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Silver nanoprisms/graphene oxide/silicon nanowires composites for R6G surface-enhanced Raman spectroscopy sensor

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ABSTRACT

In this study, Silver nanoprisms/Graphene Oxide/Silicon nanowires (AgNPr/GO/SiNWs) nanocomposites have been fabricated for Surface-Enhanced Raman Spectroscopy (SERS) of Rhodamine 6G (R6G). The SiNWs have been synthesized using the metal-assisted chemical etching method. The surface morphologies of the SiNWs samples have been investigated using scanning electron microscopy. By varying the etching time from 5 to 30 min, the nanowire lengths have been tuned from 2 to 10 µm. While the average nanowire diameter remained unaffected (30-60 nm) with the increase in etching time, increments of nanowires length were found to alter the bundle morphology. The final SERS structure is obtained by depositing the GO layer followed by AgNPr. The obtained SERS sensor exhibited an enhanced efficiency as compared to AgNPr/SiNW matrix. The results demonstrate that a maximum efficiency factor of 6.1×10^{10} could be achieved with sensor fabricated with 30 min etched SiNWs.

Keywords: *Surface enhanced Raman spectroscopy; silicon nanowires; silver nanoprisms; etching time graphene oxide.*

1. INTRODUCTION

Surface-enhanced Raman spectroscopy (SERS) is an excellent tool for amplifying Raman signals which enable to sense of substances even down to single-molecule level [1, 2]. Various chemical or biological molecules can be detected at high sensitivity of $10^{14}\sim10^{14}$ by adsorbing on metal nanoparticles (MNPs) matrix. MNPs such as gold, silver and copper are widely employed as SERS substrates owing to their localized surface plasmonic (LSP) resonance, which gives rise to "hot spots" [3, 4]. Silver nanoparticles are usually preferred than gold or copper due to their simple and low-cost synthesis in various shapes offering enhanced LSP resonance [5]. Despite of the enormous progress in this area, design of reproducible and stable SERS substrates remains major challenge [6]. In this context, remarkable research efforts have been devoted to looking after optimized matrices with ultra-sensitivity and high specificity for SERS applications.

Silicon nanowires (SiNWs) are one of the promising candidates since it can serve as host matrix for metal-nanoparticles (MNPs) in order to enhance further the SERS signal [7-10]. SiNWs are one-dimensional nanostructure, which has fascinated massive research groups in various fields due to its unique electronic, optical and mechanical properties [11, 12]. The huge surface area and nanoscale confinements made them excellent candidates for sensor applications. In addition, the Si-nanowires can be fabricated by simple and cost-effective technique like metal assisted chemical etching (MACE) process [13]. Micro-architecture of SiNWs could be modulated by varying parameters such as etching time and etching solution. Recent studies have shown that silicon nanowires functionalized with metal nanoparticles can exhibit ultrahigh sensitivity along with excellent reproducibility [8, 14]. These composite structures could show high enhancement factor as the hotspots are located at the interface between the metal nanoparticle and semiconducting silicon nanowires, which could further enhance their detection limit.

Encapsulation of the MNPs by graphene or graphene oxide (GO) has been proved to be an excellent approach to produce highly sensitive SERS devices [15, 16]. The GO possess high chemical stability due to active oxygen sites [17]. The integration of a GO layer in the SERS device has been considered useful for protecting the metal nanoparticles from oxidation [18, 19]. Currently, we have tried to evaluate SERS efficiency of AgNPr/GO/SiNWs nanocomposites for different etching times. Initially, SiNWs were prepared by silver assisted chemical etching method and the morphological properties such as length and diameter of nanowires were studied by varying etching time. Hybrid AgNPr/GO/SiNWs were fabricated and SERS of different compositions was assessed by using R6G as probe molecule.

2. MATERIALS AND METHODS

Silicon wafer (p-type, 100) having thickness of 675 ± 25 µm was received from TED PELLA, USA. Hydrofluoric acid (ACS grade, 48%) and anhydrous glacial acetic acid (ACS grade, 100%) were obtained from Merck, USA. Nitric acid (ISO grade, 65%), Rhodamine 6G (R6G) and sodium borohydride from Sigma-Aldrich and silver nitrate (ACS grade) from Alfa-Aesar were also utilized for the study.

