Supporting Information

Tailoring plasmonic properties of gold nanohole arrays for surface-enhanced Raman scattering

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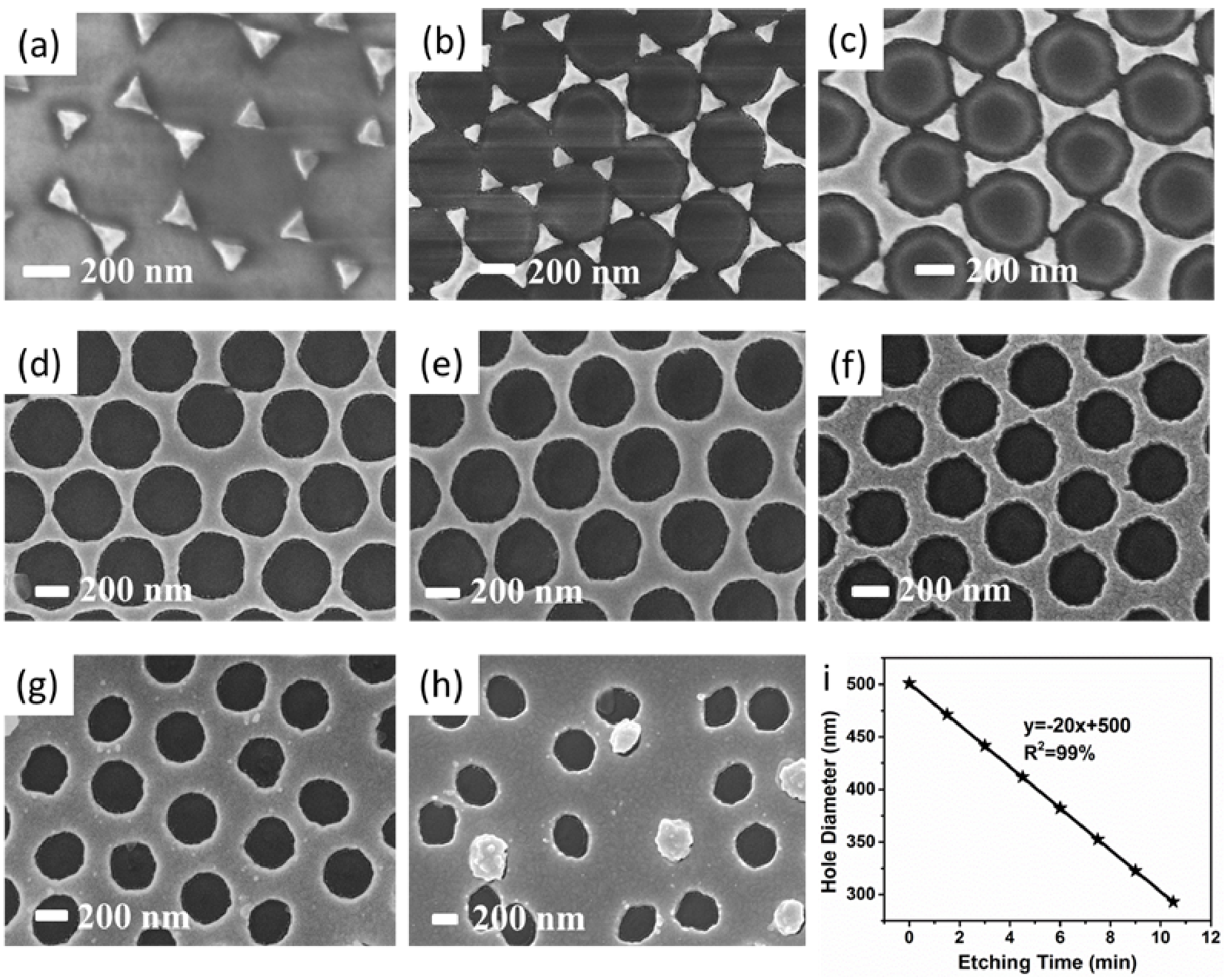

Figure S1 SEM images for 500 nm periodicity template. (a-h) Gold nanoarrays with a periodicity of 500 nm and hole diameters of 500 nm, 470 nm, 440 nm, 410 nm, 380 nm, 350 nm, 320 nm, 290 nm, and a film thickness of 50 nm; (i) linear relationship between the hole diameter and the etching time. For reference, the percentage of defects for the 440 nm hole size was ~50% from the SEM images.

