Pillar-cap shaped arrays of Ag/SiO₂ multilayers after annealing treatment as a SERS –active substrate

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Abstract

The “pillar-cap” shaped arrays of Ag/SiO₂ multilayers were prepared on 2D PS template by sputtering Ag and SiO₂ materials alternatively. Annealing under argon accelerated the interface diffusion between Ag and SiO₂ sublayers. Some Ag nanoparticles squeezed into SiO₂ sublayer through the pinholes in SiO₂ sublayer and the corona-like structure consisting of SiO₂-trapped Ag nanoparticles formed on the surfaces of the pillar-cap arrays. The sizes of Ag nanoparticles varied from 2 nm to 5 nm, depending on the annealing temperature. The separations of 1-2 nm SiO₂ were generated between Ag particles and underlying Ag sublayer, which provided a lot of hot spot sites for SERS. This fabrication method could avoid the unnecessary and cumbersome stages in chemical surface modification, which made the substrate a promising candidate for the SERS detection.

Keywords: *SERS-active substrate, Pinholes, Ag nanoparticles, Hot spots*

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1. Introduction

At the surface of some metals, the coherent oscillations of the conduction electrons could be driven by light, which will lead to an enormous electromagnetic (EM) field enhancement in the close vicinity of the metal surface. And this is called as localized surface plasma (LSPs) [1-3]. Usually the great EM field enhancement is particularly strong at “hot spots”, like sharp tips or corners [4, 5], interparticles gaps [6-8] and nanopores [9, 10], and so on. These intense fields have found applications in highly popular technique of surface-enhanced Raman scattering (SERS) which is an emerging technique for fast, sensitive and nondestructive analysis [11]. Researches related to SERS have attracted the intense research efforts and yielded a variety of novel SERS platforms for different applications in chemistry, physics, medicine and biology [12–14]. The morphology, the material choices and nanostructure design have significant effects on SERS properties. A large variety of nanostructures, such as nanotips [15], nanobowls [16], and nanowires [17,18], have been extensively reported. At present, the major challenge for SERS substrate is how to create the substrate of good sensitivity, reproducibility and stability by a low cost and easy handling method. To achieve this purpose, various nanotechnologies have been developed, including chemical self-assembly, electron-beam lithography, electromigration, nanosphere lithography (NSL), and electrochemical metal growth [19-22]. In these techniques mentioned, NSL is the most promising one due to its fast preparation on large scale at low cost.

Noble metal nanostructures, particularly those made of Au and Ag, have shown

excellent SERS sensitivity because of their unique characteristics of localized surface plasmon resonance [23-26]. To realize the specific purpose, new composite and hybrid structured materials with high SERS sensitivity have been designed. Some nanostructures obtained by combining nanomaterials of the different composites present unique possibilities which could not be directly obtained in the single constituent, for example, TiO_2 -Ag [27-30], Au-Ag [31], SiO_2 -Ag [32] composite. It has been reported that the introduction of a dielectric layer SiO_2 not only protects Ag from oxidation but also enhances the SERS signals [33, 34].

In this paper, our strategy focuses on a minimum fabrication cost and simple procedure and great accessibility for the formation of optimized SERS substrate by heating Ag/ SiO_2 multilayer. This method provides multi-diffusion interfaces between Ag and SiO_2 hybrid structures. During annealing process, Ag squeezes into SiO_2 sublayer through the pinholes at the interfaces. The corona-like structures are generated with abundant hotspots between Ag nanoparticles. The distribution dependences of Ag particles trapped in SiO_2 on annealing temperatures were discussed.

2. Experimental section

2.1 Materials

The 10 wt % aqueous solution of monodisperse polystyrene (PS) colloid particles with average diameter 200 nm and density 1.05 g/cm^3 were purchased from Duke scientific corporation. 4-mercaptobenzoic acid (MBA, 99%), sodium dodecyl sulfate (analytic reagent, AR) were purchased from Sigma-Aldrich Co., Ltd. and used as

received. NH_4OH (25%), H_2O_2 (30%) and the ethanol (AR) were purchased from Sinopharm Chemical Reagent Co.,Ltd.