SiNWs samples were synthesized by MaCE method using single side polished silicon wafer (1.5 cm x 1.5 cm). First of all, Si wafers were ultrasonically cleaned in acetone and ethanol for 5

min each, followed by dipping in an acid solution of HNO_3, HF and CH_3COOH (64%, 16%, 20% respectively) for 1 min, and thoroughly rinsed in deionized water and dried. Subsequently, they were immersed in an aqueous solution of 4.8 M HF and 0.02 M $AgNO_3$ for 1 minute to induce the deposition of silver nanoparticles (AgNP) on Si. In the etching step, the substrates were immersed in an aqueous mixture of 4.8 M of HF and 0.2 M of H_2O_2 for times ranging between 5 and 30 min, which turns them into a brownish color. The samples were then immersed in HNO_3:H_2O solution (1:1) to remove silver particles. After final rinsing and drying operations, the substrates turned black with a layer of SiNWs. Silver nanoprisms (AgNPr) and Graphene oxide (GO) were synthesized using a chemical reduction process and Hummers' method, respectively [20, 21]. Initially, SiNWs sample was subjected to spin coating by a GO/water solution at 2000 rpm for 30 sec. Then AgNPr solution is drop casted on GO/SiNWs and allowed to dry at 50°C for 20 min. The process is repeated for three times to ensure proper AgNPr density on final AgNPr/GO/SiNWs substrates.

Surface microstructure and elemental analysis of SiNWs were investigated using a Testscan Vega 3 SEM equipped with an Oxford instruments EDS detector. SERS measurements were performed on a Renishaw UK Raman microscope using 488 nm laser excitation of power of 100 µW with 50x objective (~1 μm^2 spot size) with 10 seconds integration time.

3. RESULTS

SEM analysis confirmed the deposition of the silver nanoparticles after immersion in $AgNO_3$/HF solution for 1 minute (Figure 1 (a)). It has been seen that dense silver depositions are distributed uniformly on silicon surface, which might be detrimental in regulating nanowire structure. It was reported that high density Ag NPs creates better-isolated nanowire structure while low-density Ag NPs result in only isolated pores [22]. Analysis of size distribution has shown that the majority of particles have 50-350 nm as average size (Figure 1 (b)). According to the earlier studies, the size of Ag NPs has a significant role in nanowire formation as etching rate reduces with an increase in lateral size of metal NPs [23].

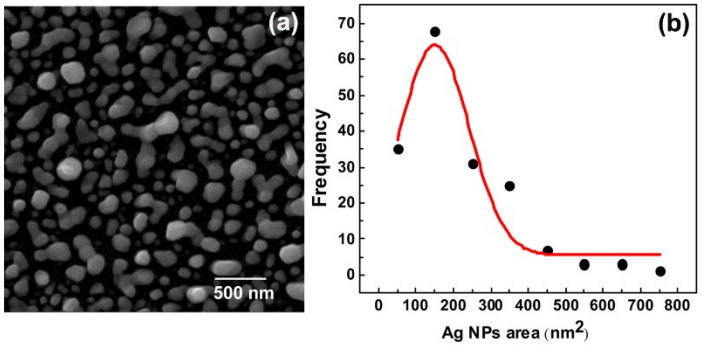

Figure 1. SEM scan for Ag-NPs deposited on Si substrate (a) and the corresponding size distribution (b).

Typical SEM micrographs depicting cross-section and top surface morphology of SiNWs prior and after removal of the Ag NPs are shown in Figure 2, which corresponds to 20 min etching time. It is evidenced that vertically aligned nanowires are successfully formed by an optimized MaCE process. The dense nanowires have been associated with some dendritic Ag NPs at the bottom of nanowires as shown in Figure 2 (a). Further the removal of Ag NPs from SiNWs has been achieved by immersing them in HNO_3/H_2O solution for 10 minutes. The corresponding cross-sectional SEM image confirms the lack of any traces of AgNPs (Figure 2(b)). The measured SiNWs length from both images before and after removal of the AgNPs is found to be maintained as ~7µm (Figure 2 (a) and (b)). We have also observed that successive increase in etching time from 5 to 30 min resulted in enhancement of SiNW length from ~2 to 10 µm (data not shown). However, the diameter of individual nanowire remained in the range of 30-60 nm, which implied that etching time does not impart a significant effect on nanowire diameter.

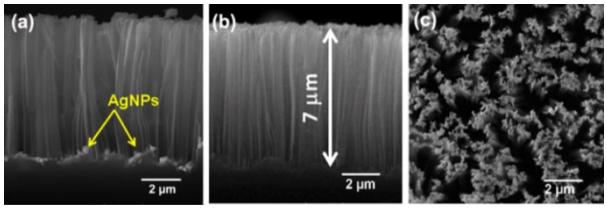

Figure 2. Cross-sectional SEM image of the SiNWs-20min sample before (a) and after (b) removal of the AgNPs and top view of the same sample after removal of the AgNPs (c).

