

SIZE CONTROL OF ZnO NANOROD PREPARED BY HYDROTHERMAL PROCESS FOR REUSABLE SERS APPLICATIONS

Nampueng Pangpaiboon¹, Phatsarathon Noitae¹, Sukon Kalasung², Chanunthorn Chananonnawathorn², Viyapol Patthanasettakul², Mati Horprathum², Saksorn Limwichean^{2,*}, Pitak Eiamchai², and Noppadon Nuntawong³

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Abstract

Surface Enhanced Raman Scattering (SERS) is a sensitive surface used to amplify the Raman signal of Raman spectroscopy. The enhancement of SERS sensitivity can reach up to a million times because of the surface Plasmon resonance of noble metal decorated on SERS substrate. Reusable SERS was originated to reduce production cost and extend life time; however, the ability to enhance Raman signal of reusable SERS is still less than the original SERS. In this work, the optimum performance to enhance the Raman signal of the reusable SERS will be investigated. Diameter and length of ZnO nanorods, grown as SERS substrates, are varied. ZnO nanorods are grown by hydrothermal process with different concentrations of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) mix with hexamethylenetetramine ($\text{CH}_2)_6\text{N}_4$ between 2.5-70 mM. Field Emission Scanning Electron Microscope (FE-SEM) images show that diameters and lengths of ZnO nanorods are directly proportional to the concentrations of the solution. Afterwards, gold nanoparticles are decorated on the nanorods by magnetron sputtering technique. The hot spot of gold nanoparticles is changed according to the different appearance of ZnO nanorods which affects the Raman signal. Performance to enhance the Raman signal is examined by dropping methylene blue (MB) on reusable SERS and analysing with Raman technique. UV light is used to activate the self-cleaning property of the reusable SERS. From the results, all reusable SERS can enhance the Raman signal. The reusable SERS substrate with the highest concentration, 70 mM, demonstrates the highest performance to enhance Raman signal even in a small amount of instant solution.

Keywords: Reusable SERS, Raman signal, ZnO nanorods, Hydrothermal process, Self-cleaning

¹ Department of Industrial Physics and Medical Instrumentation, Faculty of Applied Science, King Mongkut's University of Technology North Bangkok, Bangkok, 10800, Thailand.

² Optical Thin-Film Technology Laboratory, National Electronics and Computer Technology Center, Pathumthani, 12121, Thailand. E-mail: saksorn.limwichean@nectec.or.th

³ Carbon-based Devices and Nanoelectronics Laboratory, National Electronics and Computer Technology Center, Pathumthani, 12121, Thailand.

* Corresponding author

Introduction

Surface-Enhance Raman Scattering (SERS) is a technique using a sensitive surface to amplify the Raman signal of Raman spectroscopy. The SERS has been widely used for detecting chemical and biological molecules especially in a small quantity molecule (Kattumenu *et al.*, 2011; Kosuda *et al.*, 2011; Lin *et al.*, 2012; Yi *et al.*, 2014). The enhancement of SERS sensitivity can reach up to a million times because of the surface Plasmon resonance of noble metal decorated on SERS substrate (Nuntawong *et al.*, 2010; Dong *et al.*, 2014). Distance between noble metal nanoparticles is called the “hot spot”. Usually, the hot spot at about 50 nm results in high performance to enhance the Raman signal (Tang *et al.*, 2012; Min *et al.*, 2018). SERS can substantially improve the limit of detection for specific elements and allows the small amounts of sample substances to be detected and identified. However, SERS has a high production cost and SERS is a single-use. The reusable SERS is being developed as a new creation of the original SERS (Pangpaiboon *et al.*, 2018).