Ag (99.99%) and SiO_2 (99.99%)targets were purchased from Beijing TIANRY Science & Technology Developing Center. Silicon wafer purchased from Hefei kejing materials technology Co., Ltd, with the crystal orientation $\langle 100 \rangle$. The silicon wafer thickness is 0.52 mm and the diameter is 4 inch. Deionized water ($18.0 \text{ M}\Omega \text{ cm}^{-1}$) was used throughout the present study.

2.2 Assemble of PS arrays.

The silicon wafer were boiled in the solution of NH_4OH , H_2O_2 , and H_2O (volume ratio 1:2:6) for 5 minutes. Then they were ultrasonically cleaned for 10-15 minutes in the deionized water and the ethanol alternatively for three times. Then Si wafers were kept in 10% sodium dodecyl sulfate(SDS) solution to become hydrophilic after 24h, and then Si wafers were stored in the deionized water. Ethanol and polystyrene solution were mixed with volume ratio 1:1. Subsequently we dropped 8 μl of diluted polystyrene solution onto the hydrophilic Si wafer, and then the Si wafers covered by PS mixture were slowly immersed into the glass vessel (20 cm * 20cm) filled with deionized water. The PS particles formed the unordered monolayer films on the water surface. After that, 8 μl of 2% sodium dodecyl sulfate solution was added onto the water surface to drive the monolayer films into the highly ordered patterns. The monolayer films of the 2D PS arrays were picked up by the hydrophilic Si wafers.

2.3 Preparation of [Ag 30 nm/ SiO_2 5 nm] n (n=1-4) multilayer nanostructure.

First, 30 nm Ag layer was deposited onto PS template of colloidal bead diameter

200 nm, and then 5 nm SiO₂ layer was deposited onto the Ag layer surface. By sputtering Ag and SiO₂ targets alternatively, [Ag 30 nm/SiO₂ 5 nm]_n multilayers were prepared with different recycle periods. The thickness of multilayer is larger than the radius of PS when the recycle periods are 4, so that the shape of multilayer array looks like pillar-cap, that is, the body is pillar-shaped and the top is cap-shaped. The multilayer preparation was performed in a magnetron sputtering system of ATC 1800-F. The base pressure is 2×10^{-6} Pa and the argon pressure is 0.6 Pa during film deposition. The distance of targets to substrate is 8 cm. The sputtering powers of Ag and SiO₂ targets are 20 W and 72 W respectively. The deposition rate is 0.059 nm/s and 0.0054 nm/s for Ag and SiO₂. The substrate was cooled by recycled water so that its temperature is kept under about 30 °C during sputtering which can be neglected for heat effect of substrate.

2.4 Annealing of Ag/SiO₂ multilayer nanostructure.

The as-fabricated Ag/SiO₂ multilayers were immersed into tetrahydrofuran for 24 h to remove PS particles. Then the substrates were annealed at 200 °C, 400 °C, 600 °C, 700 °C respectively for 1 hour under argon. The heating rate is 2 °C/min, and the argon gas flux is 0.8 L/min.

2.5 Probe molecules absorption.

4-mercaptobenzoic acid (MBA) solution was used as probe molecules, and the concentration was 10^{-3} mol/L. The Ag/SiO₂ multilayer substrates were immersed in probe molecule solution for 30 minutes and then were washed thoroughly with ethanol and deionized water repeatedly to remove unabsorbed probe molecules. The

samples were finally gently dried with N₂ gas.

2.6 Characterization of substrates and SERS.

Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) are used to investigate the morphology and microstructure of the Ag/SiO₂ arrays. The SEM images were operating at 15.0 kV with a JEOL 6500F, a high-resolution (1.5 nm) thermal field emission electron microscope. TEM and high resolution transmission electron microscopy (HRTEM) images were obtained with JEM-2100F, and the energy is 200 keV. Raman spectra were measured in a Renishaw Raman system model 2000 confocal microscopy spectrometer equipped with a charge-coupled device (CCD) detector and a holographic notch filter. Radiation of 532 nm was used for the SERS from an air cooled argon ion laser (20 mW). The microscope was used to focus the laser beam onto a spot of the diameter 1 μ m with a 50 $\times$ long-range objective, a Leica DMLM system. The equipment is in a 180 $^\circ$ backscattering geometry and the time to collecting signal was set at 10 s. The XPS was obtained using a Thermo Scientific ESACLAB 250Xi A1440 system, calibrated by carbon (C1s = 284.6 eV). The analyzing spot size is 500 μ m, Al K α and the energy step size is set up as 1.0 eV.

