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# Copper Nanoparticles Grafted on a Silicon Wafer and Their Excellent Surface-Enhanced Raman Scattering

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Copper nanoparticles grafted on a silicon wafer are fabricated by reducing copper ions with silicon–hydrogen bonds and assembling them in situ on the Si wafer. The nanoparticles, with an average size of 20 nm, grow uniformly and densely on the Si wafer, and they are used as substrates for surface-enhanced Raman scattering. These substrates exhibit excellent enhancement in the low concentration detection ($1 \times 10^{-9}$ M) of rhodamine 6G with an enhancement factor (EF) of $2.29 \times 10^7$ and a relative standard deviation (RSD) of <20%. They are also employed to detect sudan-I dye with distinguished sensitivity and uniformity. The results are interesting and significant because Cu substrates are otherwise thought to be poor. These effects might provide new ways to think about surface-enhanced Raman scattering based on Cu substrates.

## 1. Introduction

Surface-enhanced Raman scattering (SERS), a powerful analytic technology, is observed primarily on the surface of coinage metals (Au, Ag, and Cu). These three metals match the plasmon resonance condition very well and are able to produce an efficient SERS effect in the visible and/or near-IR ranges.

Among them, copper substrates have their own unique advantages. Although silver gives the largest enhancement and its surface plasmon resonance condition is reached for a wide range of visible light, silver substrates have been found to be very unstable over time, even if covered with a film of another metal;[1] on the contrary, some copper substrates have been shown to remain steady with time,[2] showing a better SERS than silver substrates. As copper plays a key role in adsorption and electrocatalytic/catalytic reactions, it is particularly suitable

for studying various surface phenomena in these systems, using SERS techniques.[3]

Copper substrates have been thought to have less significant SERS effects, a poor thermal stability, and to be hard to synthesize chemically.[4] In fact, this was a misunderstanding. Suitable copper substrates can exhibit a high sensitivity, as well as good stability and reproducibility. Here, we present a one-step assembly of highly ordered copper nanoparticles (NPs) without any templates or surfactants. The Cu NPs are grown epitaxially on a Si wafer via the reduction of the silicon–hydrogen bond,[5] which keeps them from growing larger under laser irradiation in the SERS detection. The average size of the Cu NPs was 20 nm, and a Si wafer with these NPs attached on its surface was employed as a SERS substrate to detect rhodamine 6G (R6G) and sudan I (SDI). The results show that the prepared substrates performed with a satisfying sensitivity and uniformity.

## 2. Results and Discussion

### 2.1. Characterization of the Au NPs and Au-NP Assembly

**Figure 1**a shows the X-ray diffraction (XRD) pattern of the Cu NPs grown on a Si wafer. In addition to the diffraction peak of the Si, the peaks centered at 43.6 and 50.7° may be indexed as the (111) and (200) crystal planes of Cu (JCPDS 04-0836), respectively.

Figure 1b shows an SEM image of the product, revealing the uniform Cu NPs grown on the Si wafer. In order to determine the size of the Cu NPs, an AFM image (Figure 1c) was captured, showing densely packed Cu NPs with an average diameter of 20 nm.

The assembly of Cu NPs may be explained as follows: a Si wafer usually has a thin oxide layer covering its surface. It would be coated with silicon–hydrogen (Si–H) bonds if the oxide were removed by HF. The silicon–hydrogen bond (Si–H) has the ability to reduce noble metal ions.[5] Therefore, Cu NPs may be grown in situ and assembled densely on a Si wafer. We call this process silicon–hydrogen bond assembly.

This method can result in a uniform assembly up to wafer scale. Furthermore, it is easy to operate and control. More importantly, it was found that the Cu NPs do not aggregate easily or grow larger in the SERS detection, which is key for the excellent sensitivity, stability and uniformity of the substrates.

To evaluate the SERS effect of the Cu-NP assembly, Raman spectra were collected, employing R6G as the probe molecule, owing to its well-established vibrational characteristics.

