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Surface-enhanced Raman scattering from bowtie nanoaperture arrays

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ABSTRACT

This paper is dedicated to Professor P.R. Norton on the occasion of his 75th birthday, in honor of his profound contributions to Surface Science. Bowtie nanoaperture arrays with different tip-to-tip distances were fabricated on thin gold film by focused ion beam (FIB) milling. White light transmission spectra for all the bowtie nanoaperture arrays were collected and the relationship between the tip-to-tip distance and the surface plasmon resonance (SPR) frequency was evaluated. Finite-difference time domain (FDTD) simulations were carried out for the white light transmission and for the local field intensity with the aim of correlating the optical transmission peaks to the tip-to-tip distances. Surface-enhanced Raman scattering (SERS) was collected from bowtie nanoaperture arrays coated with rhodamine 6G. It was found that the SERS properties vary with the tip-to-tip distances of the bowties of same aperture size and same periodicity. The relationships between SERS, SPR frequency and the local field intensity are discussed.

1. Introduction

Surface-enhanced Raman scattering (SERS) enables a million-fold average increase [1,2] of the Raman signal. Although charge-transfer resonances [3,4] might also play a role, the amplification of local electromagnetic fields provides the main contribution to the overall enhancement [5,6]. The potential for applying the SERS technique for high sensitive (at single molecule level [7–9]) analytical [10,1] and bioanalytical [12] detection drives the pursuit of new types of SERS substrates with controllable and reproducible enhancements. Several works related to the fabrication of noble metal nanostructures with various shapes, sizes, and aggregate states for SERS applications have been published in recent years [11,13–21].

The huge local electromagnetic field amplification responsible for SERS originates from the excitation of surface plasmon (SP) oscillations [1,2]. For instance, when two metallic nanoparticles supporting SPs are close enough to allow coupling, an electromagnetic hotspot is created in between the particles. The local electromagnetic field is amplified by a few orders of magnitude within the hotspot region. Molecules adsorbed on hotspots experience the enhanced field, leading to an amplification of their Raman scattering (the SERS phenomenon) [1,2]. The hotspot area is just a few square nanometers, and the field enhancement drops exponentially with the distance from the center of the spot. The small size and large spatial variation of the field enhancement in the hotspot leads to challenges related to the preparation of stable and reproducible SERS substrates from chemically synthesized nanoparticles. For instance, most wet chemistry procedures yield distributions of nanoparticle shapes and sizes, resulting in batch-to-batch variations in SERS performance [12,16,22]. Although several advances in nanoparticles synthesis and self-assembly has generated SERS substrates with narrow spatial and sample-to-sample variations in SERS intensities [14,23], fabricated SERS substrates with a stable and reproducible distribution of hotspots have the potential to provide a better performance in terms of reproducibility [10,24,25].

Ordered circular nanoaperture arrays have been reported as a promising [26–31] SERS substrate for several applications [32,33]. These arrays of nanoholes on gold films support surface plasmon resonance (SPR), which leads to the local electromagnetic field amplification required for SERS. The SPR properties of the ordered circular nanoapertures can be tuned by their geometric characteristics and by the illumination conditions [28,34–39]. Fabrication methods for the preparation of nanoaperture arrays that do not involve expensive ion beam milling have been proposed [27,35]. However, the SERS enhancement factor for circular nanoapertures is typically smaller than observed from random metallic nanostructures. Several groups have suggested a variety of aperture shapes to allow an increase in SERS efficiency relative to the circular apertures [39–42]. Although bowtie (BT) nanostructures generated by triangular nanoparticle dimers [43–47] provided strong hotspot

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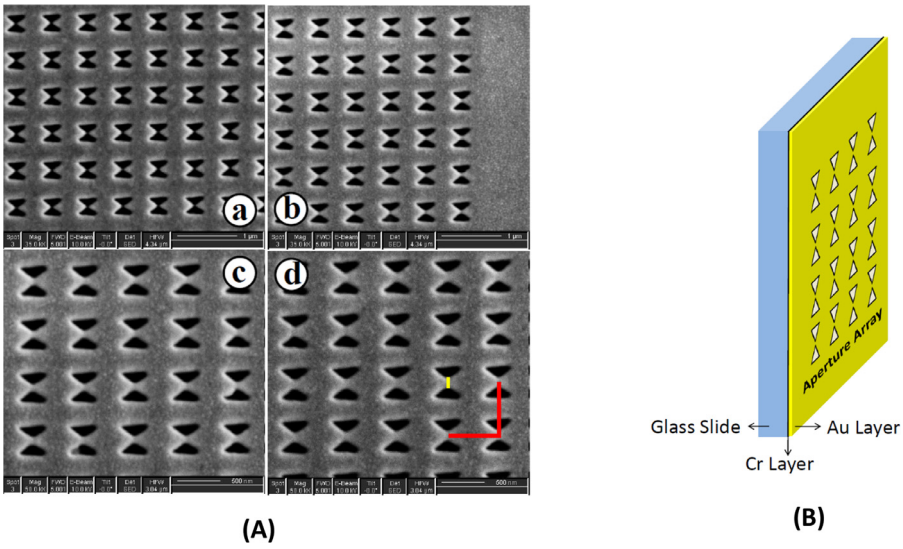

