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The size effect of silver nanocubes on gap-mode surface enhanced Raman scattering substrate

Kai-Wei Tsai^a, Kundan Sivashanmugan^a, Chen-Hsueh Lin^a, Po-Ju Tsai^a, Shu-Chun Cheng^a, Yung-Chiang Lan^b, Tsan-Yao Chen^c, Ten-Chin Wen^{a,d,*}^a Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan^b Department of Photonics, National Cheng Kung University, Tainan 70101, Taiwan^c Department of Engineering and System Science, National Tsing Hua University, Hsinchu 30013, Taiwan^d Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan 70101, Taiwan

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ABSTRACT

This study demonstrates the size effect of silver nanocubes with the namely dimension 50 and 70 nm atop the massed silver surface (denoted, 50-NcIM and 70-NcIM) on surface enhanced Raman scattering (SERS) by using rhodamine 6G and melamine with the irradiation of 532, 633, and 780 nm lasers. In addition, the NcIM substrate was exhibited a strong SERS effect under 633 and 780 nm laser irradiation. The enhancement factors of 50-NcIM and 70-NcIM samples were reached nearly 10^9 and 10^8 , respectively. The simulation results show that plasmonic cavities (PC) derived from 50-NcIM and 70-NcIM respectively possess the stronger electromagnetic field density and the larger extended PC area under 633 and 780 nm laser irradiation, interpreting the experimental results well.

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1. Introduction

Surface enhanced Raman scattering (SERS) is a powerful tool for detecting analytes in extremely low concentration for obtaining molecular-specific information [1–6]. To enhance the intensity of Raman signal, electromagnetic (EM) mechanism via localized surface plasmons resonance (LSPR) is an effective way to largely increase the SERS signal because the concentration of the local EM fields in the near field of the nanogaps between nanoparticles (NPs). The hot spot effect created by the closely spaced noble metal NPs (dimer or trimer) can be applied for SERS sensing due to the effective increase in the electric field between the NPs via the plasmons coupling of each NPs [7–9].

In order to fabricate a high sensitive, reproducible, and reliable SERS substrate via LSPR, focused ion beam technology had been applied to create regular array of nanostructured noble metals on the substrates for SERS sensing due to the large area of hot spot created between consecutive metal nanostructures (NSs) [10–12]. E-beam lithography can also create regular array of metals atop substrates for SERS application [13,14]. However, the production

cost and time consuming of these methods hindered the application for commercial and disposable use.

The NP-insulator-metal (NIM) configuration has been attracted much attention due to its easy control for the large area of hot spot by using a dielectric spacer between metal NPs and massed metal surfaces. The size of spacer should be smaller than 5 nm to construct effective EM field enhancement for molecular sensing. The dielectric spacer such as SiO_2 , Al_2O_3 , and polyelectrolyte had been used for creating coupling LSPR between metal NPs and massed metal surfaces named as the plasmonic cavity (PC) resonance [15–17]. In addition to using dielectric spacer, the PC resonance can also be created via self-assembled the metal NPs atop the metal surfaces [18–20]. Self-assembled monolayer technology enables us to fabricate SERS substrates with high density of silver nanocubes (Ag NCs) and precise nanogaps. However, spraying metal NPs atop substrates has the advantages such as large area, easy processing, and time saving for preparing SERS substrates with the NIM geometry [21–25]. In addition, spraying technique can be highly contribute the formation of PC by varying the process condition and factors. However, NPs aggregations on metal surface is still the key disadvantage in the development of spraying method. In this context, this paper focused on the development of higher order individual PC based SERS-active substrate. The wavelength of PC resonance can be tunable via changing the size of gap in NIM, size and shape of NPs. In this study, the PC derived by positioning Ag

* Corresponding author at: Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan. Fax: +886 6 2344496.

E-mail address: tcwen@mail.ncku.edu.tw (T.-C. Wen).

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NCs with the namely dimension 50 and 70 nm atop Ag surfaces were used to maximize the SERS intensity under the irradiation of 532, 633, and 780 nm lasers. The simulation of absorption spectra and the EM field density around Ag NCs also were investigated via finite difference time domain (FDTD) method for further confirmation the size effect of Ag NCs on the PC.

2. Experimental section

2.1. Synthesis of Ag nanocubes

The Ag NCs were synthesized via polyol method [26]. The 5 ml ethylene glycol (EG) was preheated in a round-bottom flask in oil bath with 150 °C treatment. The 0.06 ml sodium hydrosulfide solution (3 mM, dissolved in EG) was injected into the flask immediately when temperature was elevated to 150 °C. After 4 min, 0.5 ml hydrochloric acid solution (3 mM in EG) and 1.25 ml poly(vinyl pyrrolidone) (20 mg/ml in EG) solution were added into the flask, respectively. Another 4 min passed, the reaction time was controlled in 90 and 100 min respectively for small and large size Ag NCs after 0.4 ml silver trifluoroacetate (282 mM in EG) was added into the solution. All Ag NCs solution was purified via centrifugation before substrate fabrication. The morphology of the as-prepared Ag NCs was examined by transmission electron microscope (TEM).

