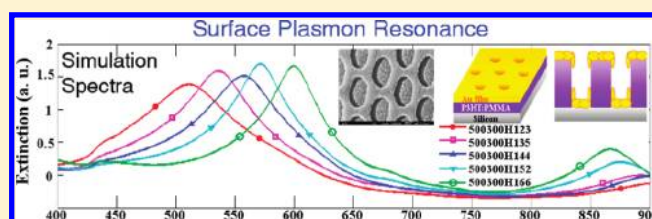


# Effects of Gold Film Morphology on Surface Plasmon Resonance Using Periodic P3HT:PMMA/Au Nanostructures on Silicon Substrate for Surface-Enhanced Raman Scattering

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Supporting Information

**ABSTRACT:** We study the effects of the morphology of gold film on the unusual modulation of surface plasmon resonance (SPR) and surface-enhanced Raman scattering (SERS) using the periodic nanostructures of P3HT:PMMA/Au on the silicon substrate. The periodic structures of cylindrical holes with triangular lattice were fabricated first by e-beam lithography using a photoluminescent resist of P3HT:PMMA at a thickness of  $\sim 100$ – $200$  nm, and the structures were then coated with gold of  $\sim 20$  nm thickness. The geometries and structures of the samples were studied by atomic force microscopy and scanning electron microscopy. The relationships between the geometry and the resonance were investigated by the extinction spectra and confocal Raman mapping. The results show that the resonance wavelength of the extinction peak is blue shifted, and its width becomes wider when the hole diameter of the structure increases or the lattice constant decreases. However, the extinction peak is red shifted when the thickness of the periodic nanostructures increases due to the surface plasmon resonance, localized surface plasmon resonances, and coupling between neighboring holes. The finite-difference time-domain (FDTD) method was adopted to simulate different nanostructures, and we found that the morphology and location of gold film on the periodic structure of P3HT:PMMA film played a vital role in the extinction spectra of the composite film of P3HT:PMMA/Au. A large enhancement of Raman scattering was observed when the SERS and SPR were correlated in the nanostructure at the exciting wavelength of 632.8 nm. This study provides a useful strategy to modulate the extinction spectra and enhance the intensity of Raman spectra by changing the nanostructures. The observed SERS will be useful for the design and fabrication of functional devices and sensors.



## 1. INTRODUCTION

Recently, study of surface plasmon resonances (SPR) and its applications has rapidly increased because of the development of nanomaterials and nanofabrication technologies. Many different geometries of plasmonic nanostructures using a periodic array of nanostructures in metallic films<sup>1–3</sup> and metallic nanoparticles<sup>4–6</sup> have been studied. It has been shown that nanoholes and nanoparticles can raise intriguing SPR in periodic array nanostructures. While the electromagnetic field in a small cavity (or hole) in Au film behaves as a light source along the rim of a hole<sup>7</sup> and causes the localized surface plasmon, the nanohole arrays in metallic film can yield higher transmission than a single cavity. In 2D cylindrical nanohole arrays SPR strongly depends on the geometries of the structures, such as the spacing between holes (i.e., the lattice constant),<sup>8</sup> shape of hole,<sup>9</sup> depth of hole,<sup>10</sup> lattice type,<sup>11</sup> and dielectric constants of materials.<sup>12</sup> Also, a cavity resonant mode was found in 2D cylindrical nanohole arrays.<sup>13</sup> The different physical mechanisms for various resonances have been described by several analytical studies.<sup>8,14,15</sup> The resonances in quasi-3D plasmonic crystals are more complicated because they include both the resonances formed in 2D cylindrical and the coupling between the metallic films.<sup>16–19</sup> The resonances of the nanostructures can be modified by controlling

the geometric parameters, and this becomes a useful method to modulate the optical properties and design devices suitable for specific applications, like sensing or detecting.<sup>20,21</sup>

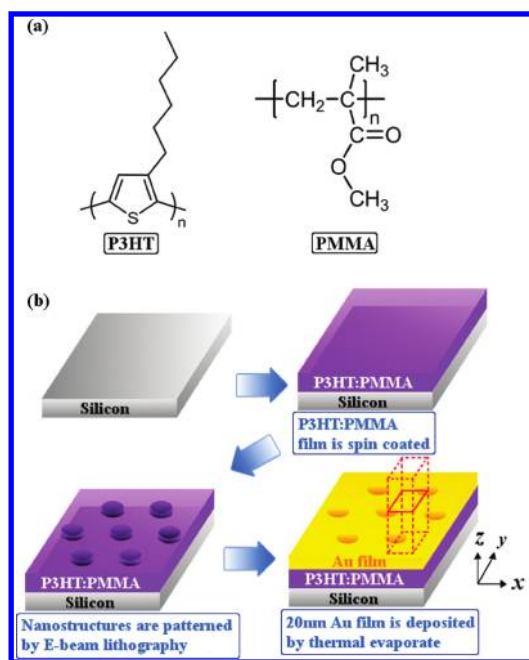
Surface-enhanced Raman scattering (SERS) is one of the most important applications in SPR studies because it can have strong field enhancement for sensing and detecting the chemical or biological samples. The SERS signals can be enhanced by the strong local electromagnetic field due to the localized surface plasmon resonances (LSPR) coupled with the vibration intensities of the molecules near the nanostructures.<sup>22</sup> The SERS signal intensities are related to the nanostructure sizes,<sup>23</sup> shapes,<sup>24</sup> and distributions.<sup>25</sup> The studies of SERS include not only the periodic structures in metallic thin films but also the metallic nanoparticles.<sup>26–28</sup>

We developed a photoluminescent electron-beam resist by blending poly(3-hexyl thiophene) and poly(methyl methacrylate) (P3HT:PMMA = 1:50 wt ratio), and it has both good thermal stability and high optical resolution.<sup>29</sup> The chemical structures of P3HT and PMMA are shown in Figure 1a. P3HT is a

