Low-concentration organic molecules detection via surface-enhanced Raman spectroscopy effect using Ag nanoparticles-coated silicon nanowire arrays

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Abstract
In this report we present the initial results of the use of Ag nanoparticles (AgNPs)-coated silicon nanowire (SiNW) arrays for detection of organic molecules using the surface-enhanced Raman spectroscopy (SERS) effect. The SiNW arrays were prepared by metal-assisted chemical etching (MACE) and the AgNPs were deposited on the SiNW arrays through immersion of SiNW arrays in the HF/AgNO₃ solution. Specifically, results showed that very low concentration (about 10⁻⁷–10⁻⁵ mol l⁻¹) of malachite green dropped on the surface of the AgNPs-coated SiNW arrays can be detected.

Keywords: SiNW, arrays, SERS, Ag-nanoparticles, malachite green

Classification number: 5.08

1. Introduction
Surface-enhanced Raman scattering (SERS) spectroscopy, a technique that was developed to detect extremely small quantities of molecules by determining their characteristic Raman signals, is now widely used in different fields such as biology, chemistry, medicine etc. Typically, the SERS effect occurs when a group of molecules is adsorbed onto a rough surface of a free electron metal such as Au, Ag, or Cu. It is generally believed that the amplification of Raman scattering in SERS effect is generated by two mechanisms: (i) electromagnetic field enhancement through the localization of optical fields in metallic nanostructures, and (ii) chemical or electronic enhancement due to the increase of Raman scattering cross-section when some molecules or lattices are in contact with metal nanostructures. For the electromagnetic field mechanism of enhancement, the SERS intensity can be enhanced substantially when two or more nanoparticles are brought closely together [1–4]. The small areas formed between those closely neighbored nanoparticles are called ‘hot spots’, where the Raman signal is locally enhanced due to the excitation of the surface plasmon resonance. The polarization of the incident light also plays an important role, since the electromagnetic field is greatly enhanced when it is polarized parallel to the axis of a particle dimer, while the field is diminished for a perpendicular polarization [3]. The chemical mechanism is much less well understood, but it is often attributed to a charge transfer intermediate state which takes place at the strong electron coupling between the analyte and the metal surface. There have been many experimental demonstrations confirming that both mechanisms play an important role in SERS effects, however, it is generally believed that electromagnetic enhancement contributes a greater part than chemical enhancement [1].
To enable SERS technique for practical applications, SERS substrates need to be reproducible, highly sensitive and easily fabricated. The most common types of SERS substrate are metallic nanoparticles in a colloidal solution. These SERS substrates have been reported to provide a remarkable enhancement of Raman signal. However, with colloidal solutions it is a challenge to bring the metal nanoparticles sufficiently close to each other to form hot spots around the analyte, while at the same time preventing the formation of large conglomerations of nanoparticles before the analyte is introduced [5]. Moreover, metal nanoparticles are prone to be uncontrollably and randomly aggregated in a solution phase, yielding relatively unstable and irreproducible SERS signals [6]. Several lithographic techniques (such as electron beam lithography, nanoimprinting, etc) have been employed for the production of uniform and controllable SERS substrates with fully controlled shape and size. This helps us to reach a controlled electromagnetic coupling between metal particles, so that this coupling will have a dominant contribution to the SERS efficiency. Despite the high efficiency of such substrates, the involved technology presents some drawbacks concerned with cost and complexity. Recently, silicon nanowires (SiNWs) decorated with metal nanoparticles (e.g. AuNPs and AgNPs) have been developed as high-performance SERS platform with excellent reproducibility, since the metal nanoparticles are tightly immobilized by SiNWs, effectively preventing random aggregation of the nanoparticles [3, 4, 7, 8]. As a result, such SiNWs-based SERS substrates have been utilized for wide-ranging sensing applications. Recent investigations further revealed that SiNWs-based substrates are advantageous in markedly magnifying the SERS signals since a large amount of SERS hot spots are prone to be generated on such nanowire-based substrates.