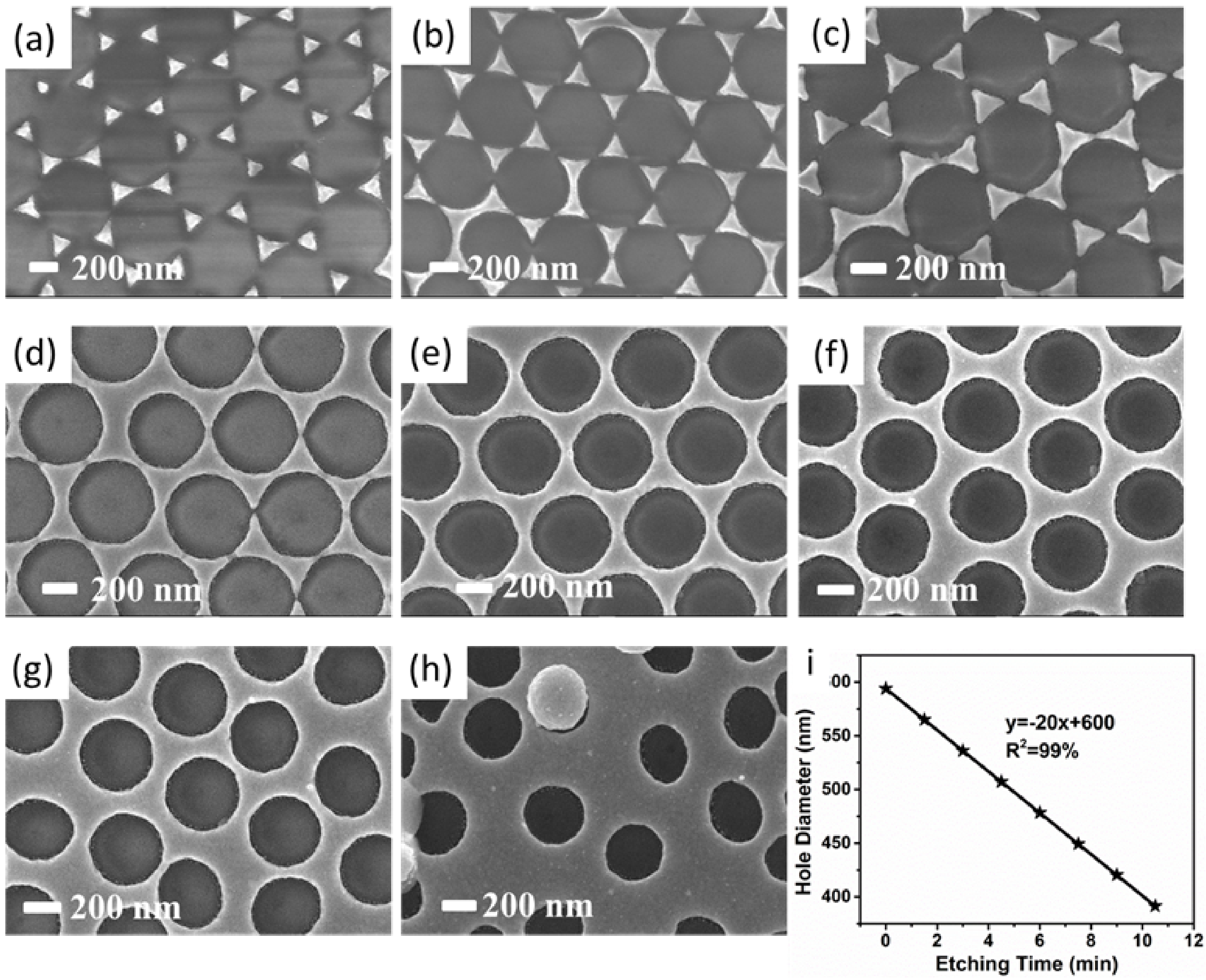

Figure S2 SEM images for 600 nm periodicity template. (a-h) Gold nanoarrays with a periodicity of 600 nm and hole diameters of 600 nm, 570 nm, 540 nm, 510 nm, 480 nm, 450 nm, 420 nm, 390 nm, and a film thickness of 50 nm; (i) linear relationship between the hole diameter and the etching time. For reference, the percentage of defects for the 540 nm hole size was ~85% from the SEM images.