At first, the reusable SERS was created by using ZnO nanorods structure as a substrate and decorated with noble metal nanoparticles (Pangpaiboon *et al.*, 2018). The ZnO nanorods were grown by hydrothermal process and Au nanoparticles were decorated by sputtering technique. Heights of ZnO nanorods templates were controlled at about 1,144 nm and the deposition time of Au sputtering were varied from 15 to 450 s. The SERS can be reused because of a photocatalytic property of ZnO (Chen *et al.*, 2012; Ruiz Peralta *et al.*, 2012; Kuriakose *et al.*, 2014; Chen *et al.*, 2017). The results showed that Au decorating time at 270 sec is the best condition, the SERS can enhance Raman scattering and can be reusable. However, because of the unchanging size of ZnO nanorod, the effect of the morphology of ZnO template has not been studied. Therefore, the optimum performance of the reusable SERS has not been discovered yet.

In this research, the ability to enhance the Raman signal of the reusable SERS has been improved. Effects of ZnO template morphology on the Raman signal enhancement have been studied. ZnO nanorod substrates is grown by varying the concentration of two precursors of ZnO nanorods, which are zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine ($\text{CH}_2)_6\text{N}_4$. They are mixed at a 1:1 ratio with concentrations between 2.5–70 mM. Sputtering time at 270 sec is used for depositing Au nanoparticles on ZnO nanorod substrate. Diameters and lengths of ZnO nanorods affect hot spots. The ability to enhance the Raman signal is examined by dropping indicator substances

on the reusable SERS template and analyzing with Raman technique. UV light is used to activate the self-cleaning property of the reusable SERS. Finally, we expected to find the optimum precursor concentration of ZnO nanorod to enhance Raman signal and, in the end, the excellent reusable SERS was invented.

Materials and Methods

Reusable SERS chips are created on silicon substrate at 2×2 cm in size. ZnO seed layer is sputtered by using Zn sputtering target purity 99.99% and flowing oxygen into sputtering system on silicon wafer. Sputtering process is operated at 8×10^{-6} mTorr under 40 sccm of argon gas and 80 sccm of oxygen gas. ZnO seed layer thickness is 80 nm by using sputtering time for 13 min (Kalasung *et al.*, 2013). After that, ZnO nanorods (NRs) on ZnO seed layer substrate are grown by hydrothermal process. The length, diameter and distance of ZnO NRs are controlled by varying concentrations between two precursors, which are zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$). Two precursor solutions are mixed together with 1:1 ratio in DI water at 2.5, 5, 10, 30, 50, and 70 mM concentrations. The bottle with mixed solution is tightly sealed with parafilm to prevent chemical evaporation. The solution is stirred with magnetic bar on magnetic stirrer by using 450 rpm rotation rate for 2 h. The 2×2 cm substrate with ZnO seed layer is used to grow ZnO nanorods. The substrate is mounted on the centre of a 5.5 cm glass slide by vacuum tape. The sample substrate is dipped into the solution bottle with 45° placement. The bottle is place in an autoclave with growth temperature at 90°C and growth time at 6 h to grow ZnO NRs (Kalasung *et al.*, 2013). The bottle is taken out from the autoclave and the sample is rinsed by DI water then dried on hot plate. The ZnO NRs structures are characterized by Field Emission Electron Microscopy (FE-SEM) to check an alignment of the nanorods.

After ZnO NRs template growth, Au nanoparticles (NPs) are deposited on ZnO nanorod templates, all concentrations of the solution, by DC magnetron sputtering system. Sputtering time for deposition is 270 sec which is the best condition to enhance Raman signal (Pangpaiboon *et al.*, 2018). Au with purity 99.99% is used as a sputtering target. Sputtering process is operated at 8×10^{-6} mTorr under 40 sccm of argon gas, 80 watt of power, and 270 sec of deposition time. FE-SEM is used to characterize the physical structures of Au-ZnO NRs.