3. Results and discussions

3.1 Microstructure profile of pillar-cap array

The schematics of ordered Ag/SiO₂ multilayer pillar-cap arrays are illustrated in figure 1. 2D PS array with bead diameter 200 nm is prepared on Si substrate by self-assembly technique and Ag/SiO₂ multilayer is deposited onto the PS array by

magnetic control sputtering method (Fig. 1a). To avoid organic contamination during the following annealing, PS colloidal sphere is removed by the tetrahydrofuran solution etching. These PS spheres serve as a sacrificial layer to preserve the close-packed nanostructure arrays with curved surfaces. The PS-free samples are annealed under argon at different temperatures for 1 h. The pillar-cap nanostructure array over cm^2 -sized ordered areas is obtained on the Si substrate. And different annealing temperatures lead to the different microstructures, as shown in fig.1b and c. The SEM image of the large ordered areas for the pillar-cap array is given in fig.1d

SEM and TEM are used to investigate microstructure of $[\text{Ag } 30 \text{ nm}/\text{SiO}_2 \text{ } 5 \text{ nm}]_4$ pillar-cap array. The SEM section view and TEM image show the pillar-like units are composed of 4 nanocaps, each of which overlaps another. Because neighbor Ag layers are separated by SiO_2 layer, the interfaces between Ag and SiO_2 are distinguished obviously due to the different properties of Ag and SiO_2 , which indicates the SiO_2 insertion can avoid the agglomeration of Ag particles. TEM image also confirms that alternately grown Ag and SiO_2 layers form Ag/ SiO_2 multilayer pillar-cap array (fig. 2b). And HRTEM image in figure 2c shows Ag layer is covered by amorphous SiO_2 layer and the thickness of SiO_2 is about 5 nm.

3.2 Influences of annealing temperature

Figure 3 shows the SEM images and SERS spectra of $[\text{Ag } 30 \text{ nm}/\text{SiO}_2 \text{ } 5 \text{ nm}]_4$ array at different annealing temperatures. In the SERS spectra, the peak at 1075 cm^{-1} , which has been assigned to the in-plane ring breathing mode coupled with $\nu(\text{C-S})$, is used to study the evolution of the peak intensity for different substrates [35]. SEM

images show the annealed pillar-cap arrays retain the perfect close-packed nanostructure as that the as-fabricated samples even when the annealing temperatures reach 700 °C, which indicates the annealing does not destroy the ordered pattern because of the SiO₂ working as the supporting framework. But the sample morphology changes with the increasing temperature. Compared to the as-fabricated array, the surface roughness for annealed samples is obviously larger. The rough surface acts as the hot spot sites for localization of electromagnetic fields, which enhances Raman signals of analyte molecules (Fig. 3f). When annealing at 200 °C, many tiny particles appear on the multilayer surface. The particles gradually grow and agglomerate into big clusters with the increasing temperature. When the annealing temperature reaches 600 °C, the sizes of the cluster are about 20-30 nm and many interstitial regions exist between the clusters, and the maximum rough surfaces are obtained. Under this annealing temperature, the Raman intensity significantly is enhanced, which is ascribed to the high-density hot spots on pillar-cap array surfaces. The SERS intensity declines obviously when annealing temperature is 700 °C, which is caused by the declined surface roughness (Fig. 3f).

3.3 Influences of cycle periods

To further investigate the effects of annealing on the SERS of the pillar-cap array with multilayer structure, [Ag 30 nm/SiO₂ 5 nm]_n (n=1-4) multilayers with different cycle periods are annealed at 600 °C. Figure 4 shows SERS spectra from the as-fabricated and annealed multilayer array, in which the Ag monolayer films are also given. Compared to Ag monolayer film, the as-fabricated Ag/SiO₂ bilayers with one