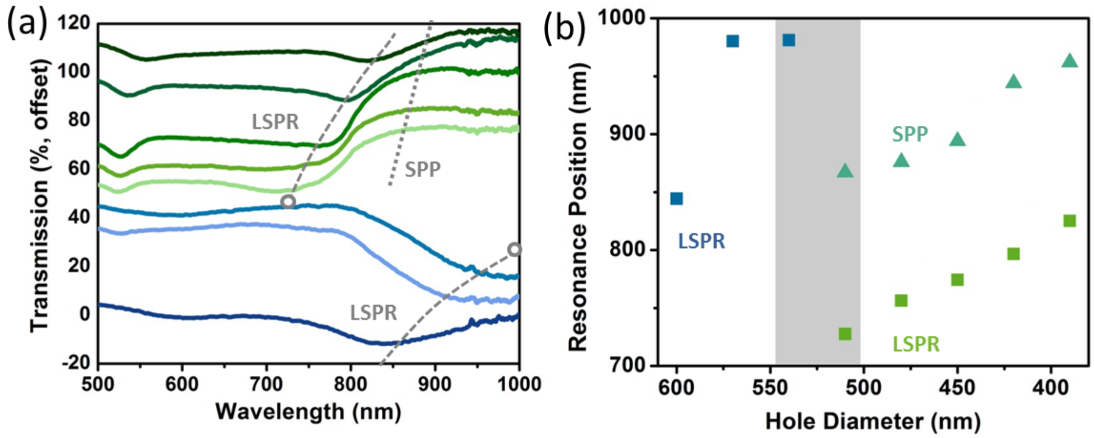

Figure S3 Change in optical modes at transition zone for 600 nm periodicity. (a) The transmission is shown for a set of hole sizes covering 600 nm to 390 nm in 30 nm intervals. (b) The estimated peak position of the LSPR and SPP peaks for each hole diameter with a fixed periodicity of 600 nm.