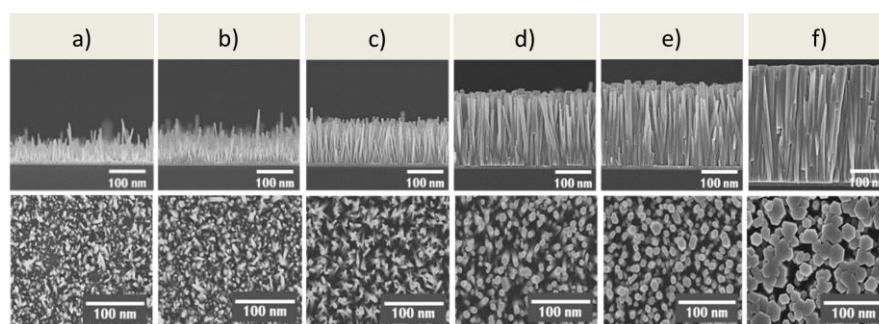


Figure 1. Cross-section and top surface morphologies of ZnO nanorods in different concentrations a) 2.5 mM, b) 5 mM, c) 10 mM, d) 30 mM, e) 50 mM, and f) 70 mM

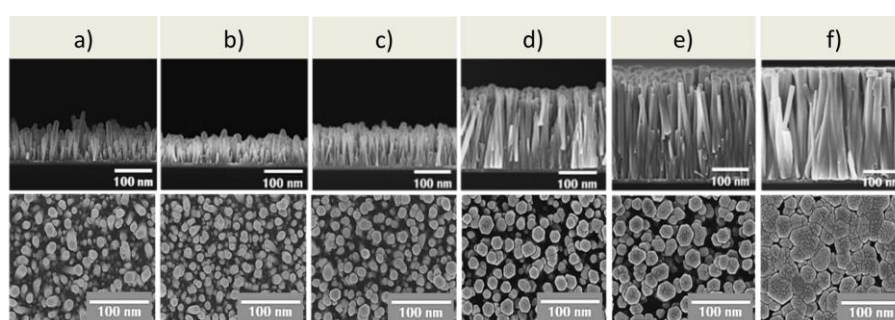


Figure 2. Cross-section and top surface morphologies of Au nanoparticles deposition for 270 seconds on ZnO nanorods in difference concentration a) 2.5 mM, b) 5 mM, c) 10 mM, d) 30 mM, e) 50 mM, and f) 70 mM

Afterwards, the Raman enhancement of the reusable SERS is tested by using Renishaw Raman spectroscopy. All the reusable SERS with varied concentrations of precursor are tested for the ability to enhance the Raman signal. Testing chemical solution is methylene blue (MB) solution at 1×10^{-5} M concentration. About 2 μ L of the methylene blue is dropped on the reusable SERS and left until the solution is dry. After that, the templates with MB stain are examined by Raman spectroscopy with 785 nm of laser wavelength. In each test, all SERS are measured in at least 3 positions and average for presenting MB Raman spectrum. The reusable SERS at 2.5, 30, and 70 mM concentration of ZnO NRs templates are tested with a limit of detection to enhance Raman signal. To find the best condition for creating the reusable SERS, Methylene blue (MB) and rhodamine 6G (R6G) solutions are used to obtain a limit of detection. At first, the solution substance with concentration 1×10^{-5} M is used, and then the concentration is reduced until the Raman spectrum is not present. In addition, after the performance testing, the reusable SERS templates are cleaned by activation with UV light for 10 min and then measure MB and R6G Raman spectrum. If the SERS show a peak of substances Raman

spectrum, the surface is cleaned more with UV light for 10 min and the spectrum measured again. This process continuously repeats until the substances Raman spectrums disappear. When the SERS are completely cleaned, MB and R6G solutions are dropped on the SERS at same position again. MB and R6G Raman spectrums examined by the reusable SERS indicate the performance of SERS after self-cleaning. This process is called 1 cycle of reusable.

