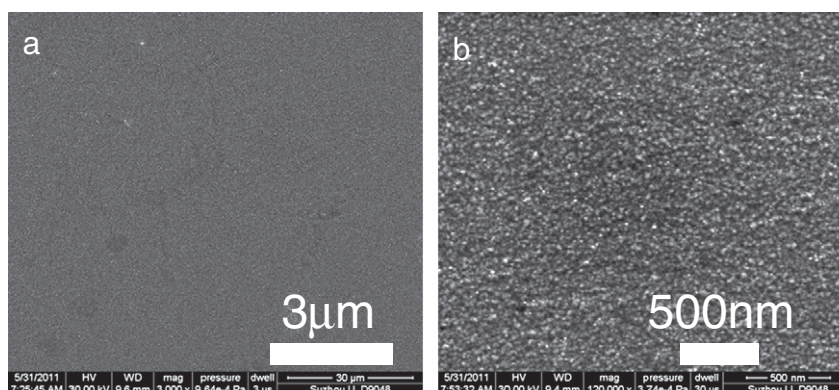


Fig. 2. Au NPs growing on Si wafer: SEM images (a) in a low magnification, and (b) in a high magnification.

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