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**Figure 1.** (a) Chemical structures of P3HT and PMMA. (b) Schematic illustration of the fabrication procedure of P3HT:PMMA/Au hybrid film with periodic nanostructure. The rectangle box marked by the dashed lines in the bottom right figure is our computation domain, and the rectangle marked by solid lines is located at the interface between the gold film and air.

photoluminescent polymer due to its conjugated double bond. Both polymers will decompose under electron-beam irradiation; thus, a positive photoluminescent pattern can be generated from the blend of P3HT and PMMA. In this study, we used this resist to fabricate several plasmonic gold nanostructures with different structural parameters, including the space between holes and the diameter and the depth of the hole. The optical properties of fabricated samples were evaluated by their extinction spectra and SERS signals. Using the finite-difference time-domain (FDTD) method the light intensity distributions of different structures were simulated, and their resonance behaviors were studied. The simulation results were compared with the experimental results. Also, the physical mechanisms were described based on both experimental observations and numerical studies. The results provide a useful strategy to fabricate new optical devices using periodic P3HT:PMMA/Au nanostructures.

## 2. EXPERIMENTAL METHODS

**2.1. Preparation of P3HT:PMMA/Au with Periodic Nanostructures.** A mixture of P3HT and PMMA (P3HT:PMMA = 1:50 by weight) electron-beam photoresist was prepared by dissolving 0.04 wt % of P3HT ( $M_w$  7000; PDI 1.2, RR 95% synthesized in our laboratory) and 2 wt % of PMMA ( $M_w$  996 000, Aldrich) in chlorobenzene. The solution was then stirred for 48 h in room temperature, and it was filtrated before use (0.22  $\mu\text{m}$  filter). The fabrication procedure of the P3HT:PMMA/Au nanostructure is schematically shown in Figure 1b.

First, the silicon wafer was washed with acetone, ethanol, and deionized water sequentially to remove surface impurities and then dried by nitrogen. The P3HT:PMMA photoresist solution was then spin coated at a specific speed for 90 s to form the

desired photoresist thickness and baked at 180  $^{\circ}\text{C}$  for 10 min. In this case, average film thicknesses of 166, 152, 144, 135, and 123 nm were obtained for a spin rate of 600, 800, 1000, 1200, and 1400 rpm, respectively. High-resolution nanolithography was performed using the Elionix ELS-7000 electron-beam lithography machine to write the designed patterns across a 150  $\mu\text{m}$   $\times$  150  $\mu\text{m}$  field with 2.5 nm beam step size (periodic range is 50  $\mu\text{m}$   $\times$  50  $\mu\text{m}$   $\approx$  9600 holes). The electron-beam writer system was operated at 100 kV with a beam current of 0.1 nA. A P3HT:PMMA-coated Si was irradiated with a dose time of 0.6  $\mu\text{s}$  to obtain 16 different design patterns. Methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA) were used to develop the P3HT:PMMA resist at 25  $^{\circ}\text{C}$  for 40 s with a volume ratio of MIBK:IPA = 1:3. Then, the sample was placed into the IPA solution for 20 s to remove excess reagent and washed with deionized water to complete the imaging process. Finally, a 20 nm thick Au film was deposited on the patterned P3HT:PMMA structures using a thermal evaporator (Kaoduen, Taiwan) to obtain P3HT:PMMA/Au periodic nanostructures.

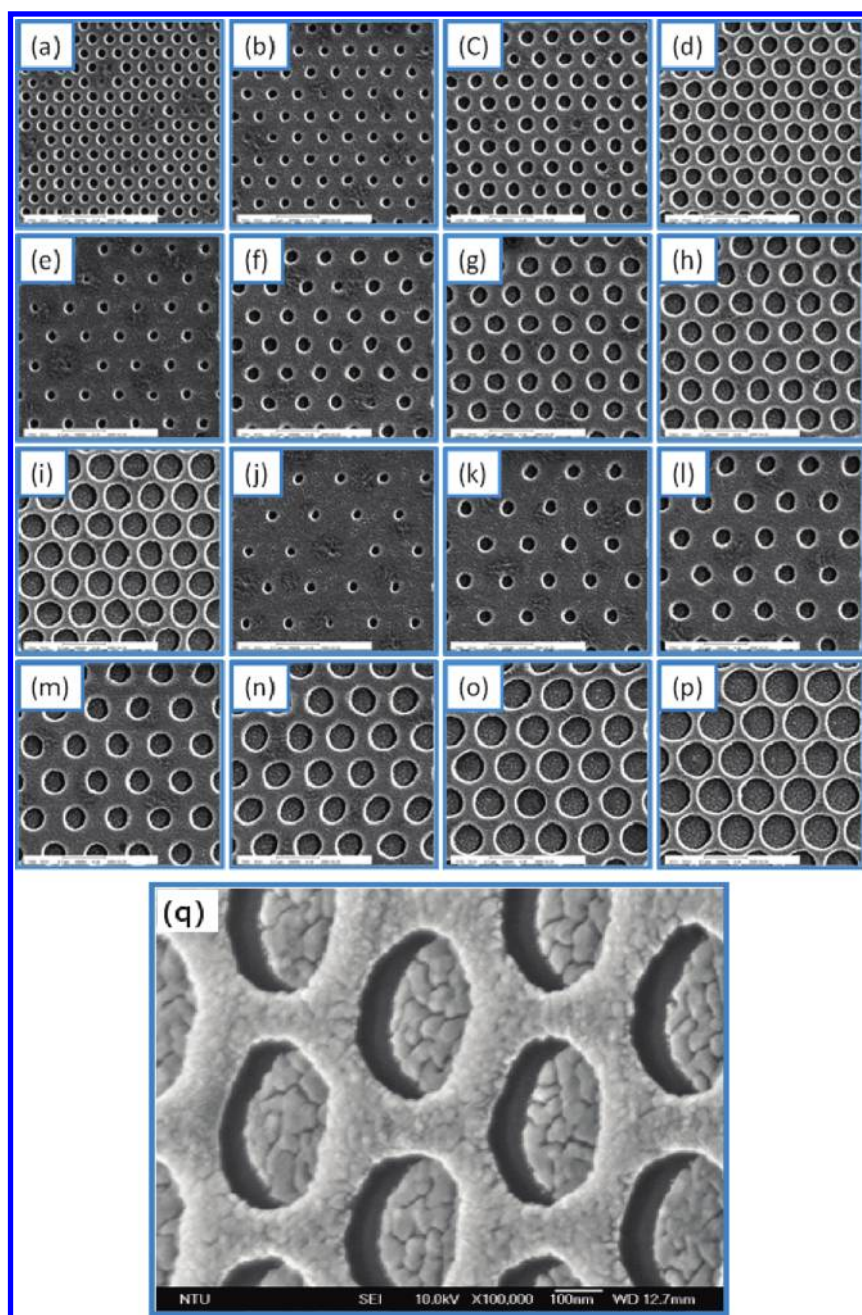
**2.2. Measurement Setup.** Extinction spectra of P3HT:PMMA/Au patterns were measured using a spectral microreflectometer (Mission Peak Optics, MP100-ME) equipped with an optical microscope. The unpolarized light was focused on the samples to measure the reflected light with wavelengths ranging from ultraviolet to near-infrared light (250–1000 nm). To obtain the extinction spectra of P3HT:PMMA/Au periodic structures, the light intensity of ambient environment ( $D_\lambda$ ) was measured first and the reflected light intensity of bare silicon wafer ( $R_\lambda$ ) was measured as a reference point. Then, the reflected light intensities of P3HT:PMMA/Au periodic arrays ( $S_\lambda$ ) were measured. The extinction spectrum  $A_\lambda$  can be calculated using the following equation