thin SiO₂ layer have the largest SERS intensity. And the SERS intensity decreases dramatically when the cycle period of the multilayers increase, which is ascribed to the decrease of the hotspot density due to the linkage of adjacent nanocaps with each other when the thickness of film is larger than the radius of PS [36]. In contrast to the as-fabricated multilayer, the annealed multilayers with different periods exhibit the significant enhancements in SERS activity except for the monolayer Ag film. The SERS intensity increases gradually with the SiO₂ introduction and increasing cycle period. It is interesting that the strongest SERS signals are found in the annealed array with cycle period $n=4$, which means the weakest SERS signals in as-fabricated multilayer. Meanwhile, it is notable that Ag monolayer has only one Raman peak at 1078 cm⁻¹, lower than that of the as-fabricated monolayer Ag film. When SiO₂ layer is absent, the periodical structure of the monolayer Ag may be destroyed during annealing and the surface morphology is similar to the flat Ag film, which lead to the obvious decrease of Raman intensity. We believe that the annealing accelerates the diffusion between Ag layer and SiO₂ layer and changes the microstructures and morphologies of the array. At the same time, the SiO₂ dielectric layer plays an important role in the SERS enhancement during annealing.

3.4 Mechanism of microstructure evolution under annealing

Compared to the as-fabricated nanostructure, the distributions of Ag and SiO₂ and the surface morphology of multilayers change after annealing. Figure 5a-d give the TEM and HRTEM images for [Ag/SiO₂] multilayer annealed at 400 °C and 600 °C respectively. After annealing, the interfaces between Ag and SiO₂ layers become

unclear, and many Ag particles appear in the amorphous SiO₂ layer. SiO₂-trapped Ag particles look like the corona surrounding the pillar-cap units, as can be seen in TEM images (Fig 5a and 5c). We believe that during the annealing, heating energy and the stress applied by the curved interface drive the interface diffusion between Ag and SiO₂ layers. The Ag diffusion is accelerated when annealed. In this case, the pinholes in SiO₂ layer are chosen as the tunnel for Ag to squeeze into the SiO₂ sublayer. When the annealing temperature is higher, Ag diffusion is faster and more Ag metal comes through the pinholes. Therefore, higher annealing temperature leads to bigger Ag particles (reference to the schematic in Fig. 1b and 1c). The Ag nanoparticles are trapped in SiO₂ layer to form a corona-like structure. HRTEM image shows the Ag nanoparticles are around 2 nm trapped in SiO₂ layers at 400 °C, which are highlighted by the red circles as shown in figure 5b. When temperatures increase from 400 °C to 600 °C, the Ag nanoparticles grow from 2 nm to 5 nm (Fig. 5d). The corona-like structures consisting of SiO₂-trapped Ag nanoparticles form with many built-in hot spots. The electromagnetic field excited by the surface plasma from core Ag particles can be transferred to the SiO₂ layer and the field intensity can also be adjusted and controlled by insulator SiO₂ layer, which results in a remarkable Raman signal enhancements.

3.5 Analysis of Ag chemical state by XPS

XPS are used to reveal the oxide state of Ag and the result is shown in figure 6. Ag 3d_{5/2} and Ag 3d_{3/2} peaks are located at 368.3 eV and 374.3 eV respectively for the multilayer annealed below 700 °C. These peak positions are similar to the ones

observed for bulk Ag [37, 38]. A tiny shift of the Ag 3d XPS peaks position is observed as a function of annealing temperature, which could be attributed to the interaction between Ag and its environment that leads to a tiny amount of Ag oxides at the surface of Ag [39, 40]. When the annealing temperature reaches 700 °C, the Ag peaks move towards to the lower energy position and the Ag 3d 5/2 peak located at 367.9 eV belongs to Ag-O bonding in Ag₂O. These results show that the introduction of SiO₂ protects the Ag particles from oxidation when annealing temperature is lower than 700 °C in our experiment. The Ag oxides formation is another reason for the decline of SERS intensity at 700 °C.

3.6 Uniformity and reproducibility

Figure 7 shows the uniformity and reproducibility for the [Ag 30 nm/SiO₂ 5 nm]₄ nanostructure annealed at 600 °C. To do this, SERS spectra of MBA molecules on the multilayer nanostructure are examined at ten different points. SERS spectra show almost identical intensities and shapes, indicating the uniform enhancement over the entire substrate. The relative standard deviation of the intensity is calculated to be 6.2% with respect to the average intensity of the band at 1075 cm⁻¹ indicating the SERS enhancements are uniform across the sample surface, which means our SERS substrate is suitable for the practical use in biological and chemical sensing devices.

