

Tuning SERS properties of pattern-based MWNTs-AuNPs substrates by adjustment of the pattern spacings

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ABSTRACT

Vertically-aligned multi-walled carbon nanotubes (MWNTs) arrays were designed with different pattern spacings on silicon wafer and tunable three-dimensional (3D) surface-enhanced Raman scattering (SERS) substrates were fabricated by decorating the patterned MWNTs arrays with gold nanoparticles (AuNPs) via magnetron sputtering and annealing. SERS substrates with large amounts of “hot spots” were achieved by adjusting the thickness of sputtered gold film. The microstructure of MWNTs-AuNPs hybrid materials were examined under scanning electron microscopy (SEM) and transmission electron microscope (TEM). The Raman scattering behavior of MWNTs arrays was systematically investigated. Surface-enhanced Raman scattering property of MWNTs-AuNPs was demonstrated using molecular probes Rhodamine 6G (R6G) solutions as standard analyte and the pattern spacing was found to significantly affect Raman intensity. MWNTs-AuNPs substrates with pattern spacing of 100 nm were used to evaluate the SERS property of the material and the detection concentration level was found as low as 10^{-10} M.

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1. Introduction

With the rapid development of modern laser technology and nanotechnology, scientists have made considerable progress in ultra-sensitive detection analysis technologies for obtainment of information from small material volumes [1]. Among the technologies, surface-enhanced Raman scattering (SERS) spectroscopy is renowned not only as nondestructive but also as extremely high sensitive [2,3]. SERS can be employed in a broad spectrum of applications including, chemical and biological sensing [4,5] and single-molecule detection [6,7].

Progress in SERS is inseparable from progress in the development of SERS substrates wherein fabrication of highly-efficient and stable substrates has emerged as a crucial research field [8,9]. The “hot spots”, which exist in the nanogaps between metal nanoparticles, can create regions of intense local fields and are regarded as the key to fabricate the ideal SERS substrate. To allow collection

and detection of as much scattered light as possible as well as to achieve more “hot spots” on the SERS substrate, the preparation of three-dimensional (3D) SERS substrates have been proposed [10–13]. Since Planeix announced the synthesis and application of noble metal nanomaterials/carbon nanotube (CNT) nanocomposites in 1994 [14], intense scientific effort has been exerted towards obtainment of noble metal nanoparticles with high dispersibility and small particle size on the surface of CNTs [15,16]. Advances in CNT growth techniques led to considerable increases in both production rate and product volume over the last years [17]. Various research on the growth of vertically aligned carbon nanotubes on silicon and other substrates via chemical vapor deposition (CVD) have been systematically investigated [18,19]. Good quality CNT arrays fabricated on a variety of substrates have also been considered for promoting the 3D structure of SERS substrates [20,21]. Zhang et al. [22] reported that hybrid multi-walled carbon nanotubes (MWNTs) modified by AgNPs structures can yield extremely high SERS activity as effective 3D substrates wherein more target molecules can be observed and detected in 3D laser focus volume. 3D SERS substrates based on vertically aligned CNT

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arrays were developed by Lai et al. [23]. They reported that the formation of “hot spots” between AuNPs in the unit volume of 3D structures with high densities of gold nanoparticles, generates more effective Raman scattering enhancement performance. Yet to date, the control of metal nanoparticles parameters, such as particle size, shape, type, were systematically investigated and confirmed to affect the Raman property of SERS substrate. To the best of our knowledge, tuning surface-enhanced Raman properties of CNT-based SERS substrate by adjusting the effect of CNTs' parameters, which acts as a carrier of precious metal particles, has not been systematically investigated [22,23]. Moreover, it is still an appealing and ongoing challenge to achieve fine control (or “tuning”) over the arrangement and spacing of nanostructured materials for optimized SERS [24]. This combined with the current need for further improvement in the performance of SERS technique through the development of efficient SERS substrates, has been the motivation behind the present study.

The present paper investigated the efficiency of gold nanoparticle (AuNPs)-covered patterned MWNTs arrays as 3D SERS substrates. The arrays were initially synthesized by CVD on locally confined catalyst-modified areas. The patterned arrays were decorated with AuNPs by magnetron sputtering with subsequent annealing to fabricate the final substrates. By adjustment of pattern spacings, 3D SERS substrates with tunable surface-enhanced Raman scattering properties were achieved. The microstructure of patterned MWNTs arrays and MWNTs-AuNPs was investigated under scanning electron microscopy (SEM), transmission electron microscope (TEM), and Raman measurements. The crystallinity and integrity of different patterned MWNTs arrays were analyzed. The surface-enhanced Raman scattering property of MWNTs-AuNPs was investigated through the use of molecular probes Rhodamine 6G (R6G) solutions and the effect of pattern spacing on the Raman intensity was investigated. MWNTs-AuNPs substrates with pattern spacing of 100 nm were used to evaluate the SERS properties of the material and the detection concentration level was found as low as 10^{-10} M.