$$A_\lambda = -\log_{10} \left( \frac{S_\lambda - D_\lambda}{R_\lambda - D_\lambda} \right) \quad (1)$$

In order to obtain the Raman scattering lights and collect the scanning Raman mapping images, the P3HT:PMMA/Au specimens were positioned on a high-resolution piezoelectric stage of the scanning microscopy (WITec, Alpha300 S) and excited by a He–Ne laser of 632.8 nm. The laser beam was focused with a 100 $\times$  objective lens (Nikon plane objective, NA  $\approx$  0.9), and the diameter of the laser beam focus was about 1  $\mu\text{m}$ . In this study, the Raman mapping images were obtained by integrating the light intensities of the Raman scattering spectra with an integration time of 0.02 s and 200  $\times$  200 data points per image.

To obtain the actual geometry of the fabricated structures and the surface profiles atomic force microscopy (AFM, Digital Instruments, Nanoscope III A) was used to measure the surface topography of the P3HT:PMMA/Au periodic structures. Also, a field-emission scanning electron microscopy (FE-SEM, Elionix, ERA-8800FE) was used to observe the nanostructures of the P3HT:PMMA/Au patterns. These imaging geometries were used for our numerical simulations and theoretical studies.

**2.3. Simulation Setup.** The Lumerical FDTD Solutions, commercial software based on the FDTD method, was adopted to simulate the extinction spectrum using eq 1, and the results were compared with the experimental data. In our simulations,  $D_\lambda = 0$  because there was no light intensity of ambient environment. Because of the periodic structure, the rectangle box marked by the dash lines in Figure 1b was adopted as the unit



**Figure 2.** SEM images of P3HT:PMMA/Au hybrid films with different patterns: (a) 200100, (b) 300100, (c) 300150, (d) 300200, (e) 400100, (f) 400150, (g) 400200, (h) 400250, (i) 400300, (j) 500100, (k) 500150, (l) 500200, (m) 500250, (n) 500300, (o) 500350, and (p) 500400, and (q) is the zoom in of (n) with an inclined angle. The sizes of images from a to p are  $2.5 \mu\text{m} \times 2.5 \mu\text{m}$ . The film thickness of P3HT:PMMA of all samples is fixed at nominal 144 nm.

cell of our computation domain and the appropriate periodic boundary conditions were used. For  $x$  polarization, the symmetric boundary conditions were set at the front- and backside surfaces of the unit cell and the antisymmetric boundary conditions were set at the other two side surfaces. For  $y$  polarization, the symmetric and antisymmetric boundary conditions were exchanged at the four side surfaces as compared to  $x$  polarization. The rectangle marked by solid lines in Figure 1b is located at the interface between the gold film and air in our computation domain. The incident plane wave with a wavelength from 300 to 1000 nm was illuminated vertically from the top, i.e., in the

negative  $z$  direction as shown in Figure 1b. The perfectly matched layers were used on the top and bottom surfaces of the simulation domain to simulate the infinite volumes of the air and the silicon material, respectively. The nonuniform mesh was chosen in the entire simulation domain for higher numerical accuracy. The reflections of energies from the planar silicon substrate and the structure of P3HT:PMMA/Au film were simulated and substituted in eq 1 to calculate the extinction. Because the incident light source is unpolarized, the average of the simulation results for the cases of  $x$  polarization and  $y$  polarization was taken. The refractive indexes of gold and silicon were selected from Palik's