Results and Discussion

Physical morphologies of the reusable SERS templates are characterized by FE-SEM. The results of ZnO NRs templates at 2.5, 5, 10, 30, 50, and 70 mM concentrations are presented in Figures 1(a)-1(f). FE-SEM images show cross-sections and top surfaces of all ZnO nanorod templates. The concentration affects the length, diameter and distance between ZnO nanorods. At 2.5 and 5 mM concentration, the needle shapes of ZnO nanorods are formed because of small amounts of precursor, as shown in Figures 1(a) and 2(b). Increasing concentration of the solutions to 10-70 mM, ZnO

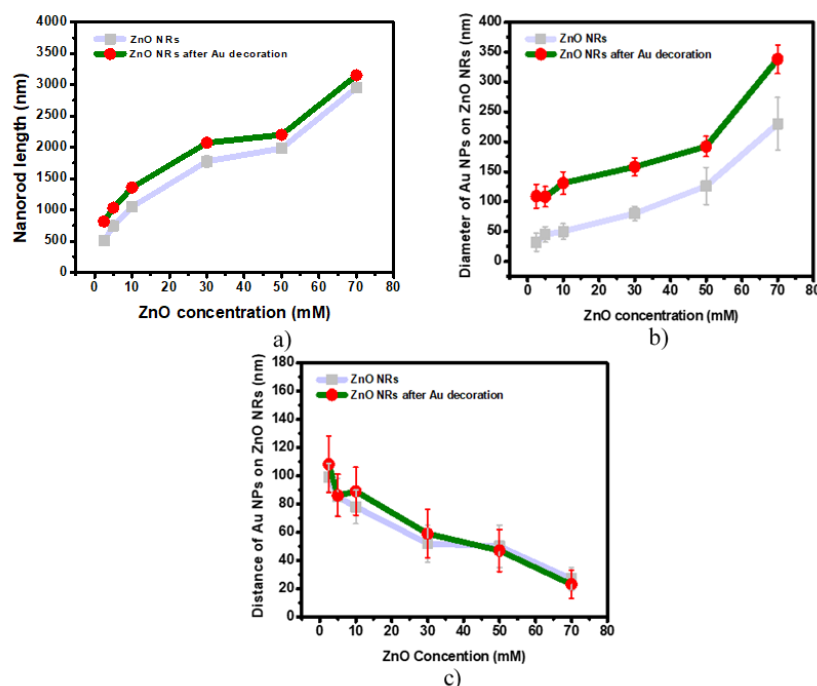


Figure 3. Relationships between ZnO concentrations and a) nanorod lengths, b) nanorod diameters, and c) distances between nanorods of ZnO NRs and Au-ZnO NRs

nanorods show a hexagonal structure. Lengths and diameters of nanorods increase with increasing concentration. However, distances between nanorods are inversely proportional to precursor concentration of the solutions, as shown in Figures 1(c) to 1(f).

After ZnO NRs growth, Au NPs are deposited on all ZnO NRs templates. FE-SEM images, in Figure 2, show cross-section and top surfaces of Au NPs deposited on all concentrations of ZnO templates. At 2.5, 5, 10, and 30 mM of ZnO NRs, Au NPs cover up throughout the nanorods, as shown in Figure 2 a) to d), because the nanoparticles have enough spaces to deposit. At 50 and 70 mM concentrations, observably, Au NPs cover up only at the top dome because the nanorods are large and merging with each other, as shown in Figures 2(e) and 2(f). Therefore, the difference in length of 70 mM ZnO NRs, before and after Au sputtering, is less than the others because of the greater area for Au deposition.

The relationships between shape of ZnO NRs and Au-ZnO NRs at all precursor concentrations are shown in Figure 3. The concentration strongly affects the shape of ZnO NRs, both in diameter and in length. When precursor concentration increases, diameter and length of NRs increase also. ZnO NRs lengths are 506, 745, 1,050, 1,775, 1,984, and 2,955 nm as increasing precursor concentration. Au-ZnO NRs lengths are 815, 1,034, 1,358, 2,072, 2,201, and 3,153 nm, as shown in Figure 3(a). Diameters of