Fig. 1. (A) SEM images of bowtie nanoaperture arrays with: a) 0 nm, b) 50 nm, c) 75 nm, and d) 110 nm tip-to-tip distances (shown as a yellow line). All the arrays have the same 600 nm periodicity (shown as the red lines); (B) schematic view of the glass slide bearing the bowtie nanoaperture array in its center. A thin adhesive layer of Cr was in between the Au layer and the glass slide. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

localization [48–53], the use of bowtie-shaped apertures is less common [54]. In this work, BT nanoaperture arrays with fixed periodicity and varied tip-to-tip distances have been fabricated and characterized. Their properties as SERS substrates have been evaluated using electromagnetic calculations. The results presented here provide insights into the plasmonic modes that play a role in the SERS from shaped apertures.

2. Materials and methods

2.1. Bowtie nanoaperture arrays

Four different types of BT nanoaperture arrays with variable tip-to-tip distances (0, 50, 75 and 110 nm, respectively) were fabricated using FEI 235 focused ion beam (FIB) milling and imaged in a field emission scanning electron microscope (SEM) present in the same system (dual beam instrument). A glass slide coated with a 5 nm thick chromium adhesion layer and a 100 nm thick gold layer was used to fabricate the nanoapertures. The slides were commercially acquired from Evaporated Metal Films.

Back facing triangle pairs were defined as a BT nanoaperture unit. Fig. 1(A) shows the as-fabricated bowtie nanoaperture arrays. These apertures were drilled through the gold film to reach the glass slide. The shape and topographical features of the bowtie nanoaperture arrays is seen in Fig. 1. The distance between two neighboring BT units was defined as the periodicity (shown by the red lines in Fig. 1(A)). All the four arrays shared the same 600 nm periodicity. In each BT aperture unit, the length of the base of all triangular apertures was about 300 nm with heights of approximately 150 nm (within 10%). The tip-to-tip distances were designed to vary from one array sample to another, ranging from 0 nm (barely connected) to 110 nm. Variation of the tip-to-tip distance can be used for tuning the SPR peaks [44,45,51].

2.2. Optical and spectroscopic measurements

White light transmission spectroscopy was used to characterize the SPR properties of all the BT nanoaperture arrays discussed in Fig. 1. Detailed experimental and data manipulation procedures can be found in a previous publication [33].The transmission peak of the gold layer and the dark noise have been removed from the final transmission spectrum using a background subtraction procedure.

SERS measurements were carried out using a Renishaw inVia Raman microscope system. A cw He–Ne laser with excitation wavelength of 632.8 nm was used. Notice that this wavelength (632.8 nm) is not resonant with the R6G electronic transition (~530 nm). Fig. 2 shows the schematic view of the SERS setup. A Teflon cell with the glass slide bearing the BT nanoaperture array was used to hold the analyte solution. A 63× (NA = 0.75) water immersion objective lens was used to collect the Raman signals. The laser spot (~3 μm^2) was focused on the surface of the BT nanoaperture arrays. Normal Raman spectra were taken with the laser spot focused on the plain gold surface to compare with the Raman signal from the BT nanoaperture arrays.

2.3. Numerical simulations

Numerical simulations were carried out using the FDTD method. The simulations modelled the optical transmission and local field enhancement properties of all the arrays. The simulations were performed using the commercial Lumerical software. The simulations considered the nanostructures immersed in aqueous solutions ($n = 1.33$). Details of the numerical approach can be found elsewhere [55,56].

2.4. Chemicals

Rhodamine 6G (R6G-CAS 989-38-8, Sigma-Aldrich) was used as the molecular probe (analyte) for all the SERS spectroscopy measurements. A final concentration of 10 μM R6G aqueous solution was used. The R6G molecule contains a xanthene group and a carboxyphenyl group (shown in Fig. 2). These two major π systems act as the chromophores, and R6G in aqueous solution displays a large absorption peak at 530 nm and a vibronic shoulder around 470 nm [57,58].

3. Results and discussion

3.1. Optical transmission

Fig. 3A shows the white light transmission spectra (using unpolarised light) through all the BT nanoaperture arrays. Two transmission peaks (labelled as Peak 1 (short wavelength) and Peak 2 (long wavelength)) are seen in all spectra. Both peaks are attributed to the extraordinary optical transmission (EOT) phenomenon [59], in which the SPR of the