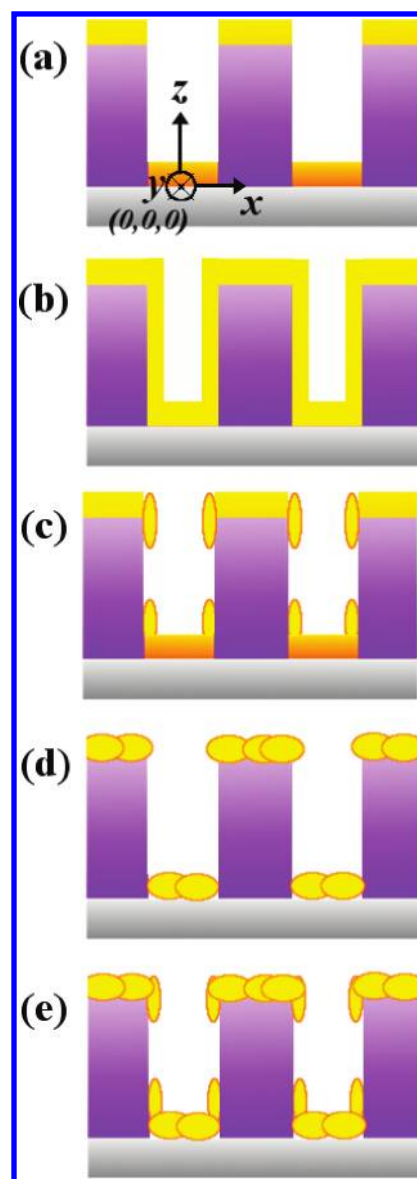
handbook,<sup>30</sup> and the refractive index of P3HT:PMMA was estimated to be 1.5 from Kasarova's study.<sup>31</sup>

### 3. RESULTS AND DISCUSSION

The objective of this research is to study the effects of gold film morphology on surface plasmon resonance and surface-enhanced Raman scattering of polymer/Au nanostructures. To have a precise control of the hole size in the fabricated structures, the electron-beam lithography technique was employed to fabricate the nanostructures. Instead of the commercial PMMA electron-beam resist, the P3HT:PMMA photoluminescent electron-beam resist was used in this study mainly because the fabricated nanostructures could emit light and provide the SERS results. Electron-beam lithography is expensive in general, and it is not for large-area or large-volume production, such as SERS sensors applications. However, it is a good research tool for the fundamental study of the structure parameter effects. To fabricate the array structures for large area, cost-effective methods such as nanoimprint, optical lithography, etc. have been used.

In this study, two parameters, the spacing between the holes (i.e., the lattice constant) and the diameter of the hole, are considered to examine the geometry effects of the designed pattern. For convenience, we named the sample by six digits with the first three digits for the lattice constant and the last three digits for the hole diameter. For example, 500300 represents the sample that has the lattice constant of periodic structure being 500 nm and the diameter of hole being 300 nm. Figure 2a–p shows SEM images of P3HT:PMMA/Au hybrid films of 144 nm thickness and with 16 different designed patterns which are (a) 200100, (b) 300100, (c) 300150, (d) 300200, (e) 400100, (f) 400150, (g) 400200, (h) 400250, (i) 400300, (j) 500100, (k) 500150, (l) 500200, (m) 500250, (n) 500300, (o) 500350, and (p) 500400. To show the details of the structure, Figure 2q is the zoom in of Figure 2n with an inclined angle, and it shows the granular nanostructures of gold film on the surface and gold disks at the bottoms of the holes. This granular structure is found to affect the extinction spectra in simulations which will be shown later. When the diameter of the hole decreases to 100 nm, there are polymer aggregates on the surface of the P3HT:PMMA/Au structure which result in a slight deformation or distortion as shown in the middle of Figure 2j. This phenomenon results from the phase separation between P3HT and PMMA during the spin-coating and postbaking process. The P3HT-rich area requires higher energy to decompose and is more difficult to develop because of the tough thiophene ring in the P3HT molecules. As shown in Figure 2j, phase separation results in the deformation structure on the patterned surface and its size is around 100–200 nm.

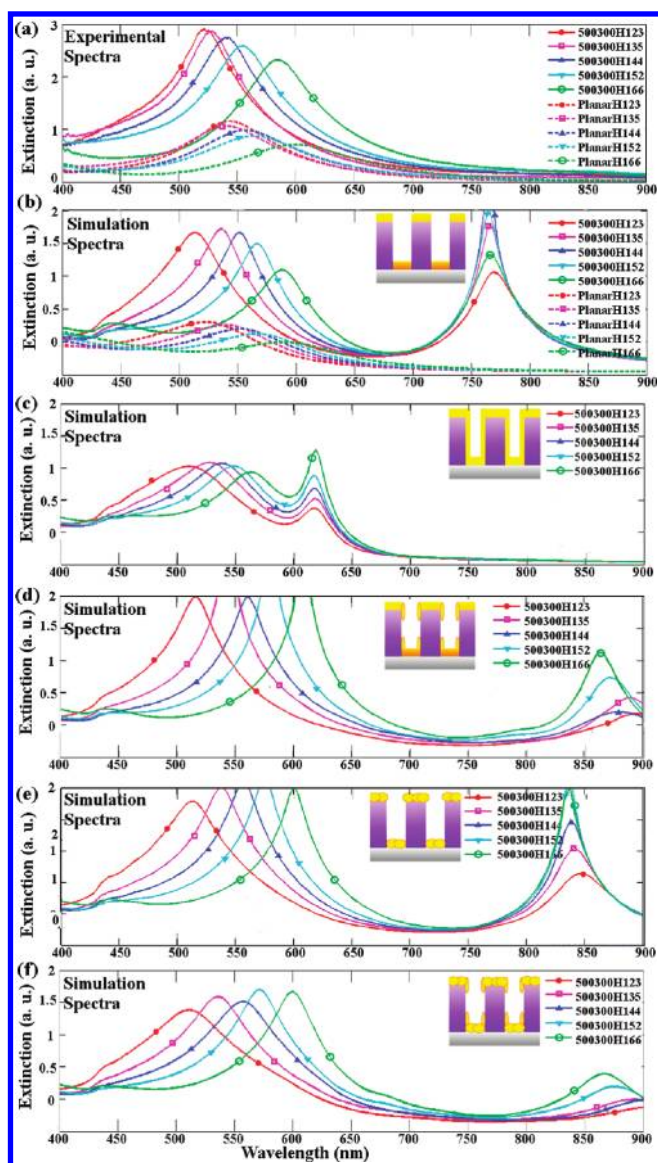
To further study the effect of film thickness on the morphology of the P3HT:PMMA periodic structure, the samples were prepared at different spin rates. The film thickness decreases with increasing spin rate because more P3HT:PMMA photoresist solution is spread out of the silicon substrate with increasing centrifugal force. Using the AFM topography images of our fabricated samples (Supporting Information, S1) we found that the film thicknesses were 166, 152, 144, 135, and 123 nm, respectively, at 600, 800, 1000, 1200, and 1400 rpm spin rates. The specimens are named according to their thicknesses as H166, H152, H144, H135, and H123, respectively. Also, it was observed from the AFM topography images (Supporting Information, S1) that the size of the P3HT-rich region decreased significantly and the surface roughness became smaller as the film