NRs increase to 32, 45, 50, 80, 126, and 230 nm. Diameters of Au-ZnO NRs are 109, 108, 131, 158, 192, and 338 nm, as shown in Figure 3(b). The expansion of nanorod diameter causes distance between NRs to decrease, reversely proportional with precursor concentrations, which are 99, 85, 78, 52, 50, and 27 nm. In Addition, distances between Au-ZnO NRs are 108, 86, 89, 59, 47, and 23 nm, as shown in Figure 3(c). However, more than shape and distance between Au-ZnO NRs, size and distance between each Au NPs may affect the Raman enhancement. Since Plasmon resonance phenomenon is caused by distance between Au NPs, hot spot, the reusable SERS can efficiently enhance the Raman signal.

After creating the reusable SERS with ZnO NRs base structure at 2.5, 5, 10, 30, 50, and 70 mM precursor concentration, the Raman enhancements of the reusable SERS have been investigated. Methylene blue at 1×10^{-5} M concentration is dropped on all reusable SERS. The Raman spectrum of MB on the reusable SERS templates at different solution concentrations is shown in Figure 4. The results confirm that all templates of reusable SERS can enhance MB Raman spectrum. The Raman shifts of methylene blue present at 448, 502, 773, 1,396, and $1,622 \text{ cm}^{-1}$. From Figure 4, the 2.5 mM template presents the lowest intensity and the 5 mM template presents higher intensity of MB Raman spectrum. At 10 and 30 mM, the templates present the highest

intensity. On the other hand, the intensities of MB Raman spectrum are reduced when the solution concentrations increase to 50 and 70 mM. However, all reusable SERS templates can enhance the Raman signal of MB solution

From the results, Figure 4, only MB couldn't identify the best condition of ZnO NRs template representing the highest enhancement of Raman signal. Therefore, three reusable SERS selected to test the limit of detection, which were 2.5, 30, and 70 mM concentrations. The MB and R6G Raman signal were measured again. However, this time, the lower concentrations of MB and R6G were used, which are 1×10^{-5} , 1×10^{-6} , and 1×10^{-7} M, as shown in Figure 5.

From the results, all three reusable SERS templates could enhance Raman signal as low as 1×10^{-6} M concentration of MB and R6G solutions, as shown in Table 1. The 70 mM template showed the best enhancement of both MB and R6G spectrums. Moreover, the 70 mM template was able to enhance R6G substance as low as 1×10^{-7} M concentration, because Au NPs roughness on the top of the nanorod helped to amplify the Raman signal of substance solution.

Afterwards, the 70 mM reusable SERS template were selected to test the self-cleaning property by dropping 1×10^{-5} M MB and R6G solution and using UV light activation. UV light decomposed the organic compounds by photocatalytic process. The 70 mM reusable SERS template takes 200 and 75 min to clean MB and R6G solution,

respectively. After the self-cleaning test was finished, the reusable property was tested by dropping the solution substances again and examining the Raman spectrum. In Figure 6, the

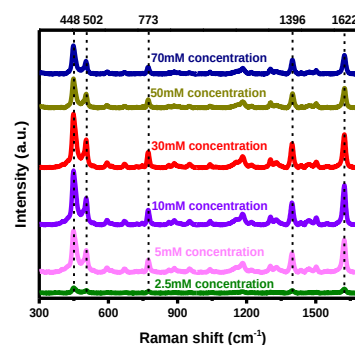


Figure 4. The Raman spectrums of methylene blue improved by SERS templates

Table 1. Limit of detection between MB and R6G solution in different precursor concentration of SERS templates

Solution	Concentration of ZnO template (mM)	Limit of detection LOD (M)
MB	2.5	10^{-6}
	30	
	70	
R6G	2.5	10^{-6}
	30	
	70	10^{-7}

