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Chemically Tuning the Localized Surface Plasmon Resonances of Gold Nanostructure Arrays

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We report on chemical etching of ordered Au nanostructure arrays to continuously tune their localized surface plasmon resonances (LSPR). Real-time extinction spectra were recorded from both Au nanodisks and nanospheres immobilized on glass substrates when immersed in Au etchant. The time-dependent LSPR frequencies, intensities, and bandwidths were studied theoretically with discrete dipole approximations and the Mie solution, and they were correlated with the evolution of the etched Au nanostructures' morphology (as examined by atomic force microscopy). Since this chemical etching method can conveniently and accurately tune LSPR, it offers precise control of plasmonic properties and can be useful in applications such as surface-enhanced Raman spectroscopy and molecular resonance spectroscopy.

1. Introduction

Noble metal nanoparticles exhibit collective oscillations of the conduction electrons. These oscillations are known as surface plasmons. Localized surface plasmon resonances (LSPR) occur when the nanoparticles are illuminated by a specific wavelength of light and the excitations of surface plasmons are localized within the nanoparticles.^{1,2} The LSPR properties of noble metal nanostructures have been of tremendous importance to applications such as nanophotonic devices and circuits,^{3–12} biological sensing and imaging,^{13–19} surface-enhanced spectroscopy,^{20–23} surface plasmon-enhanced optical tweezers,^{24,25} plasmonic nanolithography,^{26,27} and metamaterials.^{28,29} The ability to fine-tune the LSPR properties by varying size, shape, composition, and surrounding medium has been a key factor in advancing and optimizing these applications. For example, in plasmon-enhanced solar cells, the LSPR spectrum of the cells' metal nanostructures must encompass the solar spectrum for maximal use of the solar energy and enhanced energy conversion efficiency.³⁰ The highest enhancement factor for surface-enhanced Raman spectroscopy (SERS) can be observed when the LSPR peak wavelength of the metal nanostructures is between the wavelength of the excitation light source and that of the light emitted from the analytes.³¹

Thus far, researchers have developed myriad approaches to fabricate surface-immobilized metal nanostructure arrays with desirable LSPR properties.^{32–34} A typical approach to form these nanostructure arrays is to transfer chemically synthesized nanoparticles from suspensions to solid substrates.³⁵ Chemical synthesis allows precise control of the sizes, shapes, and crystal structures of the metal nanoparticles.^{36–39} However, changes in environments and interactions of nanoparticles caused by the transferring process make it difficult to fabricate structures with reproducible plasmonic properties.³⁵ Lithographic approaches such as electron-beam lithography (EBL), focused ion beam

lithography, and soft lithography directly yield metal nanostructures on substrates via selective etching or deposition processes; such approaches are capable of generating arbitrary patterns with specific sizes, shapes, and orientations.^{40,41} A particularly versatile lithographic technique is nanosphere lithography (NSL), where a template formed by the self-assembly of monodisperse nanospheres on flat surfaces acts as an etching/deposition mask. NSL is a low-cost, high-throughput method for producing ordered, geometrically tunable nanostructure arrays.^{42,43} By controlling the amount of material etched from substrates or the amount of deposited metal, one may readily fabricate metal nanostructures of LSPR properties adjustable over a wide range. However, these lithographic techniques face the same challenges as the chemical synthesis method: the deviations of the nanostructures' shapes and sizes within different batches cause the LSPR properties to be inconsistent among different batches.

To address these challenges and thus allow for precisely prescribed LSPR properties of metal nanostructure arrays immobilized on substrates, effective postprocessing techniques are needed. Along this line, Van Duyne et al. have reported both electrochemical etching of NSL-fabricated hexagonal arrays of Ag nanoprisms on indium tin oxide (ITO) substrates⁴⁴ as well as reactive ion etching (RIE) of glass substrates for anchored Ag nanoprisms with the tunable embedded depth.⁴⁵ Härtling et al. have reported photochemical tuning of both individual colloidal Au nanospheres and EBL-fabricated single ellipsoidal nanodisks.⁴⁶ Here we report controlled chemical tuning of the LSPR properties of immobilized hexagonal arrays of NSL-fabricated Au nanodisks and nanospheres. This chemical etching technique features a simple experimental setup, allows for fine adjustment of the LSPR peak position, and is useful for applications where precisely prescribed plasmonic properties are needed.