**Figure 3.** Cross sections of the hybrid films with different gold structures, where (a) the gold films are on the top surfaces and the gold disks on the bottom of the holes, (b) the continuous gold film is along the sidewalls in addition to the structure of a, (c) the sticking nanoparticles are at the top and bottom rims of the hole in addition to the structure of a, (d) the granular gold structures are on the top surfaces and bottom of the holes, and (e) the sticking nanoparticles are at the top and bottom rims of the hole in addition to the structure of d.

thickness decreased. Thus, the film thickness and distributions of the P3HT-rich area can be controlled by the spin rate during the coating process.

The  $\sim 20$  nm Au film was thermally evaporated on the patterned P3HT:PMMA that had a thickness of 100–200 nm. The vacuum evaporation process is a line of sight, and the Au film was not uniformly coated around the contour of patterned P3HT:PMMA, especially the inside wall of the hole as shown in Figure 2q. It is difficult to observe the coating morphology inside the hole. For comparison, we assume five different cross sections along the centers of the holes in our simulations as shown in Figure 3. In Figure 3a the structure has the top gold film



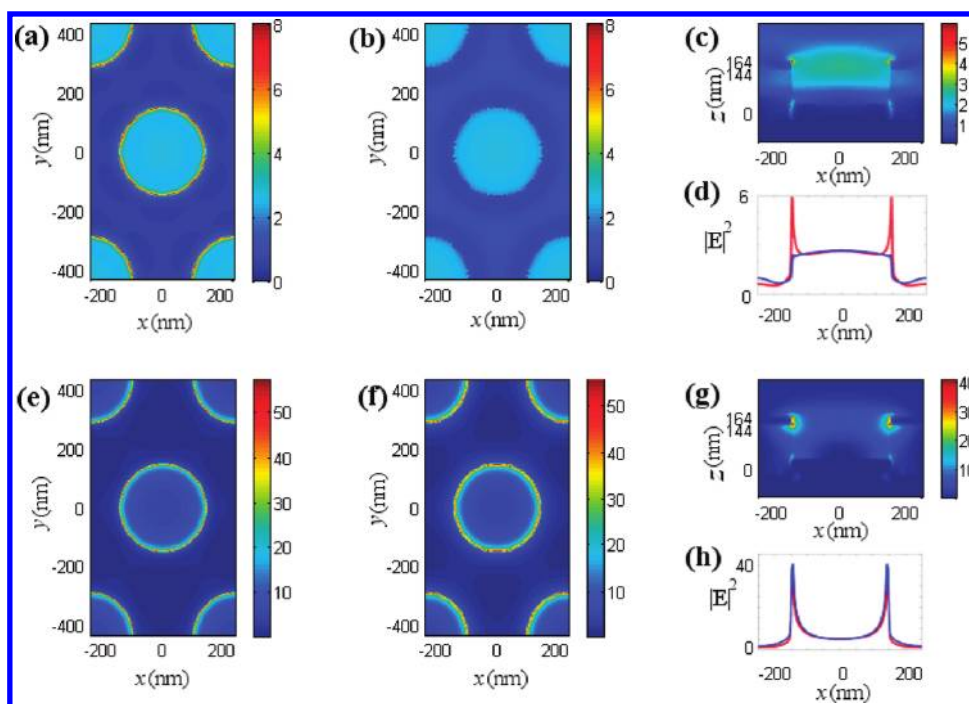
**Figure 4.** Extinction spectra of periodic arrays with different structures and thicknesses, (a) experimental result and (b–f) the corresponding simulation results in Figures 3a–e. (b) Simulation results for planar films are also shown.

and bottom gold disks without any gold sticking on the side walls of the holes. In Figure 3b the 20 nm gold films are uniformly coated on the side walls of the holes. Stimulated by the granular structure of gold shown in Figure 2q, a string of gold nanoparticles sticking along the top and bottom rims of the holes was assumed in Figure 3c. Specifically, we assumed the ellipsoidal geometry for the gold nanoparticles with the minor axis oriented in the thickness direction and the radii as 10, 20, and 30 nm in our simulations. In Figure 3d the gold film is assumed to have the granular structure without any gold on the side walls of the holes, and the granular structure is composed of gold nanoparticles in random arrangements, and the gaps between nanoparticles are much smaller than the sizes of the nanoparticles. The ellipsoidal geometry is adopted for the gold nanoparticles with the minor axis oriented in the thickness direction. The radii of the ellipsoidal gold nanoparticle for the granular structures on the top surfaces and the bottom of the holes are 15, 40, and 40 nm.