The top surface morphology shows a nanoforest structure with persistent formation of bundles (Figure 2 (c)). Moreover, we noted a significant increase in the bundle size with increments of etching time (data not shown). While lowest etched SiNWs are characterized by narrower bundle size distribution, the highest etching time generated broader sized nanowires. The linear dependence of nanowire length on the etching time could account for this observation. The flexibility of nanowires could also be enhanced with etching time as longer wires are formed at high etching times [24]. Subsequently longer nanowires can overcome the surface tensional forces and eventually they tend to get together to form the bundles due to van der Walls forces. The subsequent changes in topology of nanowires have found to affect the surface roughness parameters due to the fornation of large sized bundles). Yet, SiNWs is consistent and maintains structural integrity at all etching times.

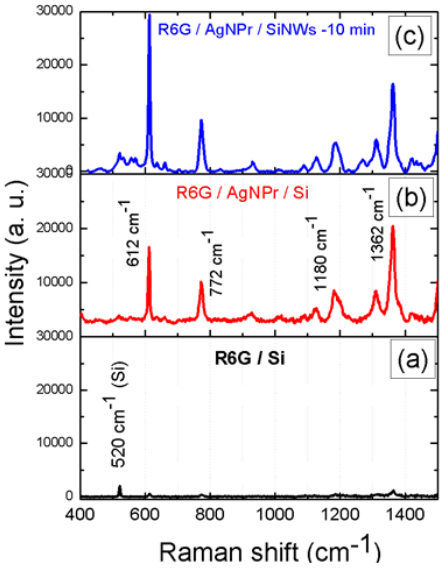

Figure 3. Raman spectra of R6G deposited on various substrates such as Si substrate (a), AgNPr/Si (b) and AgNPr/SiNWs (c).

Raman spectra of R6G deposited on different substrates have been recorded by keeping exposure time as 10 seconds and a laser power as 0.1% for comparison. First of all, 7 µl of R6G/ethanol solution was drop casted on the composite substrates and dried properly prior to the Raman analysis. It is clear from Figure 3 (a) that Raman peaks corresponding to R6G deposited on Si substrate are too weak, which indicates that the detection of R6G is quite difficult in the absence of nanoparticles system like AgNPr. Obviously, R6G/AgNPr/Si and R6G/AgNPr/SiNWs composites demonstrated characteristic peaks at 612, 774, 1362, 1509, and 1650 cm^{-1} as seen in Figure 3 (b) and (c) respectively; as these are reported as fingerprint peaks for R6G loaded substrates in earlier studies [25]. Further analysis showed that the intensity of the peak corresponding to R6G at 612 cm^{-1} is found to be the highest for R6G/AgNPr/SiNWs compared to R6G/AgNPr/Si. This indicates that expected localized surface Plasmon effect of AgNPr on flat Si might be further enhanced by combining with SiNWs having large surface area to volume ratio. While high surface area of SiNWs could provide space for more AgNPr for generating efficient hotspots that produce better SERS response; the detection levels could be enhanced much as more R6G molecules can also be adsorbed on the SiNWs substrates [14, 18]. Besides, the effect of the etching time of the SiNWs on Raman scattering of R6G was systematically investigated as illustrated in Figure 4 (left panel and right panel represents Si/SiNWs composites with AgNPr alone and AgNPr /GO, respectively). From left panel, it can be seen that the intensity at 612 cm^{-1} is increased for 5 to 10 min of etching, thereafter declined for 15 to 30 min. On moving to right panel, it is clearly visible that the corresponding Raman peak got enhanced after incorporation of GO. The highest peak intensity at 612 cm^{-1} has enhanced with etching time increases and the highest one is obtained for 30 min.

SERS efficiency factors (EF) were calculated following the method used by D'Andrea et al. [10]. By comparing the Raman and the fluorescence cross sections, σ_R and σ_F, respectively [2, 26]. The signal intensities ratio per molecule and per watt power is related to the ratio between cross sections as below:

$$\frac{I_{SERS}}{I_F} = EF\frac{I_{Raman}}{I_F} = EF\frac{\sigma_{Raman}}{\sigma_F} = EF \times 10^{-9} \qquad (1)$$

$$\eta = 10^9 \frac{I_{SERS}}{I_F} \qquad (2)$$

where I_{SERS} is the SERS intensity of the 612 cm^{-1} mode for an excitation wavelength at 488 nm, and I_F is the intensity of the fluorescence background intensities coming from the corresponding sample at the same wavelength.