2. Experimental Details

Ordered Au nanodisk arrays of various diameters and periods were fabricated on glass substrates by a previously reported

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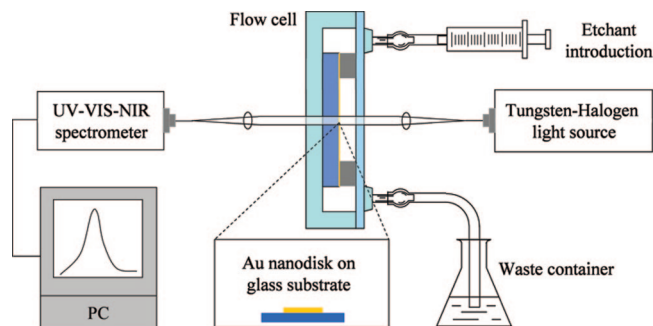


Figure 1. Schematic of experimental setup for real-time chemical etching of Au nanostructure arrays.

integrated NSL/RIE technique.⁴⁷ The fabrication procedure is as follows: (a) a Au thin film of controlled thickness was deposited onto a precleaned glass substrate with Cr as an adhesion layer; (b) a self-assembled monolayer (SAM) of close-packed polystyrene (PS) nanospheres was formed on the Au surface; (c) O₂ RIE was carried out to morph the close-packed PS nanosphere monolayer into arrays of separated nanoellipses, followed by Ar RIE to selectively etch a portion of the Au and Cr film that was not protected by the nanoellipses; (d) a Au nanodisk array was formed on the substrate after the remaining PS was selectively removed by immersing the substrates in toluene with ultrasound for 3 min. Au nanodisks of different diameters and heights were fabricated by controlling the thickness of the Au thin films as well as the RIE parameters.⁴⁷ When Cr was not deposited on the glass substrate as an adhesion layer, the Au nanodisks were transformed into Au nanospheres upon 2 h of thermal annealing at 500 °C. The shape transformation arose from the sample's tendency to minimize its surface free energy and change into a more-stable spherical shape.⁴⁸

Real-time chemical etching of the Au nanostructures was carried out in a flow cell (Starna Cells, Inc., Atascadero, CA). A schematic of the experimental setup is shown in Figure 1. The hexagonal arrays of Au nanodisks or nanospheres fabricated on glass substrates were fixed at the bottom of the flow cell. The cell was aligned vertical to the probe light so that the light was incident normal to the substrates. The probe light was coupled out of the tungsten-halogen light source with an optical fiber. Au etchant solution was introduced into the cell with a syringe via the inlet, and it was collected in a waste container at the outlet after the reaction. Two typical Au etchant solutions were investigated: K₂S₂O₃/KOH/K₃Fe(CN)₆/K₄Fe(CN)₆ = 0.1/1.0/0.01/0.001 M (identified as "Etchant 1") and KI/I₂/H₂O = 1 g/0.25 g/800 mL (identified as "Etchant 2"). The extinction spectra were recorded with a UV-vis-NIR spectrometer (Ocean Optics).

3. Results and Discussion

By combining LSPR spectroscopy and atomic force microscopy (AFM), we investigated the relation between structures and optical properties for the chemically etched Au nanostructure arrays. Figure 2a shows the evolution of the extinction spectrum of a Au nanodisk array immersed in Etchant 1 as a function of immersion time for intervals of 0.5 min. Figure 2b is an AFM image of the hexagonal array before chemical etching, where the nanodisks are of mean diameter 140 ± 14 nm, of height 20 ± 2 nm, and of period 320 ± 32 nm. Figures 2c and 2d are AFM images of the nanodisks after 0.5 and 1.5 min chemical etching, respectively. Cross-sectional analyses (data not shown) based on these AFM images indicated that the chemical etching caused simultaneous reduction of both the