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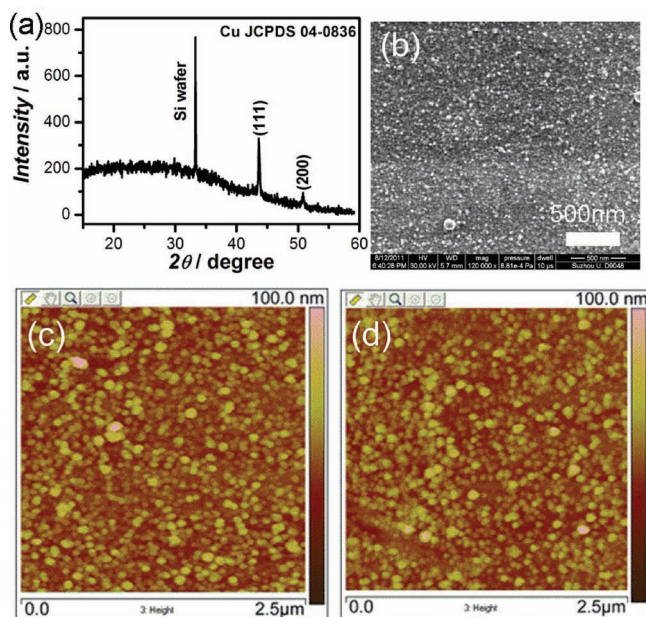E-mail: apannale@cityu.edu.hk

**Figure 1.** a,b) XRD pattern (a) and SEM image (b) of Cu NPs grown on a Si wafer. c,d) AFM images of Cu NPs grown on Si wafer before (c) and after (d) SERS detection.

The substrate was first immersed in a $1 \times 10^{-9}$ M R6G methanol solution for 1 h, and rinsed with ethanol. After drying, SERS detection was conducted. It was interesting to find that the results exhibited an outstanding SERS effect (upper part of **Figure 2**):
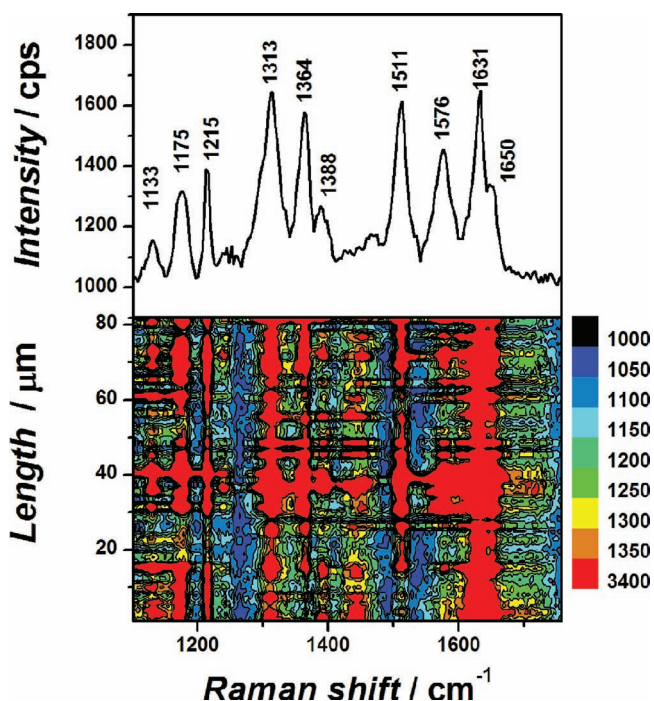


**Figure 2.** The Raman spectrum of an R6G methanol solution ($1 \times 10^{-9}$ M) on a Cu-NP assembly as the substrate (upper part) and the SERS contour (lower part).

the main vibrations of the R6G at 1364, 1511, 1576, 1650 cm$^{-1}$ were present, similar to that described in previous reports.[6] There was also a band centered at 1133 cm$^{-1}$, which was barely observable in the normal Raman spectrum. The appearance of this band proved the enhancement effect of the substrate.

This high SERS activity deserved further investigation, because copper substrates have been regarded as being poor. It is obvious that the excellent activity was beneficial from the large electromagnetic field coupling at the junctions of the NPs.[7] There were about 260 Cu particles in a square micrometer area, based on the AFM image in Figure 1c. The diameter of the laser was calculated to be 0.86 μm, according to the formula:[8] $D = 1.22\, \lambda/NA$, where $\lambda$ is the wavelength of the laser used and NA is the numerical aperture of the objective. Thus, the laser spot covered more than 100 Au NPs ($\pi(0.86/2)^2 \times 260 = 151$), which ensured the sensitivity and reproducibility of the SERS.