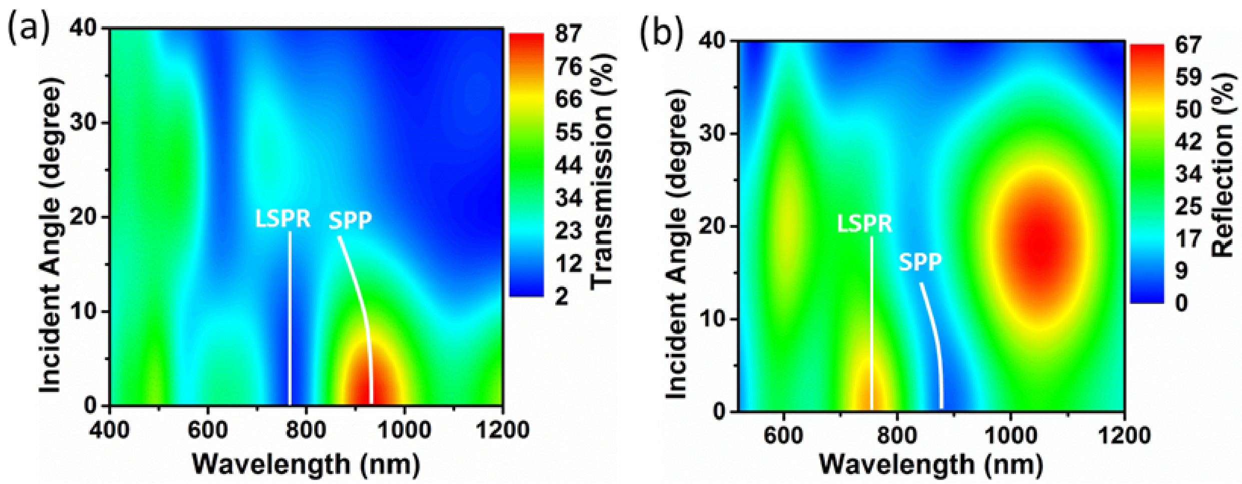

Figure S4 Change in LSPR and SPP with incident angle. (a) The transmission and (b) reflection show that the LSPR is relatively unaffected by the input angle while the SPP shifts due to the momentum matching condition changing.

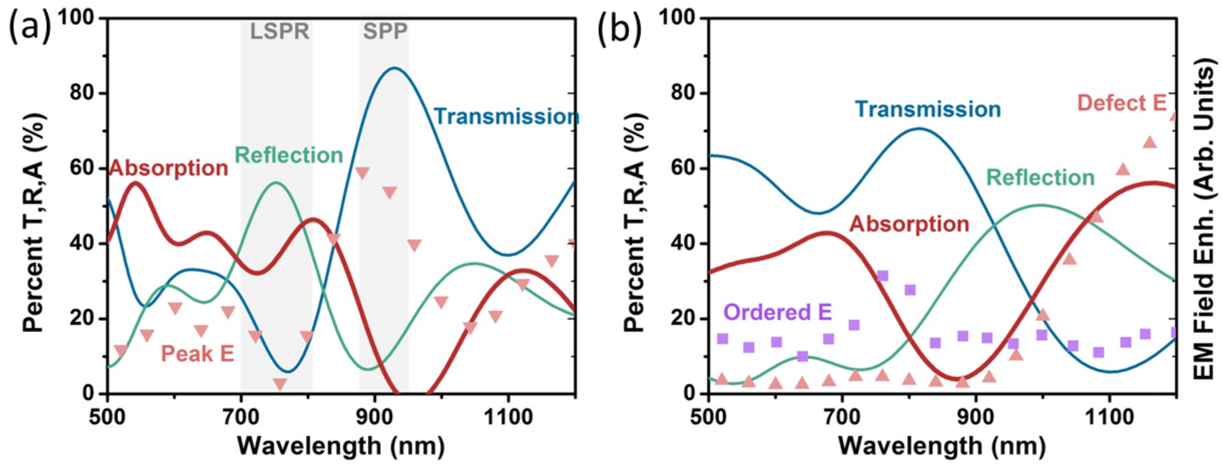

Figure S5 Comparison of optical modes and resulting EM field enhancement for 600 nm periodicity. The transmission (T), reflection (R), and absorption (A=1-T-R) is compared to the peak EM field enhancement for an (a) ordered and (b) 'gap' defective pattern for a 600 nm template with 420 nm, 540 nm hole size, and 50 nm gap defects, respectively.