height and diameter of the nanodisks. The overall size of the nanodisks decreased as chemical etching proceeded. When the Au nanodisks were completely etched away, the sample consisted of only the glass substrate which exhibited no extinction band (image not shown). Each LSPR spectrum in Figure 2a exhibited a single in-plane dipole resonance band.⁴⁹ No out-of-plane dipole resonance was excited at the shorter wavelength because the probe light was incident normal to the nanodisks and had only an in-plane electric field. Prior to chemical etching, the Au nanodisk array exhibited a LSPR peak wavelength at 701 nm. As the etching time increased, the LSPR peak shifted toward longer wavelengths, the bandwidth broadened, and the peak intensity decreased. The decrease in peak intensity was due to the reduction of the diameter of the nanodisks after further chemical etching. The redshifting and broadening of the LSPR spectra during the chemical etching process could be caused by the increased diameter/height ratio of the nanodisks (i.e., the disks would become more and more oblate),⁵⁰ the changed coupling effect among the neighboring nanodisks, or the increased influence of the Cr adhesion layer. We observed similar changes in the LSPR of Au nanodisk arrays when we used Etchant 2 (data not shown).

Next, we studied the LSPR spectra of a hexagonal array of Au nanospheres that featured similar particle size and array period. The Au nanosphere array was fabricated by forming a Au nanodisk array without the Cr adhesion layer and then transforming the nanodisks to nanospheres via thermal annealing (as mentioned in Experimental Details). Figure 3a shows the evolution of the extinction spectra of the Au nanosphere array immersed in Etchant 1 as a function of immersion time. The inset shows the AFM image of Au nanospheres before chemical etching, with a mean diameter of 121 ± 40 nm. Similar to the LSPR spectra of the Au nanodisk array, the LSPR peak intensity from the Au nanosphere array decreased as the etching time increased. This is because the mean size of the nanospheres decreased as the etching time increased. Figure 3b shows the variations of the LSPR peak wavelength and full width at half-maximum (fwhm) as a function of etching time. Unlike Figure 2a, the LSPR peak of the Au nanosphere array remains almost constant initially and then gradually blueshifts continuously as the etching proceeds. The main reason for the slower etching of the nanospheres than that of the nanodisks arises from the thermal annealing of the nanospheres, making them more resistant to etching. After about 4 min, the etching rate increases and a gradual blue shift of the LSPR peak position is observed as the nanospheres become smaller. The initial reduction of the fwhm of nanospheres is most likely due to additional chemical annealing from the etching, making the nanoparticles more spherical. The following increase in the fwhm after around 4 min is most likely due to increased dispersion in nanoparticle dimensions, leading to additional inhomogeneous broadening.

To gain a better understanding of the observed LSPR behavior of the Au nanodisk array, we performed electrostatics simulations of the effects of changes in nanodisk size and shape (due to chemical etching), the Cr adhesion layer, and array coupling effect on the extinction spectra of single Au nanodisk and Au nanodisk arrays. Calculations for single Au nanodisks were performed using the Discrete Dipole Approximation (DDA) method,⁵¹ a numerical method in which an arbitrary-shaped nanoparticle is represented as a cubic lattice of many polarizable point dipoles. We used the DDSCAT program (version 6.1) by Draine and Flatau to simulate the LSPR properties of single Au nanodisks.⁵² To obtain a qualitative description of the experimental results, we constructed a three-