Malachite green (MG) is an organic compound that is used as a dye for materials such as silk, leather and paper [9]. The chemical formula of MG is C$_{23}$H$_{23}$ClN$_2$. MG is also used extensively as a fungicide and antiprotozoal agent in the fish industry throughout the world. However, this dye has generated much concern regarding its use, due to its reported toxic effects. MG recently has been reported to cause carcinogenesis, mutagenesis, chromosomal fractures and respiratory toxicity to animals exposed to it [9]. Unfortunately, in recent times MG has been used illegally to make food become green colored. This will seriously affect the quality of agricultural products. To enable SERS technique for practical applications, SERS substrates need to be reproducible, highly sensitive and easily fabricated. The most common types of SERS substrate are metallic nanoparticles in a colloidal solution. These SERS substrates have been reported to provide a remarkable enhancement of Raman signal. However, with colloidal solutions it is a challenge to bring the metal nanoparticles sufficiently close to each other to form hot spots around the analyte, while at the same time preventing the formation of large conglomerations of nanoparticles before the analyte is introduced [5]. Moreover, metal nanoparticles are prone to be uncontrollably and randomly aggregated in a solution phase, yielding relatively unstable and irreproducible SERS signals [6]. Several lithographic techniques (such as electron beam lithography, nanoimprinting, etc) have been employed for the production of uniform and controllable SERS substrates with fully controlled shape and size. This helps us to reach a controlled electromagnetic coupling between metal particles, so that this coupling will have a dominant contribution to the SERS efficiency. Despite the high efficiency of such substrates, the involved technology presents some drawbacks concerned with cost and complexity. Recently, silicon nanowires (SiNWs) decorated with metal nanoparticles (e.g. AuNPs and AgNPs) have been developed as high-performance SERS platform with excellent reproducibility, since the metal nanoparticles are tightly immobilized by SiNWs, effectively preventing random aggregation of the nanoparticles [3, 4, 7, 8]. As a result, such SiNWs-based SERS substrates have been utilized for wide-ranging sensing applications. Recent investigations further revealed that SiNWs-based substrates are advantageous in markedly magnifying the SERS signals since a large amount of SERS hot spots are prone to be generated on such nanowire-based substrates.

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2. Experimental

Aligned SiNW arrays were prepared by Ag-assisted chemical etching of Si (100) wafers with resistivity in the region of 0.5–3 Ω cm. The samples were washed with acetone and deionized water and then immersed into the HNO$_3$/H$_2$O solution with 1:1 volume ratio. The thin oxide layer formed on the surface was then dissolved in a 5% HF solution. The silver deposition step was done by embedding Si samples in the aqueous solution of HF/AgNO$_3$ with 4.6 M HF and 20 mM AgNO$_3$. The deposition time was 60 s. After silver deposition step, Si samples were washed with deionized water and then etched in the aqueous solution containing 4.8 M HF and 0.4 M H$_2$O$_2$ at room temperature for 90 min to create SiNWs. After SiNWs formation, the silver particles remaining on the samples were removed with nitric acid.

Before AgNPs deposition, the SiNW arrays were immersed into HF solution to terminate the surface of SiNWs with Si–H bonds. This was done because it is generally believed that the AgNPs for SERS were deposited on the SiNW arrays via the reaction between Ag ions and Si–H bonds on the surface of SiNWs. After rinsing with deionized water, the SiNW arrays decorated with large numbers of the Si–H bonds were immersed into the solution containing HF (0.1 M) and AgNO$_3$ (1 × 10$^{-4}$ M) at room temperature. As a result, we obtained the AgNPs attached to the surface of every SiNW to form an AgNPs-coated SiNW array. After being thoroughly washed, the SERS substrates were stored in deionized water for further use.

The structure of a representative SERS substrate, which was measured by the S-4800 Field Emission Scanning Electron Microscope (FE-SEM) (Hitachi, Japan) and JEM 1010 Transmission Electron Microscope (TEM) (Jeol, Japan) is shown in figure 1. Figure 1(a) is the top-view SEM image of this substrate. From this figure we can see that the SiNWs are uniformly distributed in the substrate surface. Figure 1(b) is the cross-sectional view SEM image of the aforementioned substrate, in which SiNWs are well separated and most of them are vertical to the wafer surface with the length of SiNWs of about 13 µm. The TEM images of representative SiNWs before and after AgNPs coating are shown in figures 1(c) and (d). From these images we can estimate that the diameters of SiNWs are in the region of 100–200 nm and can see clearly the AgNPs in the form of small black dots (with diameter in the 20–40 nm region) on the SiNW after Ag deposition. Here we can observe that the density of the AgNPs is relatively high and fairly evenly distributed across the entire surface of the SiNW.

The SERS measurements were performed by dropping 50 µl of aqueous MG solution with different concentrations onto the substrate, the spreading area is about 1 × 1 cm$^2$. After that the sample was dried in air at room temperature. The Raman scattering spectra were recorded using the LABRAM–1B (HORIBA) Raman system. The excitation wavelength was 488 nm from the argon ion laser and 632.8 nm from the He–Ne laser.