In Figure 3e, in addition to the granular structure of the film, there are gold nanoparticles sticking along the top and bottom rims of the holes.

The spectral microreflectometer equipped with an optical microscope was used to measure the extinction properties of P3HT:PMMA/Au hybrid films. Figure 4a shows the experimental results of the extinction spectra of the samples of 500300 pattern and the planar film with different film thicknesses. To explore the physical mechanisms of the measurement results, the FDTD method was applied to simulate the extinction and light intensity for different cases of P3HT:PMMA/Au hybrid films. To compare with the experimental results in Figure 4a, we simulated different cross sections of the structures from Figure 3a–e, and the corresponding simulation results are shown in Figure 4b–f. In Figure 4b not only the extinction spectra of the 500300 pattern (500300H123~H166) in Figure 3a but also the extinction spectra of the planar film (PlanarH123~H166) are simulated. The resonance peaks of extinction spectra for samples of 500300 pattern (500300H123~H166) and planar film (PlanarH123~H166) in Figure 4a and the first resonance peaks in Figure 4b all show a red shift as the film thickness increases. Comparing the simulation results in Figure 4b with the experimental results in Figure 4a, the curves for the planar film agree very well; however, the curves for the samples of the 500300 pattern show an additional peak around 760 nm in the simulation. To explore the absence of the second peak in the experiments, we also simulated different cross sections of the structures in Figure 3. Assuming that the structure has the 20 nm continuous gold films on the side walls as shown in Figure 3b, the corresponding simulation results are shown in Figure 4c and it is found that the second peaks around 760 nm disappear but the new shoulder peaks appear at about 620 nm. If the continuous gold film on the side wall in Figure 3b is replaced by strings of gold nanoparticles at the two rims as shown in Figure 3c, the corresponding simulation results are shown in Figure 4d and it is found that the intensity of the second peak decreases dramatically. The corresponding simulation results for the structure in Figure 3d are shown in Figure 4e. The intensity of the second peak is still high, but the peak shifts to a longer wavelength at about 845 nm. Considering the gold nanoparticles sticking along the side walls for the granular structures as shown in Figure 3e, its corresponding simulation results are shown in Figure 4f and shows that the intensity of the second peak decreases significantly and the peak shifts to a longer wavelength with the first peak remain the same. With the above modifications the simulation results indicate that the intensity of the second peak decreases and moves to a longer wavelength when the thickness of the film increases as shown in Figure 4f.

Compared to the experimental results in Figure 4a, the simulation results in Figure 4f show the same trend. The results suggest that the decrease of the plasmon resonances was due to the presence of the granular structure of gold nanoparticles with the gold nanoparticles sticking along the rims of the holes. Stewart et al.<sup>17</sup> also found that the field intensity decreases at the resonance peak in their structures due to the presence of small gold particles along the side wall of the nanoholes. On the basis of the simulation results in Figure 4 and the SEM photo in Figure 2q, it is suggested that the cross sections of our fabricated structures may look like the schematic drawing shown in Figure 3e. However, with the continuous gold film shown in Figure 3b, despite the appearance of a shoulder peak aside the first peak in the simulation results, the second peak disappears



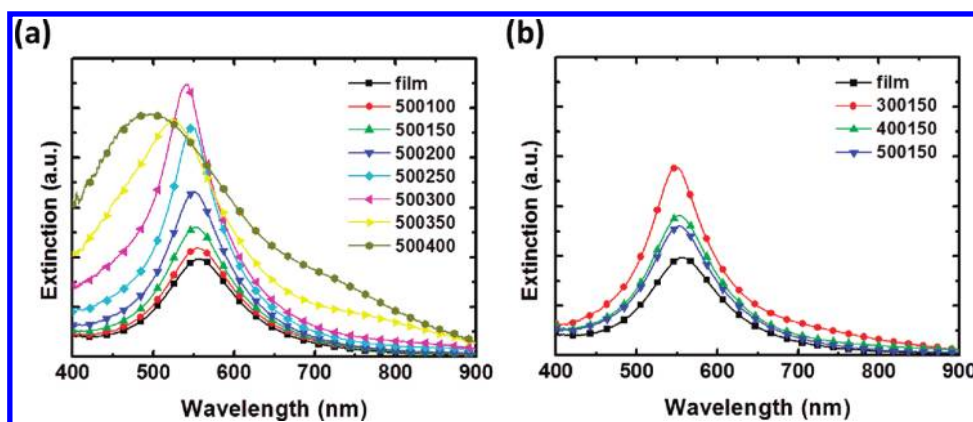
**Figure 5.** Electric field intensities ( $|E|^2$ ) distribution of patterned 500300H144 sample in Figure 4b, where a, b, c, and d are for 550 nm wavelength and e, f, g, and h are for 760 nm wavelength. (a and e) At the plane  $z = 164$  nm, i.e., the interface between air and top Au layer. (b and f) At the plane  $z = 144$  nm, i.e., the interface between the top Au layer and P3HT:PMMA. (c and g) At the plane  $y = 0$  nm which represents the diametrical section through the axis of symmetry of the hole. (d and h) Field intensity distributions at  $y = 0$  and along the  $x$  axis for  $z = 164$  (red line) and 144 nm (blue line). Gold thickness is 20 nm. Origin of the coordinate is located at the center of bottom gold disk. Simulation structure can be referred to Figure 1b.

which agrees well with experimental results. Hence, we cannot preclude the validity of the continuous gold film. Because a shoulder peak was observed in the measurements done by R. G. Nuzzo's research team,<sup>17,18</sup> in which the film thickness was 50 nm as shown in their paper,<sup>17</sup> it was conjectured that the film remained granular when the thickness is only 20 nm and became continuous when the thickness was thicker.