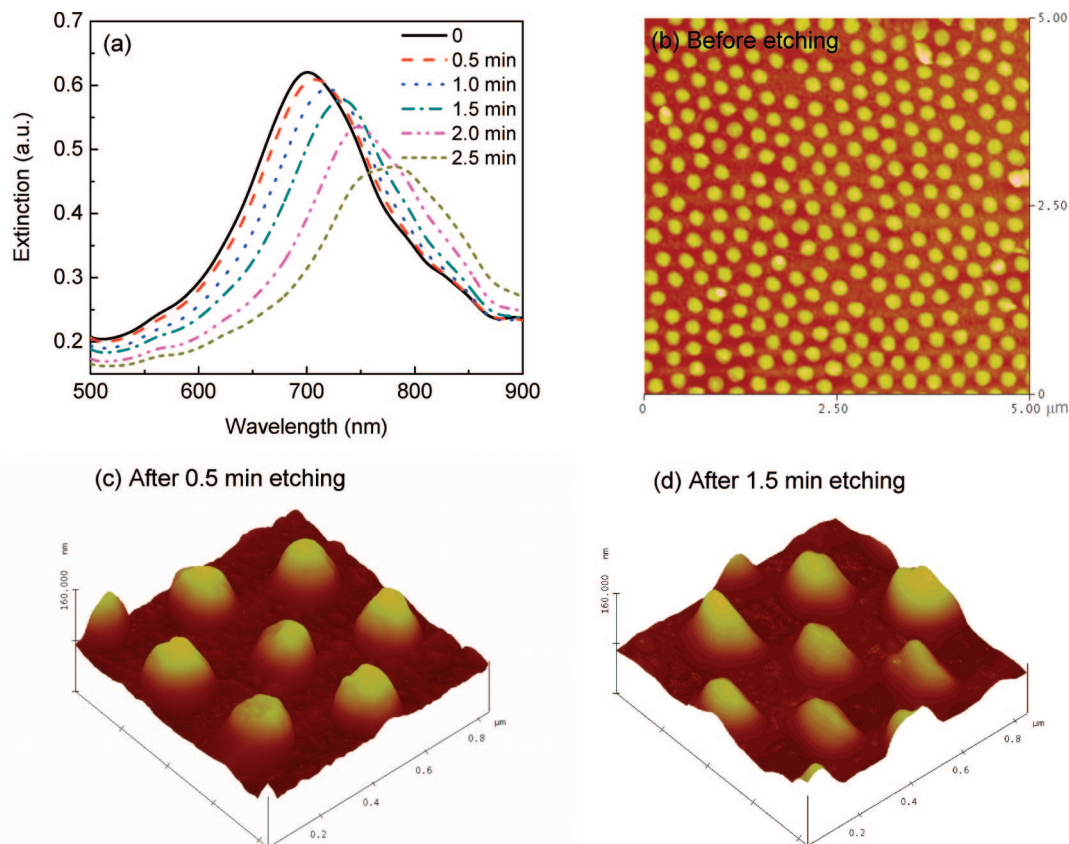


Figure 2. (a) Real-time extinction spectra recorded from Au nanodisk arrays immobilized on a glass substrate and immersed in a Au etchant solution (Etchant 1). (b) AFM image of a Au nanodisk array before chemical etching. (c and d) Three-dimensional AFM images of the Au nanodisks after 0.5 and 1.5 min chemical etching, respectively.

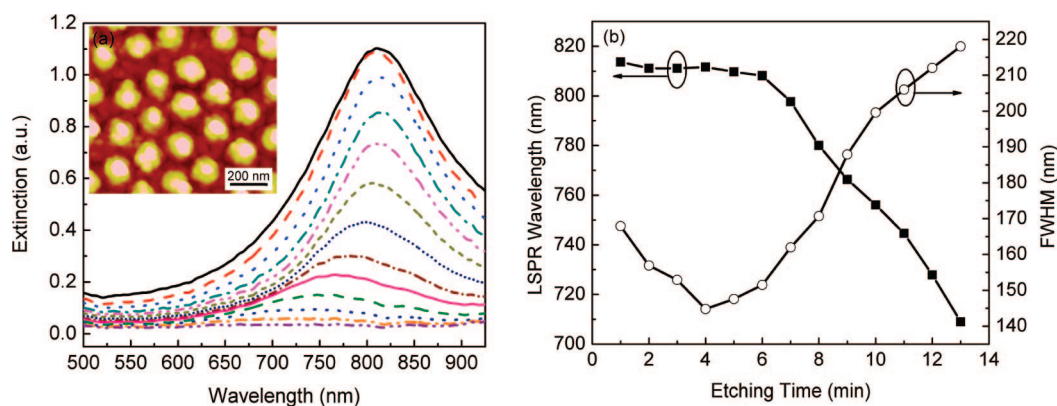


Figure 3. (a) Real-time extinction spectra recorded from a Au nanosphere array immobilized on a glass substrate and immersed in a Au etchant (Etchant 1). Inset is the AFM image of the Au nanospheres before chemical etching. (b) Variations of LSPR peak wavelength and fwhm as a function of etching time from the experimental spectra (a).

