Gold/Silicon nanowire arrays modified by Gold nanosphere as the surface-enhanced Raman spectroscopy substrate

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Abstract. Fabrication of gold coated silicon nanowires (AuSiNW) substrate is introduced in detail and a hybrid substrate is designed for surface-enhanced Raman spectroscopy (SERS). The SERS behaviors are discussed and compared by the detection of 4, 4′-Bipyridine. Gold nanoparticles is modified on the surface of AuSiNW to form the “hot gap”. Molecules captured in these “hot gap” can generate huge Raman signal. Double-fold enhancement of SERS signal has been achieved comparing with AuSiNW. The as-fabricated hybrid substrate exhibit high SERS sensitivity, long-term stability, and consistent reproducibility, highly potential for realizing a rapid, cost-effective, and label-free SERS-based biosensor.

1. Introduction
Surface-enhanced Raman spectroscopy (SERS) has gained prominence for sensitive and selective molecular identification, widely used in clinical diagnosis, food safety inspection, and environment monitoring [1-4]. Since the first demonstration of the SERS on the silver electrode in 1974 [5], many efforts have been made to fabricate a SERS substrate with ultra sensitivity, good stability, well homogeneity and perfect affinity.[6] Recently, the fast evolution of nanotechnology has reinvigorated this field. By virtue of the dramatically enhanced electromagnetic field in the proximity of nanostructured metal surfaces, ultrasensitive detection has been reported using substrates of graphene oxide/silver nanoparticles/silicon pyramid [7], gold nanoparticles (AuNPs) [8], and Gold nanostars [9]. Up to now, electromagnetic mechanism (EM) is widely accepted as the mainly mechanisms of SERS[10]. However, challenges remain in the issues of reproducibility, throughput and stringent requirements of equipment [11].

The surface plasmons can be excited between two particles by the incident light and further contribute to the EM enhancement. A metal film over nanosphere (MFON) was proposed to improve the stability of nanostructure, where Raman signal around the hot spots can be enhanced about 10^8 fold due to the coupling of localized surface plasmon resonances [12]. A recent study of AgNPs SERS substrate shows that the molecules in the hot spots have ~10^7 fold enhancement while those in not “hot” area only possess ~10^5 fold enhancement [13]. Nevertheless, the active “hot-spot” areas in SERS sensors are on the scale of nanometers, making it difficult to directly detect analyte molecules diluted to femto- or atto-molar concentrations. Efforts have been made to concentrate molecules in the desired locations of hot-spots [14]. Many methods including photolithography, reactive ion etching and metal-assisted
wet etching have been used to fabricate the silicon nanowire arrays [15]. These methods require complex steps, dangerous reagent or expensive facility.

In this letter, silicon nanowire arrays were fabricated by polymer sphere (PS) template with short assay time and high throughput. Enhancement of SERS signal of 4, 4’-Bipyridine was measured after modifying AuNP on the gold coated silicon nanowires (AuSiNW) surface. The improved SERS signal intensity using the hybrid substrate (AuNP/AuSiNW) compared to the AuSiNWs substrate was demonstrated. This result can be well extended to open an avenue for developing various SERS-based biosensors.

2. Experiment
A self-assemble at the water-air interface technique was used to produce monolayers of PS on silicon wafer. [16] After achieving the monolayer of PS on the silicon substrate, inductively coupled plasma (ICP) etching was performed to obtain the silicon nanowires (SiNW). The PSs with reduced diameter were used as mask for etching silicon nanowires with 360 nm in diameter and 650 nm in length by STS Multiplex ICP system. For the silicon etching, SF6 and C4F8 mixed gases were applied for 6 min with flow rates of 10 sccm and 4.9 sccm, respectively. Coil power and platen power were set as 400 W and 20 W, respectively. 2 min oxygen etching was performed afterwards to remove the remaining PS. The SiNWs were coated with a 3 nm ~ 5 nm Titanium film and a 20 nm thick gold film by sputtering evaporation to form AuSiNWs. Then AuSiNWs were immersed in a mixture solution of ethanol and 4, 4’-Bipyridine with 1 mmol/L for 1 h. After cleaning by pure ethanol to lift off the spare 4, 4’-Bipyridine (4,4’-bipy) molecule, the substrate was immersed in the AuNP solution for 1 h, so that the AuNP can be adsorbed on the gold film with the assistance of 4,4’-bipy.