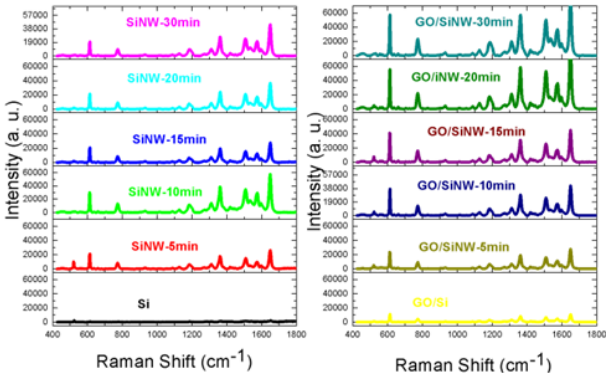

Figure 4. Left panel shows the Raman spectra of the R6G/AgNPr/SiNWs and right panel shows Raman spectra of the R6G/AgNPr/GO/SiNWs nanocomposites obtained with different etching times (5 - 30 minutes).

Figure 5 shows the evolution of the efficiency factor versus the etching time of the SiNWs. Highest SERS efficiency (3.2×10^{10}) was obtained for 10 min and decreased thereafter with higher etching time. In contrast, EF subsequently enhanced with successive increase in etching time after modifying SiNWs with GO. The highest EF value of 6.1×10^{10} has been achieved for R6G/AgNPr/GO/SiNWs - 30 min. As mentioned above, surface plasmonic effect of AgNPr plays critical role for getting SERS signal as the probe molecule recede on hot spot could be enhanced much significantly. Triangular shaped AgNPr having size range of 20-60 nm was employed for the current study, which is reported to have better SERS response than spherical Ag NPs [5, 20].

As fabricated SiNWs are characterized by bundles, Raman response is found to be influenced by the position of laser pointer either it is on bundle top or bundle valleys. Bundle top has found to accommodate larger number of AgNPr and R6G molecules compared to bundle valleys. Among different etching times, 10-min found to have better homogeneous bundle topology and hence contributed the highest SERS response. At higher etching times (15 to 30 min), formation of longer nanowires substantially increased the lateral surface area, yet the larger bundles are found to comprise the most measurable surface area.

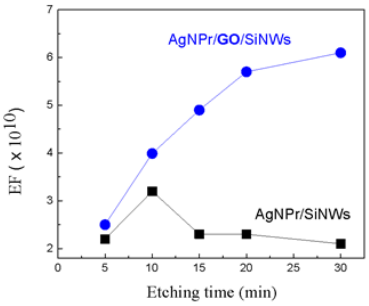

Figure 5. Evolution of the efficiency factor (EF) with the etching time for the AgNPr/SiNWs and AgNPr/GO/SiNWs nanocomposites.

A different trend of EF has been observed with etching time after incorporating GO coating to SiNWs. Studies suggested that GO can provide good SERS efficiency by quenching background fluorescence [15, 23]. We have also found greater SERS response for AgNPr/GO/SiNWs composite substrate which could arise due to synergistic effects of AgNPr and GO. The enhanced cross sectional area at higher etching time can increase GO layer. Furthermore, the incorporation of the GO layer in the composite substrates is expected to offer flat plane for the homogeneous distribution of the AgNPr that improve the stability and reproducibility of the SERS substrates [25]. Also, GO can manage the separation between neighboring AgNPrs and strongly enhance the intensities of hot spots via strong inter-coupling of LSP [16]. At higher etching times (>15min), the presence of a GO layer might help in better distribution of AgNPr, thereby preventing them from being embedded in the deep valleys of SiNWs. We attempted to study the implications of etching time on silicon nanowires topology and SERS response by integrating with AgNPr and GO. The present study gave an insight for optimizing different etching parameters in MaCE process in order to design an ideal SERS substrate. The possible outcome of this study is towards achieving a low cost, highly efficient and sensitive AgNPr/GO/SiNW SERS substrate for chemical sensing applications.

4. CONCLUSIONS

The micro-structural features of SiNWs fabricated by MaCE process were significantly affected by etching time. The NW length varying from 2 to 10 µm was achieved by tuning etching time from 5 to 30 min. The bundle formation was found to be significant at higher etching time, which in turn influences the top surface morphology of nanowires. High SERS response was demonstrated by AgNPr/GO/SiNW compared to AgNPr/SiNW composite substrates for R6G detection. SERS efficiency of 6.1×10^{10} was accomplished for AgNPr/GO/SiNW composite after 30 min etching.

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6. ACKNOWLEDGEMENTS

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