layer disk consisting of a glass substrate layer, a Cr adhesion layer, and a Au layer. Modeling the glass substrate as a small nanodisk allows for a computationally efficient way of capturing the influence of the substrate. Previously we showed that the size of the dielectric layer only had small effects on the results, whereas it was essential to include the Cr layer in the simulations.⁴⁷ All three layers of each disk were of the same diameter (see Figure 4a). The nanodisk prior to chemical etching was 140 nm in diameter and 66 nm in height (with a glass substrate layer 44 nm in height, a Cr layer 2 nm in height, and a Au layer 20 nm in height). To model the chemical etching process, we assumed that the height of the Au layer was etched away 4 nm after every minute of immersion while the height

of the glass substrate layer and Cr layer remained the same. Since the chemical etching caused an isotropic reduction of both the tops and sides of the nanodisks (based on the analyses of the AFM images), the diameter of the three-layer model nanodisk decreased at the same time by 8 nm. This isotropic reduction allowed us to adjust the nanoparticles' dimensions for each successive etching time. The wavelength-dependent dielectric constants of Au and Cr were taken from Palik,⁵³ and the refractive index of the glass substrate was assumed to be 1.52.⁴⁷ Although the experiments were carried out in aqueous solution, all our DDA calculations were done for nanodisks embedded in air. Calculations with water as the surrounding medium will shift the LSPR peak position to longer wavelength

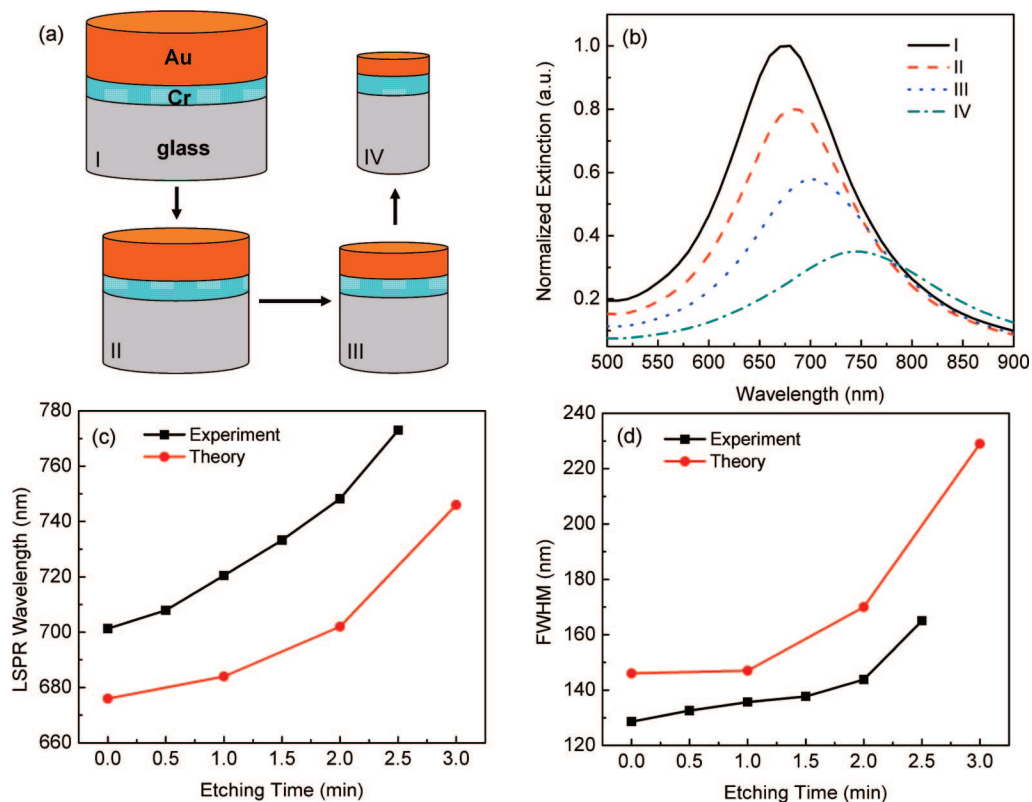


Figure 4. (a) Schematic of three-layer Au nanodisk models (with a Cr layer of 2 nm in height) employed for DDA calculations. (b) Corresponding DDA-calculated extinction spectra of the models described in part a. Variations of (c) LSPR peak wavelength and (d) fwhm as a function of etching time from both the experimental spectra (Figure 2a) and the calculated extinction spectra (b).