The enhancement factor (EF) was calculated based on the peak at 1511 cm$^{-1}$ and Equation (1):[9]

$$EF = \frac{I_{SERS}\, C_0}{I_0\, C_{SERS}} \tag{1}$$

where $C_{SERS}$ and $I_{SERS}$ are the concentration and peak intensity of Raman under SERS conditions, respectively, and $C_0$ and $I_0$ are the concentration and peak intensity of the normal Raman measurement, with a 0.01 M R6G methanol solution on a Si wafer. According to Equation (1), the EF was calculated to be $2.29 \times 10^7$ (($1600 \times 1 \times 10^{-2}$)/($700 \times 1 \times 10^{-9}$) = $2.29 \times 10^7$).

The lower part of Figure 2 reveals the remarked uniformity of the Cu-NP substrate. The SERS contour is plotted after the line mapping, which was conducted spot-to-spot for a $1 \times 10^{-9}$ M R6G methanol solution. In all of the 82 spots, each spot exhibited a favorable capability of enhancing the Raman signal of the R6G molecules.

To assess further the uniformity of these SERS signals semiquantitatively, the relative standard deviations (RSD) of the intensities of the carbon skeleton stretching modes were calculated. The values of the RSD for the vibrations at 1313, 1364, 1511 and 1650 cm$^{-1}$ (**Figure 3**) were 17.4, 18.2, 19.8, and 12.5%, respectively, which proves strongly the uniformity of the substrate.[10] The RSD of the four bands, of less than 20%, demonstrated further that the as-prepared substrate was suitable as a highly sensitive SERS substrate.[11]

For a practical application, the Cu-NP assembly was also used to detect a $1 \times 10^{-9}$ M SDI methanol solution, a harmful dye to DNA, RNA and enzymes.[9] The SERS (**Figure 4**) of the SDI ($1 \times 10^{-9}$ M) using the Cu-NP assembly as the substrate and its RSD values for the vibrations at 1352 and 1381 cm$^{-1}$ (14.5% and 14.3%) (**Figure 5**) verified further the sensitivity and uniformity of the Cu-NP assembly.

It should be pointed out that crystal lattice matching is another critical factor for the SERS effect. Si and Cu both exist in the face-centered cubic phase with crystal parameters of 0.5430 and 0.3615 nm, respectively. A simple proportional relationship between these values exists, $a_{Si}:a_{Cu} = 3:2$, with a lattice mismatch rate of less than 0.14% (($2 \times 0.5430 - 3 \times 0.3615$)/($2 \times 0.5430$) = 0.14%). The above values indicate that the Cu NPs may grow epitaxially on the Si wafer. Epitaxial growth would result in a strong adhesion between the Si wafer and the Cu NPs and prevent the NPs from aggregating or growing larger
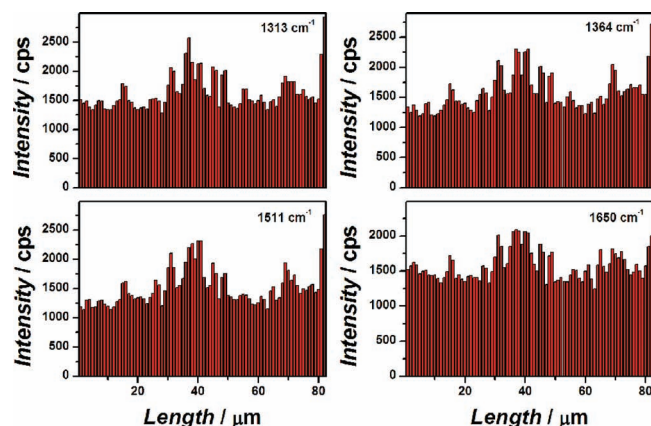
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**Figure 3.** The intensities of the main Raman vibrations of an R6G methanol solution ($1 \times 10^{-9}$ M) at 82 spots, for SERS line-scan spectra collected on the Cu-NP assembly.



**Figure 5.** The intensities of the main Raman vibrations of an SDI methanol solution ($1 \times 10^{-10}$ M) at 82 spots for the SERS line-scan spectra collected on a Cu-NP assembly.

in the SERS detection. In order to confirm this hypothesis, an AFM image of the substrate was captured after SERS detection (Figure 1d); this showed the average diameter of the Cu NPs only increased to 25 nm.

and uniformity. The process was easy to conduct and control. The unexpected results may find practical applications, such as in monitoring the adsorption or catalysis of copper with SERS technology.