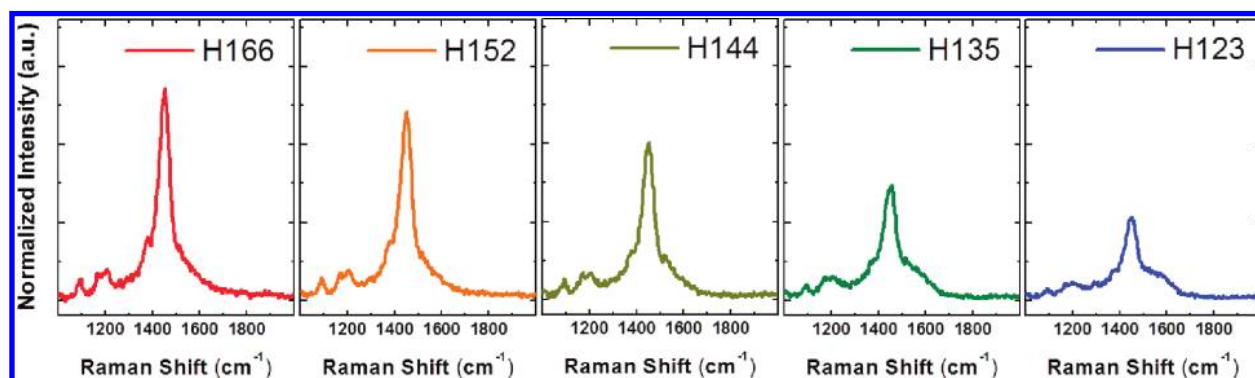
To understand why the second peak appears in the simulation (Figure 4b) but is not observed in the experiments (Figure 4a), we calculated the field intensity distributions corresponding to the first and second peaks of the 500300H144 pattern shown in Figure 4b and the simulation results are illustrated in Figure 5a–d and 5e–h, respectively. The location of the substrate surface is defined at  $z = 0$ . At the interface between air and the top Au layer (i.e., at  $z = 164$  nm), the strong field and LSPR are found at the rim of the top of the hole for both the first and the second peaks as shown in Figure 5a and 5e, respectively. However, the field intensity of the second peak in Figure 5e is stronger than that of the first peak in Figure 5a. At the interface between the top Au layer and P3HT:PMMA (i.e., at  $z = 144$  nm) there is no LSPR for the first peak in Figure 5b. For the second peak in Figure 5f it still has the strong LSPR and is similar to the results at the interface between air and the top Au layer shown in Figure 5e. To facilitate visualizing the differences between the first and the second peaks, the field intensities on the diametric cross section of the hole (i.e., at  $y = 0$ ) are shown in Figure 5c and 5g, respectively, for the first and second peaks. In Figure 5c it is found that the strong field is on the top of the hole and the weak field on the bottom of the hole. In Figure 5g strong LSPR can be observed at the two rims between air and the top Au layer and between the top Au layer and the P3HT:PMMA layer. The first peaks in Figure 4b for the

planar structures have an obvious red shift as the film thickness of P3HT:PMMA increases from 123 to 166 nm, and the same trend of the red shift is also found for the first peaks in Figure 4b for the hole array structures. This indicates that the red shift of the first peaks in Figure 4b is dominated by the film thickness but not the structure. For the second peaks, the strong LSPR field formed in the hole results in the difficulty in the propagation of the surface waves between the gold layer and the P3HT:PMMA layer as compared with the case of the first peak. Also, because of this strong LSPR at the rims of the hole as compared to the coupling between the top gold layer and the bottom gold disk, the effect of the film thickness was not obvious for the second peak shown in Figure 4b. The field intensity profiles at  $y = 0$  and  $z = 144$  and 164 nm are plotted as functions of  $x$  in Figure 5d and 5h, respectively, for the first and second peaks. While the field intensity at the rim is greatly reduced from  $z = 164$  nm to  $z = 144$  nm in Figure 5d, it remains about the same between  $z = 164$  nm and  $z = 144$  nm in Figure 5h.

To study the effects of the hole diameter and the lattice constant on the extinction spectra, the extinction measurements were performed on all the prepared samples shown in Figure 2. The variations of the measured extinction spectra of the periodic arrays with respect to the hole diameter and the lattice constant are shown in Figure 6a and 6b, respectively. These extinction peaks are actually quite complicated because they combine SPR, LSPR, and the coupling between neighboring holes. When the lattice constant is fixed at 500 nm for the cases in Figure 6a, the resonance peak is blue shifted with increasing hole diameter. With a fixed lattice constant, the boundaries of holes become closer as the hole diameter increases. Thus, the light coupling between holes becomes significant and the extinction of the



**Figure 6.** (a) Extinction spectra of P3HT:PMMA/Au hybrid films with different hole diameters at a fixed lattice constant of 500 nm. (b) Extinction spectra of P3HT:PMMA/Au hybrid films with different lattice constants at a fixed 150 nm hole diameter. Film thickness of P3HT:PMMA of all P3HT:PMMA/Au samples is fixed at nominal 144 nm.



**Figure 7.** Raman spectra of P3HT:PMMA/Au hybrid films of 500300 structure with different thicknesses. Wavelength of excited laser is 632.8 nm.

resonance peak increases when the hole diameter increases from 100 to 300 nm. However, when the hole diameter becomes too large, such as 350 and 400 nm, the extinctions of the resonance peak saturate and can not increase any more. It is observed that the width of the peak is very wide when the diameter of the hole is 350 nm or larger, and usage of such large holes should be avoided in the actual applications. On the other hand, when the diameter of the hole decreases, the extinction peak approaches the characteristic of a planar film which is dominated by SPR. When the diameter of the hole is fixed at 150 nm for the cases in Figure 6b, the resonance peak is red shifted and the width of the peak becomes narrower with increasing lattice constant because of decreasing coupling between holes. However, as the lattice constant becomes larger, the relative hole area becomes smaller which, in turn, results in less light absorption in the structures and a smaller resonance peak. Again, the SPR dominates the extinction peak when the lattice constant becomes large and the coupling between holes becomes less that approaches the characteristic of the planar film.