4. Conclusion

In summary, we have demonstrated a low-cost and easy handling method for SERS substrate of nanopillar-cap array, in which the high-density hot spots are generated by heating Ag/SiO₂ multilayer. A corona-like structure consisting of SiO₂-trapped Ag

nanoparticles forms on the surface of nanopillar-cap array after annealing. The corona-like structure and nanoparticle sizes can be modulated by annealing. With the increasing temperature, the SiO₂-trapped Ag nanoparticles grow from 2 nm to 5 nm. In comparison with as-fabricated Ag/SiO₂ multilayer, the annealed multilayers enhance the plasmon coupling and result high SERS intensity. The nanopillar-cap arrays annealed at 600 °C show the roughest surface, from which the strongest SERS signals are observed, about one order of magnitude higher than that of as-fabricated substrate. In addition, the annealed pillar-cap array shows the excellent signal reproducibility (6.2%). Our approach allows the possibility of creating nanoparticles of other metals such as Pd, Pt or Ag encaged in SiO₂ or TiO₂ for SERS-active substrate, which presents an easy and scalable fabrication technique of Ag/SiO₂ multilayer arrays for SERS application and have bearing on other plasmonic technologies, like plasmonic photocatalysis [41-42].

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References

- [1] D. Rodríguez-Fernández, J. Langer, M. Henriksen-Lacey, and L. M. Liz-Marzán, Hybrid Au–SiO₂ Core–Satellite Colloids as Switchable SERS Tags, *Chem. Mater.*, 27 (2015) 2540–2545.
- [2] M. D. Sonntag, J. M. Klingsporn, A. B. Zrimsek, B. Sharma, L. K. Ruvuna, R. P. Van Duyne, Molecular plasmonics for nanoscale spectroscopy, *Chem. Soc. Rev.*, 43(2014) 1230-1247.
- [3] Q. Fu, Z. B. Zhan, J. X. Dou, X. Z. Zheng, R. Xu, M. H. Wu, and Y. Lei, Highly Reproducible and Sensitive SERS Substrates with Ag Inter- Nanoparticle Gaps of 5 nm Fabricated by Ultrathin Aluminum Mask Technique, *ACS Appl. Mater. Interfaces*, 7 (2015) 13322–13328.
- [4] J. Fang, S. Du, S. Lebedkin, Z. Li, R. Kruk, M. Kappes, H. Hahan , Gold Mesostructures with Tailored Surface Topography and Their Self-Assembly Arrays for Surface-Enhanced Raman Spectroscopy , *Nano Lett.*, 10 (2010) 5006-5013.
- [5] R. Zhang, Y. Zhang, Z. C. Dong, S. Jiang, C. Zhang, L. G. Chen, L. Zhang, Y. Liao, J. Aizpurua, Y. Luo, J. L. Yang, and J. G. Hou, Chemical mapping of a single molecule by plasmon-enhanced Raman scattering, *Nature*, 498 (2013) 82-86.
- [6] D. K. Lim, K. S. Jeon, J. H. Hwang, H. Kim, S. Kwon, Y. D. Suh and J. M. Nam, Highly uniform and reproducible surface-enhanced Raman scattering from DNA-tailorable nanoparticles with 1-nm interior gap, *Nat. Nanotechnol.*, 6 (2011) 452-460.