## 3. Conclusions

In summary, Si–H-bond assembly is an effective and time-saving route for the growth and assembly of dense and uniform Cu NPs in situ on a silicon wafer, exhibiting excellent sensitivity
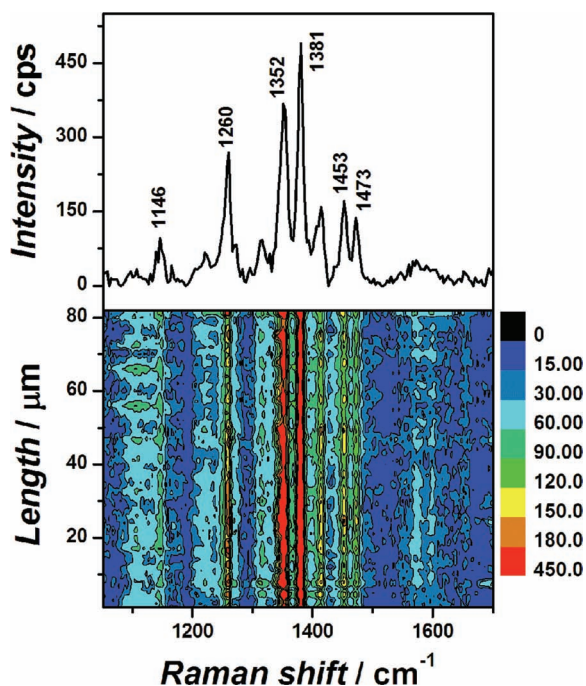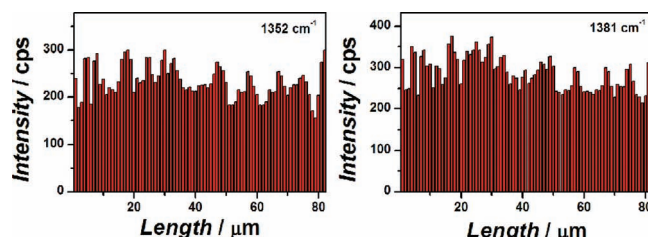
## 4. Experimental Section

*Synthesis and Characterization of Au NPs*: All of the chemical reagents were of analytical grade: they were purchased from Shanghai Chemical Company and used without further purification. The water used was doubly distilled. Silicon wafers (p type, 0.01–0.05 $\Omega$ cm) were purchased from Hefei Kejing Materials Technology Co., Ltd (China). The as-prepared products were characterized via X-ray powder diffraction (XRD), which was carried out on a Philips X'pert PRO MPD diffractometer using Cu K radiation ($\lambda = 0.15406$ nm). The morphology of the products was characterized by scanning electron microscopy (SEM), using an FEI Quanta 200F SEM instrument. The AFM measurements were conducted on a Multimode V system (Veeco, Bruker).

*Silicon–Hydrogen Bond Assisted Assembly of Cu NPs*: The silicon wafer was cut to a size of 1 cm × 1 cm and cleaned with acetone, ethanol, $H_2SO_4/H_2O_2$ and water. $Cu_2O$ (0.0143 g, $1 \times 10^{-4}$ mol), distilled water (10 mL) and HF solution (5 mL, 4%) were mixed and stirred in a Teflon beaker at room temperature. The cleaned silicon wafers were put into the above solution for just 2 s, taken out, rinsed with distilled water, and then dried at room temperature. Cu NPs were then grown on the Si wafer.

*Raman Microscopy*: Raman spectra were collected using an HR 800 Raman spectrometer (J Y, France) equipped with a synapse charge-coupled device (CCD) detector and a confocal Olympus microscope. The SERS experiments were conducted in line-mapping mode and 1 $\mu$m increments as model molecules. The spectrograph used 600 g mm$^{-1}$ gratings. The SERS spectra were collected at a 100× objective (Olympus), with a numerical aperture of 0.90, and an accumulation time of 1 s. In addition, the filter in the SERS spectra was D0.6. A 633 nm He-Ne laser was employed in all of the Raman detections.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.



**Figure 4.** The SERS spectrum of an SDI methanol solution ($1 \times 10^{-9}$ M) coated on a Cu-NP assembly as a substrate (upper part) and the SERS contour (lower part).

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