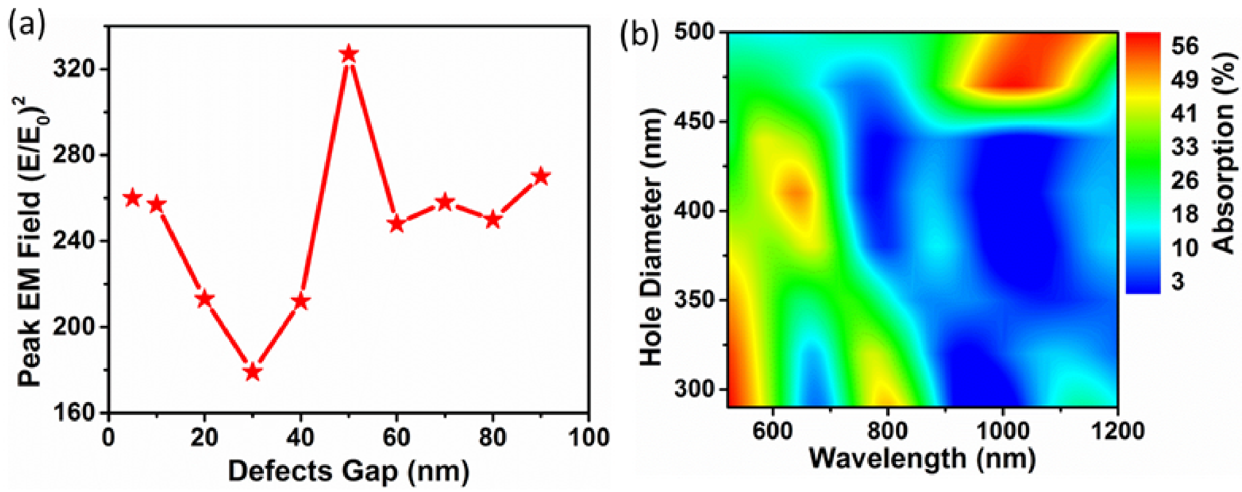

Figure S6 Conditions for EM field enhancements for 500 nm periodicity. (a) The 'gap' defect peak field is largest for a gap of ~50 nm for a hole size of 440 nm and an excitation of 785 nm. It should be noted the EM field at this excitation wavelength and condition is more focused on the edge of the nanotriangle as seen in Figure 4d, and not purely between the structures as would be expected at smaller separation distances. Instead, the introduction of 'gap' defects seems to bring the remaining nanotriangle in resonance with the excitation laser, increasing the local EM field at the edges of the pattern. Smaller gaps also produce a large EM field enhancement, however they are not found as abundantly in the NSL produced patterns as defects with ~50 nm size, see Figure S1 and S2. (b) The absorption for the ordered pattern varies spectrally for changing hole size with a fixed periodicity.

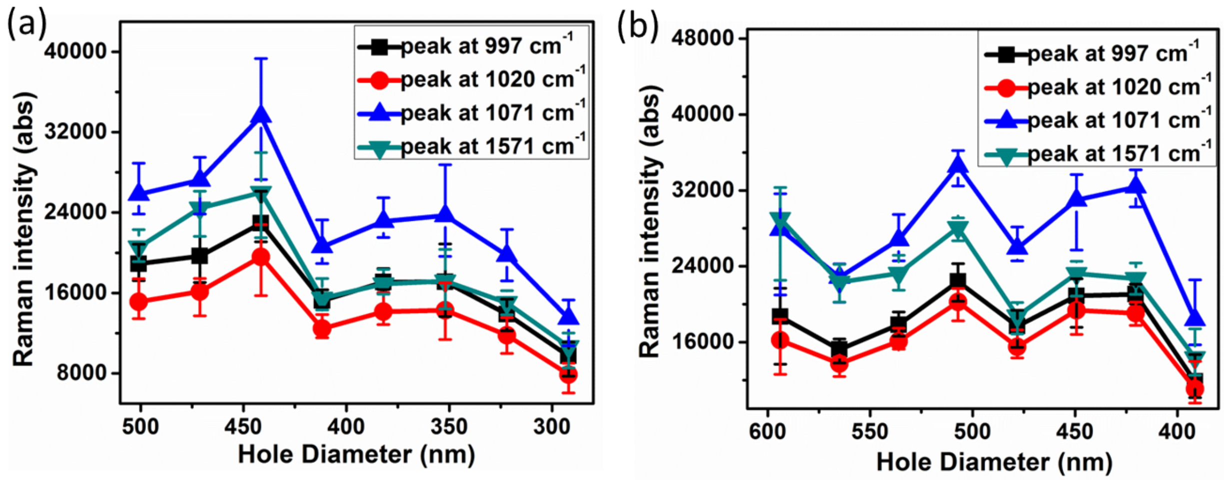

Figure S7 Measured Raman Signal The measured Raman intensity for 785 nm excitation at several nanohole sizes for (a) a 500 nm periodicity template and (b) a 600 nm periodicity template. Error bars represent the average of three measurements, each line corresponds to a different Raman transition.