2.2. Fabrication of SERS substrates

Ag thin film (~60 nm thickness) was deposited onto the cleaned indium tin oxide substrates by thermal evaporation of Ag (99.99% purity) and deposited at a controlled deposition rate. To fabricate a gap-mode on the substrates, the Ag surface was soaked in a 0.1% 1,2-ethanedithiol solution for 2 h and washed carefully to remove all unbonded 1,2-ethanedithiol. The substrates for SERS measurement were fabricated via depositing Ag NCs with 50 and 70 nm sizes by simple spray method on the 1,2-ethanedithiol assembled Ag surface (denoted, 50-NcIM and 70-NcIM) for creating large area of hot spot between Ag NCs and surfaces. The Ag NCs were deposited atop prepared Ag surface at spray rate of 0.04 ml/s from 4 mg/ml of Ag NCs solution for 100 s. The morphology and optical properties of the as-prepared substrates were characterized by scanning electron microscope (SEM), TEM and ultraviolet–visible (UV–vis) spectrophotometry.

2.3. SERS measurements

The Raman spectrum was taken by a confocal microscopic Raman spectrometer using a frequency-doubled diode-pumped Nd:YAG, He–Ne and diode lasers with excitation wave-lengths of 532, 633 and 780 nm, respectively. An air-cooled CCD was used as

the detector; the incident power was 3 mW with 20 s accumulation. The Raman spectra was calibrated via the characteristic peaks of silicon wafer at 520 cm^{-1} before each measurement. Rhodamine 6G (R6G) and melamine, used as the molecular probe, were diluted with aqueous solution to a concentration of 10^{-6} – 10^{-13} M. To verify the SERS mechanism, the NcIM substrate with the R6G and melamine containing solutions were covered with a glass slide and then rapidly measured using Raman spectroscopy. The enhancement factor (EF) and the standard deviations were averaged from ten consecutive measurements.

2.4. Simulation of electric field distribution of NcIM

All the simulation were done according the calculation of Maxwell equation via FDTD method which is done by the software named Meep [16]. The substrates used in the simulations were 50 and 70 nm Ag NCs atop the massed 60 nm thickness Ag surface with 1, 2, 2.5, and 3 nm dielectric spacer, which closely matched the experimental samples. The incident angle of x - y plane polarized excited energy source was normal to the substrate surfaces. The grid size of NCs for FDTD simulation was 0.25 nm. The surrounding boundaries were the perfectly matched layers. The absorbance spectra and EM field densities were calculated by the ratio of electric field strength under λ_{max} wave excitation.

3. Results and discussion

3.1. Characterization of NcIM substrate

Fig. 1(a) and (b) shows the TEM images of as-synthesized and homogeneously distributed Ag NCs with size of 53.70 ± 0.50 and 72.06 ± 0.77 nm (namely as 50 nm and 70 nm), respectively. The size distribution of Ag NCs are detailed in Fig. S1 in Supplementary Data (SD). By using these two sized Ag NCs, 50-NcIM and 70-NcIM SERS substrates were prepared by spraying them on the massed 1,2-ethanedithiol assembled Ag surface. The SEM images of 50 nm Ag NCs on Ag surface with 100 s of spraying time are shown in Fig. 1(c). In addition, with the spraying time of 60 s, few Ag NCs were deposited on the Ag surface and more aggregation of Ag NCs on the substrate with 120 s than 100 s of spraying time can be observed, as shown in Fig. S3 in SD. Thus, 50-NcIM and 70-NcIM substrates were prepared by spraying Ag NCs atop the massed Ag surface with 100 s spraying time for Raman measurements. Notably, the Ag NCs are randomly distributed and self-assembled on the massed Ag surface by Ag–S chemical bonds between two Ag interfaces, as detailed in our pervious publication [18]. In insert Fig. 1(c) shows that formation of nanogap (2.0 nm apart) between two metal interfaces via 1,2-ethanedithiol layer, which can generate a strong LSPR effect.

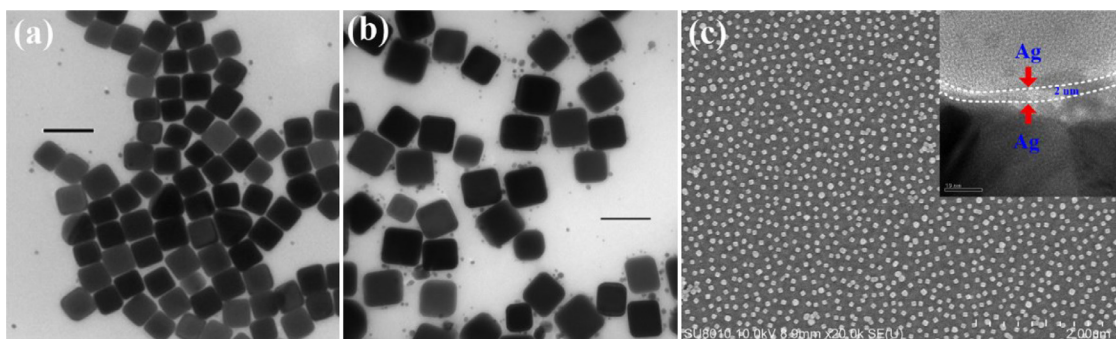


Fig. 1. The TEM images of namely (a) 50 nm (b) 70 nm Ag nanocubes. The SEM images of 50-NcIM substrate and insert TEM images shows the nanogap (2 nm) between two Ag interfaces (c).

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