2. Experimental section

2.1. Patterning of vertically aligned MWNTs arrays

The patterning process is shown in Fig. 1. Therein, mask templates with different pattern spacings (12 μm , 6 μm , 3 μm , and 100 nm) were designed and patterned Fe-catalyst was deposited on the Si wafers by standard mask lithography methods. Then the vertically aligned MWNTs arrays were grown on the modified areas by CVD in Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences. Argon with 6% hydrogen and pure ethylene were used as the forming gas and the carbon source, respectively.

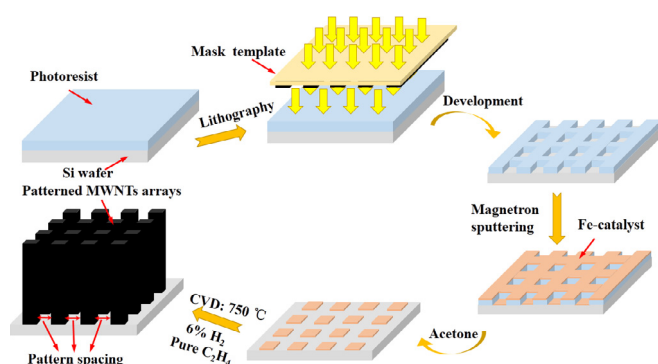


Fig. 1. Preparation process of patterning of vertically aligned MWNTs arrays. (A colour version of this figure can be viewed online.)

The total flow rate of gases was set at 1.5 L/min. The growth chamber was kept at 750 °C for 10 min. Four kinds of pristine patterned MWNTs arrays with spacings of 12 μm , 6 μm , 3 μm and 100 nm, were prepared.

2.2. Preparation of patterned MWNTs-AuNPs

The SERS substrate is shown in Fig. 2. Gold nanoparticles were deposited on the substrates by magnetron sputtering (MSP-300BT, Wiener Technology Co., Ltd, Beijing, China) followed by high temperature annealing. According to the previous reports [25,26], when the solid film was heated to a sufficiently high temperature, it will gradually turn into islands or nanoparticles due to its instability in the as-deposited state. It was found that the dewetting process of solid films normally occurs via surface diffusion and the rate of it is strongly related to the film thickness and temperature. Therefore, in order to allow achievement of SERS substrates with large numbers of “hot spots”, which exist in the nanogaps between AuNPs and also the nanogaps between AuNPs and MWNTs, the thickness of gold films was controlled by adjustment of the deposition time of magnetron sputtering and all samples were annealed at 450 °C for a duration of an hour.

2.3. Characterization and Raman measurements

The surface morphology of prepared samples was characterized using field emission gun scanning electron microscope (SEM, Hitachi S-2700, Tokyo, Japan) and transmission electron microscope (TEM, FEI Tecnai F20G2, USA). The elements of MWNTs-AuNPs were confirmed by energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments X-Max^N). The absorption spectra of pure AuNPs, pure MWNTs and MWNTs-AuNPs were measured using an ultraviolet-visible (UV-vis) spectrophotometer (Perkin-Elmer Lambda 35 UV-vis-NIR). Specimens of $5.00 \times 5.00 \text{ mm}^2$ (length $\times$ width) were used for Raman tests. For each Raman detection, 3 samples were used and each sample was tested for 3 times. SERS spectra were acquired with a confocal laser Raman spectrometer (Horiba Renishaw inVia Raman Microscope) operating an air-cooled frequency doubled Nd: YAG green laser ($\lambda = 532 \text{ nm}$, $P = 50 \text{ mW}$, 10% laser power and 10s exposure time) at room temperature. The microscope was equipped with a $50 \times$ objective lens. Relevant experiments using R6G ($\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$) as the molecular probes were conducted to analyze the SERS performance of all samples.

3. Results and discussion

3.1. Characterization of patterned MWNTs arrays

SEM images of the microstructure of MWNTs arrays with pattern spacings of 12 μm , 6 μm , 3 μm and 100 nm are shown in

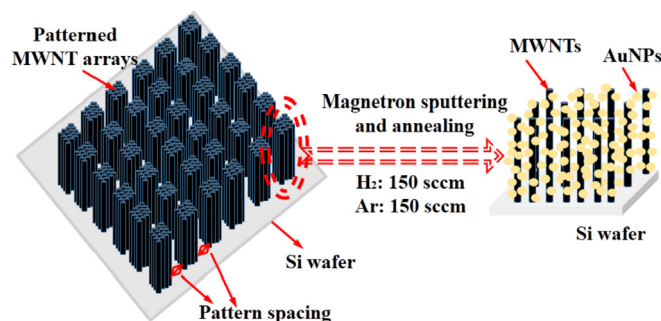


Fig. 2. Preparation process of patterned MWNTs-AuNPs. (A colour version of this figure can be viewed online.)

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