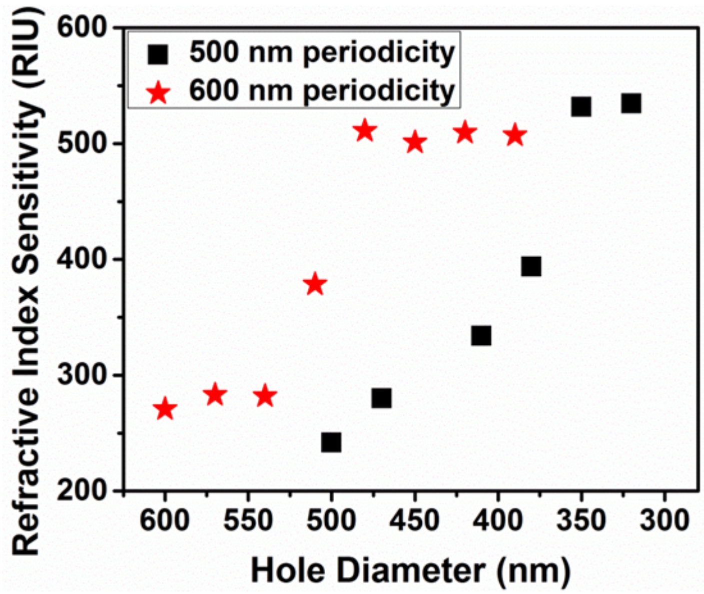

Figure S8 Refractive index sensitivity for 500 nm and 600 nm periodicity templates with varying hole size. The range over which the nanohole array is optimized for a refractive index sensor differs from a SERS sensor, as even though both effects originate in the local field, the SPP have a larger field decay length and more restrictive excitation condition, making it more sensitive than the LSPR to changes in the refractive index.

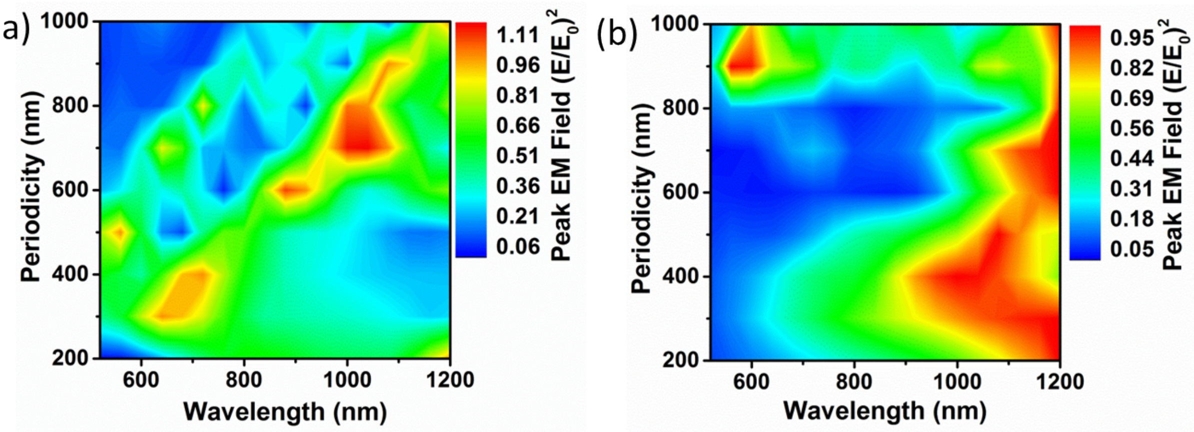

Figure S9 Additional SERS tuning curves. (a) The EM field corresponding to the optimal absorption condition. The EM field is slightly redshifted from the absorption peak. The EM field magnitude is normalized by the highest value for each periodicity (b) The 'gap' defect EM field, normalized for each periodicity individually to accentuate how the EM field changes as the template is varied.

