Applied Surface Science xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Facile fabrication of large-area and uniform silica nanospheres monolayer for efficient surface-enhanced Raman scattering

Junqi Tang, Qianrun Zhao, Ning Zhang, Shi-Qing Man*

College of Physics and Electronic Information, Yunnan Normal University, Kunming 650031, China

ARTICLE INFO

Article history:
Received 2 March 2014
Received in revised form 9 April 2014
Accepted 18 April 2014
Available online xxx

Keywords:
Surface-enhanced Raman scattering (SERS)
Silica nanosphere
Composite nanostructure
Langmuir–Blodgett (LB)

ABSTRACT

A large-area efficient surface enhanced Raman scattering (SERS) substrate was deposited by Langmuir–Blodgett (LB) assembly and followed by sputter coating process. The interparticle distance of silica nanospheres was convenient and readily regulated by controlling the surface pressure. After sputter coating with a small amount of gold, the nanocomposite film was formed. The surfaces of nanostructures were characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The applicability of the nanostructures as SERS substrates was investigated by adsorption of crystal violet (CV) molecules. Different SERS effects were observed on deposited gold nanostructure upon large-area silica nanospheres monolayer with diameter of 250, 570 and 800 nm. It was also discussed the nanospheres with diameter of 250 nm for the fabrication of ordered arrangement of monolayers at surface pressures of 10–30 mN/m. These substrates with the close-packed nanospheres and sputtering of gold were found to exhibit high and uniform enhancement of the Raman signal across the entire surface. The averaged surface enhancement factor (ASEF) was calculated and discussed. The fabricated nanocomposite structures could be utilized as low-cost SERS-active substrates for biomedical and analytical chemistry field.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Surface-enhanced Raman scattering (SERS) is as a powerful analytical tool extensively used in many areas of chemistry and biology [1,2], due to its excellent sensitivity for molecular vibrations when the analyte is close to a nanoscale rough metal surface. Presently, there are two generally acceptable mechanisms of overall SERS effect: electromagnetic (EM) enhancement and chemical (CHEM) enhancement. EM is based on laser excitation inducing localized electromagnetic field at the surface of noble metals. CHEM is associated with the charge transfer between the noble metal and adsorbate at atomic-scale roughness features [3,4].

A great deal of strategies has been employed for preparing metal nanostructure substrates with atomic scale roughness for SERS applications such as sono-electrochemical pulse deposition [5], lithographic techniques [6] and self-assemble techniques [7]. However, it is still a challenge to produce portable, stable, reproducible, inexpensive, and conveniently fabricating SERS substrates with large-area structure. The nanoparticles deposition substrates can cover a large surface area but the drawback is a random deposition of the particles, resulting in a disordered distribution of hot-spots and lithographic substrates can provide excellent control on density and position of the hot-spots, but have several limitations such as high cost, long production time, and small patterned area [8]. A number of experiments have demonstrated that Langmuir–Blodgett (LB) assembly method is a reliable technique to prepare a large-area monolayer of anisotropic building blocks [9,10].

In this context, we fabricated large area SERS substrates which provided uniform roughness and sufficient enhancement performance. Silica nanoparticles were well packed in a long range order by LB technique and subsequently covered with gold by sputter coating process. The obtained large area metal film over nanospheres (MFON) provided well uniformity and enhancement performance of Raman signal for the substrate. The surface pressure which was the main influential factor of preparation uniform large scale monolayer film was discussed in this study. Crystal violet (CV) was selected as the model molecule to measure substrates enhancement factors.

* Corresponding author at: Chenggong Campus: No. 1 Building of Ruizhi, 768# Juxian Street, Chenggong District, Kunming 650500, Yunnan, China.
Tel.: +86 871 65941177; fax: +86 871 65941177.
E-mail addresses: man_shiqing@yahoo.com, tjunqi@163.com (S.-Q. Man).

http://dx.doi.org/10.1016/j.apsusc.2014.04.143
0169-4332/© 2014 Elsevier B.V. All rights reserved.

Please cite this article in press as: J. Tang, et al., Facile fabrication of large-area and uniform silica nanospheres monolayer for efficient surface-enhanced Raman scattering, Appl. Surf. Sci. (2014), http://dx.doi.org/10.1016/j.apsusc.2014.04.143

2. Experimental

2.1. Chemicals and instrumentation

All chemicals were of analytical grade and used as received without further purification. Tetraethyl orthosilicate (TEOS, 99.9%), anhydrous ethanol (EtOH, 99.7%), ammonium hydroxide (NH_4OH, 25%) were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Crystal violet was supplied from Aladdin (Shanghai, China). Deionized water with a resistivity of 18.2 MΩ cm was obtained from a Millipore Simplicity-185 ultrapure-water purification system and used throughout the experiment. The glasses were cut into rectangles (about 25 × 20 × 1.2 mm) and cleaned by being immersed into a piranha solution (30% H_2O_2 + 70% H_2SO_4 volume ratio) at 70 °C for 3 h. Then the slides were washed with copious amounts of distilled water.

The size distribution and monodispersity of SiO_2 nanoparticles were checked by using PHILIPS TECNAI-10 transmission electron microscope (TEM) operated at an accelerating voltage of 100 kV. The Langmuir–Blodgett monolayer was prepared using a KSV mini trough (Finland) filled with deionized water. Scanning electron microscopy (SEM) was carried out on PHILIPS XL-30 ESEM with accelerating voltage of 20 kV, and used to determine the surface morphology of monolayer films deposited on glass substrates. Atomic force microscopy (AFM) was also used for surface morphology studies. The measurements were carried out in tapping mode using a Thermo Microscopes Auto-Probe CP Research AFM. The surface pressure was measured with a Wilhelmy plate. SERS measurements were performed by an Advantage-785 Raman Spectrometer equipped with a 50× objective, of focal length 50 mm (DeltaNu, America).