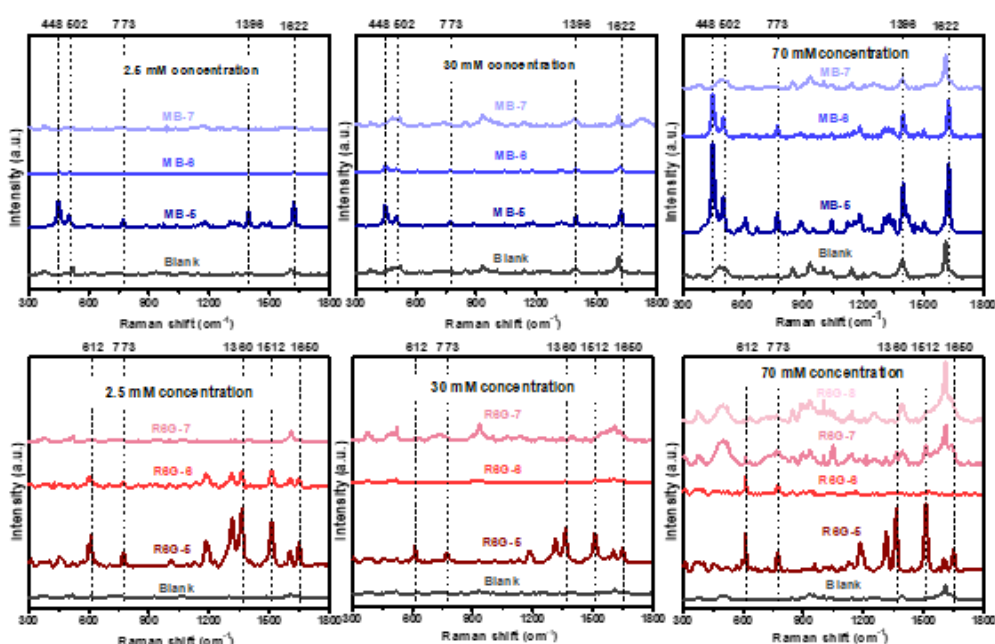


Figure 5. Raman spectrums of MB and R6G at 1×10^{-5} , 1×10^{-6} , and 1×10^{-7} M concentration of 2.5 mM, 30 mM, and 70 mM of reusable SERS template

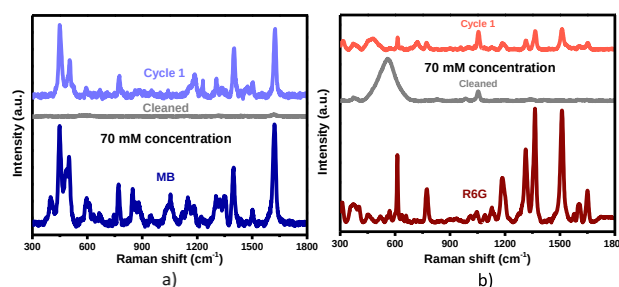


Figure 6. Raman spectrums before UV activation, after cleaned with UV activation, and after dropped solution substances again examined by the 70 mM reusable SERS templates a) MB solution b) R6G solution

results show that, the 70 mM reusable SERS templates could enhance the Raman signal after self-cleaning with UV light. The intensity of Raman enhancement by 70 mM template decreased to 30 and 58% of MB and R6G, respectively. Due to the substance stain left in the hot spot of Au nanoparticles, the Raman spectrum enhancement was dropped. However, in conclusion, our SERS could be repeated. Finally, the reusable SERS with great efficiency in Raman signal enhancement even in small amounts of substance, 10^{-7} M, was invented.

Conclusions

The reusable SERS are successfully created by control diameters and lengths of ZnO NRs. The shape of ZnO NRs affects the performance to enhance the Raman signal. Reusable SERS can enhance the Raman signal at all precursor concentration of ZnO nanorod templates. The highest performance to enhance the Raman signal occurred by ZnO nanorod template with 70 mM precursor concentration because it has a large amount of Au nanoparticles on the top of the nanorod. The 70 mM reusable SERS can enhance Raman signal as low as 1×10^{-7} M concentration of R6G substance. The reusable SERS can be self-cleaning by activation with UV light and can be repeated.

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