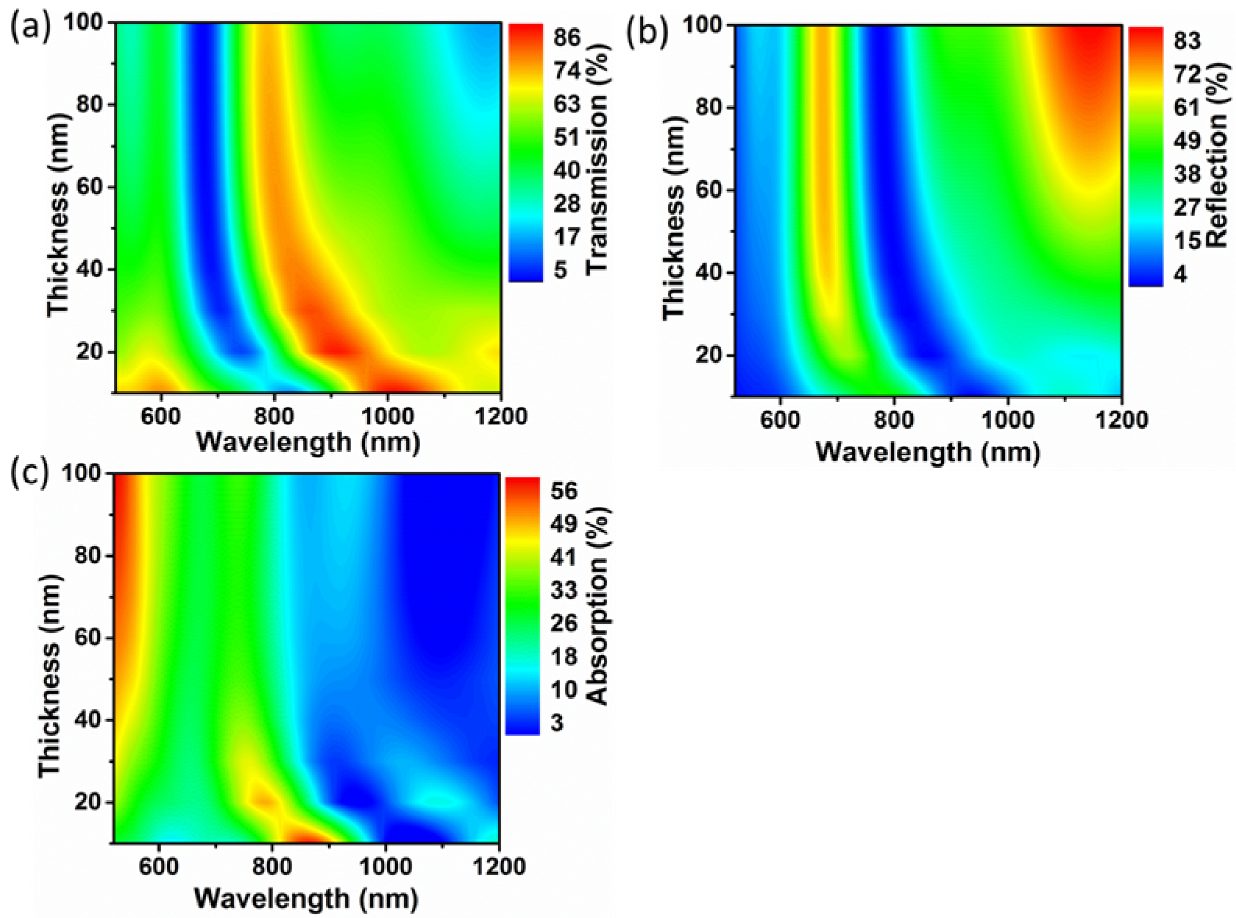

Figure S10 Effect of metal thickness on optical properties. The transmission (T), reflection (R), and absorption (A=1-T-R) is compared as the metal film thickness is changed for a 500 nm periodicity template with a hole size of 350 nm.