- [7] J. Song, B. Duan, C. Wang, J. Zhou, L. Pu, Z. Fang, P. Wang, T. T. Lim, H. Duan, SERS-Encoded Nanogapped Plasmonic Nanoparticles: Growth of Metallic Nanoshell by Templating Redox-Active Polymer Brushes, *J. Am. Chem. Soc.*, 136 (2014) 6838–6841.
- [8] J. W. Oh, D. K. Lim, G. H. Kim, Y. D. Suh, J. M. Nam, Thiolated DNA-Based Chemistry and Control in the Structure and Optical Properties of Plasmonic Nanoparticles with Ultrasmall Interior Nanogap, *J. Am. Chem. Soc.*, 136 (2014) 14052–14059.
- [9] H. Abramczyk, B. Brozek-Pluska, Raman Imaging in Biochemical and Biomedical Applications. Diagnosis and Treatment of Breast Cancer, *Chem. Rev.*, 113 (2013) 5766–5781.
- [10] Y. Wang, B. Yan, L. Chen, SERS Tags: Novel Optical Nanoprobes for Bioanalysis, *Chem. Rev.*, 113 (2013), 1391–1428.
- [11] D. Fernand, C. Pardanaud, D. Bergé-Lefranc, P. Gallice and V. Hornebecq, Adsorption of Rhodamine 6G on SiO₂ and Ag@SiO₂ Porous Solids: Coupling Thermodynamics and Raman Spectroscopy, *J. Phys. Chem. C*, 118 (2014) 15308–15314.
- [12] S. C. Xu, Y. X. Zhang, Y. Y. Luo, S. Wang, H. L. Ding, J. M. Xu and G. H. Li, Ag-decorated TiO₂ nanograss for 3D SERS-active substrate with visible light self-cleaning and reactivation, *Analyst*, 138 (2013) 4519–4525.
- [13] H. B. Tang, G. W. Meng, Q. Huang, Z. Zhang, Z. L. Huang, and C. H. Zhu, Arrays of Cone-Shaped ZnO Nanorods Decorated with Ag Nanoparticles as 3D

- Surface-Enhanced Raman Scattering Substrates for Rapid Detection of Trace Polychlorinated Biphenyls, *Adv. Funct. Mater.*, 22 (2012) 218–224.
- [14] D. Majumdar, A. Singha, P. K. Mondal and S. Kundu, DNA-Mediated Wirelike Clusters of Silver Nanoparticles: An Ultrasensitive SERS Substrate, *ACS Appl. Mater. Interfaces*, 5 (2013) 7798–7807.
- [15] W. Zhang, X. D. Cui, B. -S. Yeo, T. Schmid, C. Hafner and R. Zenobi, Nanoscale roughness on metal surfaces can increase tip-enhanced Raman scattering by an order of magnitude, *Nano.Lett.*, 7 (2007) 1401-1405.
- [16] J. Ye, P. V. Dorpe, W. V. Roy, G. Borghs, G. Maes, Fabrication, characterization, and optical properties of gold nanobowl submonolayer structures, *Langmuir*, 25 (2009) 1822-1827.
- [17] I. Yoon, T. Kang, W. Choi, J. Kim, Y. Yoo, S. -W. Joo, Q. H. Park, H. Ihee, B. Kim, Single nanowire on a film as an efficient SERS-active platform, *J. Am. Chem. Soc.*, 131 (2008) 758-762.
- [18] H. Wei, F. Hao, Y. Z. Huang, W. Z. Wang, P. Nordlander, H. X. Xu, Polarization dependence of surface-enhanced Raman scattering in gold nanoparticle– nanowire systems, *Nano. Lett.*, 8 (2008) 2497-2502.
- [19] Y. Yokota, K. Ueno, H. Misawa, Essential Nanogap Effects on Surface-Enhanced Raman Scattering Signals from Closely Spaced Gold Nanoparticles, *Chem. Commun.*, 47 (2011) 3505–3507.
- [20] H. G. Duan, H. L. Hu, K. Kumar, Z. X. Shen and J. K. W. Yang, Direct and Reliable Patterning of Plasmonic Nanostructures with Sub-10-nm Gaps, *ACS*