A schematic illustrating the process of making AuNP/AuSiNWs was shown in Figure.1. Tilt-view scanning electron microscope (SEM) image of PS was shown in Figure.2 (a). The particle size of PS is 500nm in standard. From Figure.2 (a), we can observe the PS is highly ordered and compact in a considerable area. Due to the self-assemble at the water-air interface technique, we can rapidly and conveniently get such a monolayer of PS. To fabricate expected SiNW, PS mask should be disposed of its size to obtain given duty cycle. With the help of PS mask and ICP technology, we can realize a controlled diameter and length SiNW arrays. Figure.2 (b) shows us the surface topography of AuNP/AuSiNW, we can clearly see those AuNP attached on the surface of AuSiNW with the help of 4, 4’-Bipyridine molecule. In Figure.2 (b), the diameter of the used AuNP is about 60 nm.
3. Results and discussion

4, 4′-Bipyridine was used as signal molecules and was adhered to the gold film with concentration of 1mmol/L. LabRAM HR Evolution was used to detect the SERS signal. Excitation wavelength was set to be 633 nm. SERS spectra of the AuSiNW substrate and the AuNP/AuSiNW substrate were plotted in Figure. 3.

Figure 3 shows the 4, 4′-Bipyridine molecule has three mainly Raman characteristic lines, which locates at Raman shift of $1017 \text{ cm}^{-1}$, $1295 \text{ cm}^{-1}$ and $1610 \text{ cm}^{-1}$. In view of the maximum signal intensity, we choose the signal at $1610 \text{ cm}^{-1}$ as the intercomparable points. From Figure 3, the maximum Raman intensities of the AuSiNW substrate and AuNP/AuSiNW substrate are about 1350 and 3000, which means Raman signal on AuNP/AuSiNW substrate is beyond double times magnitude larger than that of
the AuSiNW substrate. As electromagnetic mechanism (EM) is widely accepted as the mainly mechanisms of SERS, we could explain these phenomena with electromagnetic field theory. In AuSiNW substrate, the wavelength of incident light is larger than the diameter of SiNW, most resonant energy is confined on the surface and resonantly coupled to the propagating surface plasmons of the Au layer. When AuNP is attached to the surface of Au layer, a so-called “hot gap” is generated between the AuNP and the AuSiNW. The electric field at the “hot gap” can be greatly enhanced. When detected molecule is captured by this “hot gap”, more violent Raman signal can be obtained, which means lower detection concentration can be accepted. In general, we can confirm Raman signal on AuNP/AuSiNW substrate is larger than that on AuSiNW substrate. When AuNP/AuSiNW substrate is used for biomolecular detection or molecule sensor, lower detection limits can be obtained than that of the AuSiNW substrate.

4. Conclusion
In conclusion, AuNP/AuSiNWs for SERS enhancement were fabricated by rapidly assembling monolayer PS. The Raman intensity of the molecular captured in the gap between the AuNP and AuSiNW can be enhanced dramatically, almost double times larger than that of the AuSiNW substrate. The AuNP/AuSiNWs substrate can be utilized with a low detection limit and has the potential for realizing a rapid, low cost and label-free SERS based biosensor. From the result mentioned, we can prove electric field between the AuNP and AuSiNW is agminate and the Raman signal is enhanced. For the further study, target molecule and probe molecule will be introduced. Target molecule is modified on the AuNP and probe molecule is fixed on the AuSiNW, respectively.

5. Acknowledgments
This work was supported by National High Technology Research and Development Program of China (No.2014AA06A504), Science and Technology Department of Zhejiang Province(No.2014C31030), Fundamental Research Funds for Central Universities (No. 2014QNA5018), the National Natural Science Foundation of China (No. 61535010), Zhejiang Provincial Natural Science Foundation of China (No.LY16F050001).

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