The curve (a) in figure 2 shows the Raman spectrum of 50 µl of 2 × 10$^{-5}$ mol l$^{-1}$ aqueous MG solution on 1 cm$^2$ SERS substrate. Compared with the standard Raman spectrum, all well separated and strong peaks in figure 2 are the peaks of MG molecule. Especially, signals observed at 914 cm$^{-1}$ are attributed to ring skeletal radial vibration; signals at 1171 and 1294 cm$^{-1}$ come from in-plane aromatic C–H bending vibration; signals at 1366 cm$^{-1}$ are contributed
Figure 1. Top-view (a) and cross-sectional (b) SEM images of an AgNPs-coated SiNW arrays (which has been used as SERS-active substrate in Raman measurements). TEM images of some SiNWs before (c) and after (d) AgNPs deposition step.

Figure 2. Raman spectra of the samples dropped with $2 \times 10^{-5}$ mol l$^{-1}$ MG solution with different types of substrate: (a) AgNPs-coated SiNWs; (b) AgNPs-coated porous silicon; (c) AgNPs-coated flat silicon and (d) uncoated SiNWs.

from N–C stretch; signals at 1394 cm$^{-1}$ come from C–C and C–H in-plane motion (aromatic) and those at 1617 cm$^{-1}$ are assigned to N–C ($\phi$ bond) and C–C stretch [10].

To confirm the role of AgNPs in the SERS effect, we have dropped aqueous MG molecular solution onto the SiNW sample without AgNPs coating and after that performed the Raman measurements. The result (curve (d) of figure 2) shows that without AgNPs, the SERS effect did not occur. To demonstrate the superiority of the AgNPs-coated SiNW substrate in comparison with other types of substrate, the Raman measurements also have been performed after MG solution dropping on the AgNPs-coated porous silicon and flat silicon substrates. The results are also shown in figure 2 (curves (b) and (c)). Here, we can see that the SERS signals from AgNPs-coated SiNW sample are much stronger than those from AgNPs-coated porous silicon (curve (b)) and flat silicon (curve (c)) samples. We can explain why the Raman signals are greatly increased in the case of using
AgNPs-coated SiNW substrate as follows. With using the SiNW substrate, much higher density of the AgNPs is packed over a unit area of the substrate compared with porous silicon or flat silicon substrates which normally are used for SERS measurements [11]. The consequence of this is that the Raman signal increases many times. Moreover, according to the theoretical analysis [12], the characteristics of AgNPs coated on SiNWs, i.e., size, separation, and density, will provide an optimum environment for enhancement of Raman signals. The fact showed that the AgNPs cling tenaciously to the SiNWs, they do not fall off even if the SiNWs was subjected to an ultrasonic vibration. Thanks to this the AgNPs-coated SiNW substrate is very durable over time, the characteristics of the substrate do not change even when it is exposed to the air for several months. It is worth remarking that in the case of AgNPs-coated SiNW substrate, in addition to enhancement of the individual Raman bands, the background signal is also increased. This rising of the baseline signal is partially attributed to inelastic light scattering by charge carrier excitations in Ag and partially attributed to fluorescence from Si nanowire arrays under the AgNPs [13].

The next result is that the intensity of the Raman peaks decreases with decreasing of the MG concentration in the solution dropped onto the substrate. This result is illustrated by figure 3, in which the curves (a), (b) and (c) are corresponding to Raman spectra of the aqueous solution containing $2 \times 10^{-5}$, $2 \times 10^{-6}$ and $2 \times 10^{-7}$ mol l$^{-1}$ MG, respectively. In curve (c) some peaks disappeared (due to the weak intensity), but we still can use this curve to identify MG molecule.

3. Conclusion

In summary, SERS-active substrates fabricated from uniform AgNPs-coated SiNW arrays have been prepared via metal-assisted chemical etching (MACE) method. The results showed that the SERS-active substrates prepared by this method are excellent candidates for MG molecules sensing with high sensitivity, good reproducibility and excellent stability. In particular, very low concentration (about $10^{-7} - 10^{-5}$ mol l$^{-1}$) of MG dropped on the surface of the AgNPs-coated SiNW arrays can be detected. In comparison with other kinds of substrate, AgNPs-coated on SiNW arrays give much stronger Raman signals.

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