2.2. Preparation of silica nanoparticles

The preparation of silica nanoparticles with diameter of 250 nm was similar to the Stöber method and our previous report [11]. In brief, 2.5 mL of TEOS was added swiftly under rapidly stirring to a mixture of 25 mL of EtOH, 4.5 mL of H_2O and 5 mL of NH_4OH. The reaction mixture turned turbid white as SiO_2 particles formed after about 2 min. Then, the reaction with moderate stirring was allowed to continue for 2 h at room temperature. By varying the concentrations of TEOS, ammonium and water, the final particle sizes can be easily adjusted. Silica nanoparticles with 570 nm were synthesized by adding 5.5 mL EtOH and 2.5 mL of TEOS mixture to the solution containing 17 mL of EtOH, 9 mL of NH_4OH and 7.5 mL of H_2O. Larger monodisperse SiO_2 nanospheres with a diameter of 800 nm were synthesized according to the so-called seeded growth reaction [12]. A 5 mL aliquot of 570 nm silica suspensions was then used as seeds. Sequentially the seeds solution was dropwise added into the mixtures solution containing 2 mL of TEOS and 8 mL of water with vigorous stirring, and then the resulting mixture was stirred for 30 min more.

2.3. Surface-modification of silica nanoparticles

The as-synthesized silica nanosphere was centrifuged at 4000 rpm for 5 min. The precipitations were collected and ultrasonic re-suspended in ethanol. This process was repeated 3–6 times. The final precipitation was dispersed in 10 mL of ethanol. This procedure removed excess aqua ammonia and gave a homogenous solution of nanospheres. Vinyltriethoxysilane (VTES) was employed as surface modifying agent. Firstly, 50 μL of VTES was dropped in a 10 mL of ethanol and DI water mixture (v/v, 1:3), and an amount of 2 mL glacial acetic acid was added to adjust the solution pH value to ~4 and stirring for 1 h at room temperature. Secondly, 2 mL of 25% NH_4OH was added to adjust the pH value to ~10, followed by the addition of 5 mL of ethanol dispersion of silica nanospheres, and stirring was continued for 10 h. Finally, the suspensions were centrifuged at 8000 rpm for 5 min and rinsed 2 times with ethanol to remove excess reactants. The product was dried at 100 °C for 2 h to form hydrophobic silica nanospheres.

2.4. Langmuir–Blodgett assembly

The hydrophobic silica nanospheres were dispersed in 10 mL of chloroform. The suspension was spread drop-wise (typically 500 μL of 10 mg/mL concentration) on the water surface of a Langmuir–Blodgett trough by using a microsyringe. The amount of suspensions added to the trough differed with respect to particle size, and an optimal amount was decided through monitoring surface pressure area (π–A) isotherms. The nanospheres monolayer on the water surface was left 15 min waiting period to let the chloroform evaporate and reached the equilibrium state, which was compressed by a barrier with a speed of 30 cm^2/min. The surface pressure was measured with a Wilhelmy plate during the compression. The film was compressed to different surface pressures (10, 15 and 30 mN/m), and then deposited to glass substrates for further studies. Typically, the substrates were pulled by the vertical dipping method with a speed of 10 mm/min.

2.5. Sputter coating gold film on silica monolayer

Gold films were deposited onto the monolayer arrays of SiO_2 nanospheres by a conventional sputter coating. The process of putter coating was performed with a Balzers Bal-Tec SCD 005 instrument at 30 mA for 90 s.

3. Results and discussion

3.1. Transmission electron microscope images

Fig. 1 showed typical TEM images of monodisperse SiO_2 solid spheres of diameter 250, 570 and 800 nm. It was shown that the nanoparticles were uniform in size distribution with a standard deviation of about 15%.

3.2. LB films for different sizes of the silica nanoparticles

Fig. 2 showed the surface pressure–area (π–A) isotherm of SiO_2 nanospheres monolayer film obtained at subphase temperature of 20 °C and pH 7.0 and SEM images of the deposited LB monolayer of silica nanospheres. The nanoparticle layer went from a gaseous phase to a solid condensed phase characterized by a sharp increase in surface pressure, followed by monolayer collapse at even higher pressures [13]. All π–A curves displayed three phases with the monolayer compression at the air–water interface (Fig. 2 a, c and e). At the beginning of the LB compression, the average distance between silica nanospheres was quite large, so that the total trough area decreased from 240 to 110 cm^2 (diameter of 250 nm) at approximately surface pressure (π) = 0 (Fig. 2a). This region was comparable to the gaseous phase. As the barrier moved toward each other, the nanoparticles closed into a quasi-2-dimensional liquid phase. The total trough area decreased from 110 to 60 cm^2. As the total area decreased below 60 cm^2, the monolayer was compressed into a 2D-quasi solid phase. The value of pressure of the quasi-solid monolayer was observed to begin at ~10 mN/m. And the surface pressure was sharp increased from 10 to 55 mN/m. This process was because the interparticle distance became very small and indicated a densely packed monolayer of the silica particles formed. When the barrier compressed further and the surface pressure was above ~55 mN/m, some nanoparticles clusters were formed and

Please cite this article in press as: J. Tang, et al., Facile fabrication of large-area and uniform silica nanospheres monolayer for efficient surface-enhanced Raman scattering, Appl. Surf. Sci. (2014), http://dx.doi.org/10.1016/j.apsusc.2014.04.143

Download English Version:

https://daneshyari.com/en/article/5350079

Download Persian Version:

https://daneshyari.com/article/5350079

Daneshyari.com