Scanning Raman scattering mapping spectroscopy with the excited laser at a wavelength of 632.8 nm was used to study the enhancements of Raman scattering intensities of patterned P3HT:PMMA/Au structures. The methodology developed for enhanced P3HT Raman scattering on patterned metal oxide/Au structure was adapted in this study.<sup>23</sup> From the tilt angle SEM photo of patterned P3HT:PMMA/Au structure (Figure 2q) and

the FDTD study of different morphologies of the structure (Figure 4), we can conclude that P3HT:PMMA is not fully covered by the Au film because of the granular structure of the film. Also, the thickness of the gold coated on the P3HT:PMMA layer is thin in our experiments, which is about 20 nm. Although P3HT:PMMA is underneath the Au film, intense Raman and photoluminescence of the photoresist still can be observed in our structures. The emission signals near the characteristic peaks of P3HT were extracted and compared among different structures. The images of emission intensity corresponding to each designed patterns shown in Figure 2 were measured and summarized in the Supporting Information, Figure S2. The images show that the light intensities of periodic structure area are stronger than the nonpatterned area. This is due to the surface plasmon resonance effects that enhance the P3HT:PMMA emission scattering. The enhancements are observed which are increased as the hole diameter increases at a fixed lattice constant of 300, 400, and 500 nm. The results are in agreement with their extinction spectrum discussed earlier (Figure 6). The emission signals are enhanced by the presence of gold and the surface plasmon resonance of periodic arrays. The emission signals are very weak for the same structures without gold. In order to obtain the Raman only spectrum, the photoluminescence background has been subtracted from the emission spectrum. Figure 7 shows the Raman spectra of P3HT:PMMA/Au of the 500300 pattern with different thicknesses under the exciting laser of 632.8 nm.

The characteristic peak of P3HT is at about  $1442\text{ cm}^{-1}$ . The peak intensity of P3HT Raman scattering decreases as the thickness decreases when the internal standard peak of  $1100\text{ cm}^{-1}$  is used. The extinction peak wavelength is increased with increasing film thickness, and the extinction is larger as the film thickness of P3HT:PMMA increases from H123 to H166 (Figure 4a). The thickest film (H166) exhibits a strongest intensity of Raman signals due to its occurrence near the maxima extinction of 586 nm. Also, more P3HT can contribute to the Raman scattering signals as the film thickness increases. The Raman signals can be enhanced greatly for P3HT:PMMA/Au with the periodic structure of 500300H166 as compared with the structure without Au. From the Raman spectra in Figure 7, the extinction spectra in Figures 4a and 6, and the theoretical study in Figures 4 and 5, it is expected that the P3HT:PMMA/Au hybrid structure with stronger Raman signals at specific wavelength can be designed according to the physical mechanism described by the experimental and theoretical studies present here.

Because the gold granular structures have significant surface roughness which can also cause the SERS effects, it is important to distinguish the effects of surface roughness and the effects of hole array structures on the SERS signals qualitatively. In the fabrication the thickness of the P3HT:PMMA film is controlled by the spin rate of the spin coater. As the film thickness increases, i.e., the slower spin speed, P3HT can form more rich regions on the surface to result in a rougher surface. Then, it can cause the gold granular structure to have more surface roughness. Although there are other mechanisms to cause the surface roughness during fabrication, it is generally related to the spin rate, i.e., the film thickness. This can also be observed in SEM and AFM images. Thus, the SERS signals in the study of Raman spectra can also be enhanced by the surface roughness accompanied by the hole arrays. However, when the thickness of the P3HT:PMMA film is fixed and the different structures should have the same level of surface roughness which, in turn, should exhibit similar SERS signals. Because the measured Raman signal varies with the hole structure variation in each array in mapping experiments and the physical mechanism can be described well as the previous discussions, we conclude that the variation of the SERS signal measurements are dominated by the hole array structures instead of the surface roughness.

#### 4. CONCLUSIONS

In this study, P3HT:PMMA/Au hybrid materials with periodic nanostructures are fabricated by electron-beam lithography and the optical properties can be modulated by the surface plasmon resonance effects with control of the structure design. The extinction spectra of P3HT:PMMA/Au periodic nanostructures are measured by a spectral microreflectometer. The blue shift and width of the resonance peaks are proportional to the area fraction of the holes which can be controlled by either changing the diameter of the hole with the fixed lattice constant or changing the lattice constant with the fixed diameter of the hole. The SPR can also be modulated by changing the film thickness. Specifically, the Raman scattering signal is enhanced when the film thickness increases. Both the SEM and the AFM images show the granular nanostructure of the gold layer and sticking of gold nanoparticles along the top and bottom rims of the holes. Considering the actual nanostructure of periodic arrays in the FDTD simulations, the measured extinction results are verified.

A large enhancement of Raman scattering signals has been measured in this study using the P3HT:PMMA/Au periodic nanostructure as compared with the case without gold. As the thickness of the periodic structure increases, the resonance wavelength becomes closer to the excited wavelength 632.8 nm and the Raman signal becomes stronger. This study provides a useful strategy to control and modulate the extinction spectra and intensity of Raman spectra by changing the P3HT:PMMA/Au nanostructures, and it can be helpful for further designs in optical devices and sensing applications.

#### ■ ASSOCIATED CONTENT

**S Supporting Information.** AFM topography images and total emission mapping images of P3HT:PMMA hybrid films with different patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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