- Nano, 5 (2011) 7593–7600.
- [21] G. Amarandei, C. O'Dwyer, A. Arshak, D. Corcoran, Fractal Patterning of Nanoparticles on Polymer Films and Their SERS Capabilities, ACS Appl. Mater. Interfaces, 5 (2013) 8655–8662.
- [22] P. Goldberg-Oppeneheimer, S. Mahajan, U. Steiner, Hierarchical Electrohydrodynamic Structures for Surface-Enhanced Raman Scattering, Adv. Mater., 24 (2012) OP175–OP180.
- [23] V. G. Kravets, G. Zorinians, C. P. Burrows, F. Schedin, A. K. Geim, W. L. Barnes, A. N. Grigorenko, Composite Au nanostructures for fluorescence studies in visible light, Nano. Lett., 10 (2010) 874-879.
- [24] X. M. Kong, Q. Yu, X. F. Zhang, X. Z. Du, H. Gong and H. Jiang, Synthesis and application of surface enhanced Raman scattering (SERS) tags of Ag@SiO₂ core/shell nanoparticles in protein detection, J. Mater. Chem. 22 (2012) 7767–7774.
- [25] S. Pal, J. Sharma, H. Yan, and Y. Liu, Stable silver nanoparticle-DNA conjugates for directed self-assembly of core-satellite silver–gold nanoclusters, Chem. Commun., (2009) 6059–6061.
- [26] H. W. Yoo, J. M. Jung, S. K. Lee, and H. T. Jung, The fabrication of highly ordered silver nanodot patterns by platinum assisted nanoimprint lithography, Nanotechnology, 22 (2011) 095304.
- [27] J. S. Teguh, F. Liu, B. Xing, E. K. L. Yeow, Surface-Enhanced Raman Scattering (SERS) of Nitrothiophenol Isomers Chemisorbed on TiO₂, Chem. Asian J., 7

(2012) 975–981.

- [28] X. Li, H. Hu, D. Li, Z. Shen, Q. Xiong, S. Li, H. J. Fan, Ordered Array of Gold Semishells on TiO₂ Spheres: An Ultrasensitive and Recyclable SERS Substrate, *ACS Appl. Mater. Interf.*, 4 (2012) 2180–2185.
- [29] X. Li, G. Chen, L. Yang, Z. Jin and J. Liu, Multifunctional Au-Coated TiO₂ Nanotube Arrays as Recyclable SERS Substrates for Multifold Organic Pollutants Detection, *Adv. Funct. Mater.*, 20 (2010) 2815–2824.
- [30] E. Z. Tan, P.G. Yin, T. T. You, H. Wang, L. Guo, Three Dimensional Design of Large-Scale TiO₂ Nanorods Scaffold Decorated by Silver Nanoparticles as SERS Sensor for Ultrasensitive Malachite Green Detection, *ACS Appl. Mater. Interf.*, 4 (2012) 3432–3437.
- [31] H. Chang, H. Kang, J. -K. Yang, A. Jo, H. Y. Lee, Y.S. Lee, and D. H. Jeong, Ag Shell–Au Satellite Hetero-Nanostructure for Ultra-Sensitive, Reproducible and Homogeneous NIR SERS Activity, *ACS Appl. Mater. Interfaces*, 6 (2014) 11859–11863.
- [32] Y. J. Hu, Y. L. Shi, H. Jiang, G. J. Huang and C. Z. Li, Scalable Preparation of Ultrathin Silica-Coated Ag Nanoparticles for SERS Application, *ACS Appl. Mater. Interfaces*, 5 (2013) 10643–10649.
- [33] X. F. Zhang, and X. Z. Du, Carbon Nanodot-Decorated Ag@SiO₂ Nanoparticles for Fluorescence and Surface-Enhanced Raman Scattering (SERS) Immunoassays, *ACS Appl. Mater. Interfaces*, 8 (2016), 1033–1040.
- [34] T. T. B. Quyen, W. N. Su, K. J. Chen, C. J. Pan, J. Rick, C. C. Chang and B. J.

- Hwang, Au@SiO₂ core/shell nanoparticle assemblage used for highly sensitive SERS-based determination of glucose and uric acid, *J. Raman Spectrosc.*, 44 (2013) 1671–1677.
- [35] X. L. Zhang, Z. Yu, W. Ji, H. Sui, Q. Cong, X. Wang and B. Zhao, Charge-Transfer Effect on Surface-Enhanced Raman Scattering (SERS) in an Ordered Ag NPs/4-Mercaptobenzoic Acid/TiO₂ System, *J. Phys. Chem. C*, 119 (2015) 22439–22444.
- [36] M. C. Wu, M. P. Lin, S. W. Chen, P. H. Lee, J. H. Li, and W. F. Su, Surface-enhanced Raman scattering substrate based on a Ag coated monolayer array of SiO₂ spheres for organic dye detection, *RSC. Adv.*, 4 (2014) 10043-10050.
- [37] V. Uzayisenga, X. D. Lin, L. M. Li, J. R. Anema, Z. L. Yang, Y. F. Huang, H. X. Lin, S. B. Li, J. F. Li, and Z. Q. Tian, Synthesis, Characterization, and 3D-FDTD Simulation of Ag@SiO₂ Nanoparticles for Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy, *Langmuir*, 28 (2012) 9140–9146.
- [38] G. B. Hoflund, Z. F. Hazos and G. N. Salaita, Surface characterization study of Ag, AgO, and Ag₂O using x-ray photoelectron spectroscopy and electron energy-loss spectroscopy, *Phys. Rev. B*, 62 (2000) 11126 –11133.
- [39] H. H. Huang, X. P. Ni, G. L. Loy, C. H. Chew, K. L. Tan, F. C. Loh, J. F. Deng, G. Q. Xu, Photochemical formation of silver nanoparticles in poly(N-vinylpyrrolidone), *Langmuir*, 12 (1996) 909–912.
- [40] V. Uzayisenga, X.D. Lin, L.M. Li, J. R. Anema, Z.L. Yang, Y.F. Huang, H.X. Lin,

S.B. Li, J.F. Li, and Z.Q. Tian, Synthesis, Characterization, and 3D-FDTD Simulation of Ag@SiO₂Nanoparticles for Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy, *Langmuir*, 28 (2012) 9140-9146.

[41] Koichi Awazu, Makoto Fujimaki, Carsten Rockstuhl, Junji Tominaga, Hirotaka Murakami, Yoshimichi Ohki, Naoya Yoshida, and Toshiya Watanabe, A Plasmonic Photocatalyst Consisting of Silver Nanoparticles Embedded in Titanium Dioxide, *J. Am. Chem. Soc.*, 2008 (130) 1676-1680.

[42] Guido Soliveri, Valentina Pifferi, Guido Panzarasa, Silvia Ardizzone, Giuseppe Cappelletti, Daniela Meroni, Katia Sparnacci and Luigi Falciola, Self-cleaning properties in engineered sensors for dopamine electroanalytical detection *Analyst*, 2015 (140) 1486–1494.

Captions

Figure 1. Schematic diagram of the structure for pillar-cap $[\text{Ag } 30 \text{ nm}/\text{SiO}_2 \text{ } 5 \text{ nm}]_4$ arrays by nanosphere lithography (a). Different microstructures are caused by annealing at (b) low temperature and (c) high temperature. (d) Less magnified SEM image of large ordered domains

Figure 2. Section view SEM (a) and TEM (b) and HRTEM (c) images for the as-fabricated $[\text{Ag } 30 \text{ nm}/\text{SiO}_2 \text{ } 5 \text{ nm}]_4$ multilayer array.

Figure 3. SEM images and SERS spectra of $[\text{Ag } 30 \text{ nm}/\text{SiO}_2 \text{ } 5 \text{ nm}]_4$ pillar-cap array after annealing at different temperatures (a) room temperature, (b) 200°C , (c) 400°C , (d) 600°C , (e) 700°C , and (f) SERS spectra under different annealing temperatures.

Figure 4. SERS spectra for the as-fabricated (A) and the annealed $[\text{Ag } 30 \text{ nm}/\text{SiO}_2 \text{ } 5 \text{ nm}]_n$ ($n=1-4$) at 600°C (B). Curve a represents the spectrum from Ag monolayer. And curve b-e represents the spectra from samples with the cycle period 1-4.

Figure 5. TEM and HRTEM images of the microstructure for the annealed $[\text{Ag } 30 \text{ nm}/\text{SiO}_2 \text{ } 5 \text{ nm}]_4$ pillar-cap nanostructure, (a, b) 400°C , (c, d) 600°C .

Figure 6. XPS spectra of $[\text{Ag } 30 \text{ nm}/\text{SiO}_2 \text{ } 5 \text{ nm}]_4$ pillar-cap nanostructure annealed at different temperatures

Figure 7. Uniformity and reproducibility test at ten different points on the $[\text{Ag } 30 \text{ nm}/\text{SiO}_2 \text{ } 5 \text{ nm}]_4$ “pillar-cap” pair multilayer nanostructures annealed at 600°C .

Figure 1._ WYX

Figure 2._ WYX

Figure 3._ WYX

Figure 4._ WYX

Figure 5._ WYX

Figure 6._ WYX

Figure 7._ WYX