since only part of the disk (top and sidewall) was exposed to the water in our experiments, and these calculations will overestimate the effect of the surrounding medium on the LSPR behavior. Like other approximations already made in the modeling, this parameter choice for surrounding medium will not significantly alter the calculated LSPR behavior of the nanodisk array qualitatively.

Figure 4a and 4b are schematics and calculated extinction spectra of several disks: Sample I had a diameter of 140 nm and a height of 66 nm (the Au layer: 20 nm in height prior to chemical etching); Sample II had a diameter of 132 nm and a height of 62 nm (the Au layer: 16 nm in height after 1 min etching); Sample III had a diameter of 124 nm and a height of 58 nm (the Au layer: 12 nm in height after 2 min etching); Sample IV had a diameter of 116 nm and a height of 54 nm (the Au layer: 8 nm in height after 3 min etching). Similar to the experimental data shown in Figure 2a, the DDA results show that the LSPR peak wavelength redshifted, the extinction intensity per particle decreased, and the bandwidth broadened. The variations of the LSPR peak wavelength and fwhm as a function of etching time from both the experimental spectra (Figure 2a) and the calculated spectra are plotted in Figure 4c and 4d, respectively. Compared to the experimental results, the DDA calculations gave consistently shorter LSPR peak wavelengths and slightly smaller changes in the resonance wavelength upon the chemical etching process. This discrepancy can be partly attributed to the fact that experimental measurements were carried out in aqueous solutions, which usually shifted the LSPR spectra to longer wavelengths, while the DDA calculations were for disks in air. The calculated bandwidths were consistently broader than experimental results, although the change in bandwidth was similar to experimental findings. Overall, we observed a qualitative agreement between the experimental observations (Figure 2a) and the DDA results (Figure 4b).

We have previously reported⁴⁷ that the presence of a Cr adhesion layer weakens the LSPR peak intensity and broadens the LSPR bandwidth. To study the effect of the Cr adhesion layer on the observed LSPR behavior, we carried out DDA calculations of the extinction spectra for a two-layer disk with the same dimensions for the glass substrate and the Au layer but without a Cr layer (Figure 5a and 5b). We observed that the LSPR peaks redshifted significantly while the bandwidth narrowed slightly as the etching proceeded. DDA calculations of Au nanodisks only (of dimensions similar to those of the Au layer in the three-layer disk but with no glass substrate) also showed redshifting of the LSPR peak wavelength (about 100 nm in the shift) and narrowing bandwidth as etching time increased (data not shown). We also performed DDA calculations of extinction spectra for a three-layer disk, with similar dimensions for glass substrate and the Au layer but with a thicker Cr layer (4 nm in height) (Figure 5c and 5d). Here the LSPR peak wavelength redshifted slightly while the bandwidth became dramatically broader as we increased the chemical etching time. The aforementioned results show that the thickness of a Cr adhesion layer is critical to LSPR bandwidth; the observed redshifting was due to an increase in the diameter/height ratio of the nanodisks as etching proceeded. Thus the Cr adhesion layer can significantly broaden the LSPR bandwidth due to the additional absorption in the Cr layer. As the particles become smaller, the effect of the Cr layer becomes more pronounced. This was shown in the simulations with a thicker Cr layer. This effect was also recently reported by Jiao et al.⁵⁴ who did simulations of near-field resonances in bowtie antennae to study the influence of the adhesion layers.

To study the nanoparticle coupling effect on the LSPR behavior of the Au nanodisk array, we carried out Coupled Dipole Approximation (CDA) calculations.⁵⁵ The CDA is similar to the DDA method but for one difference: in CDA one

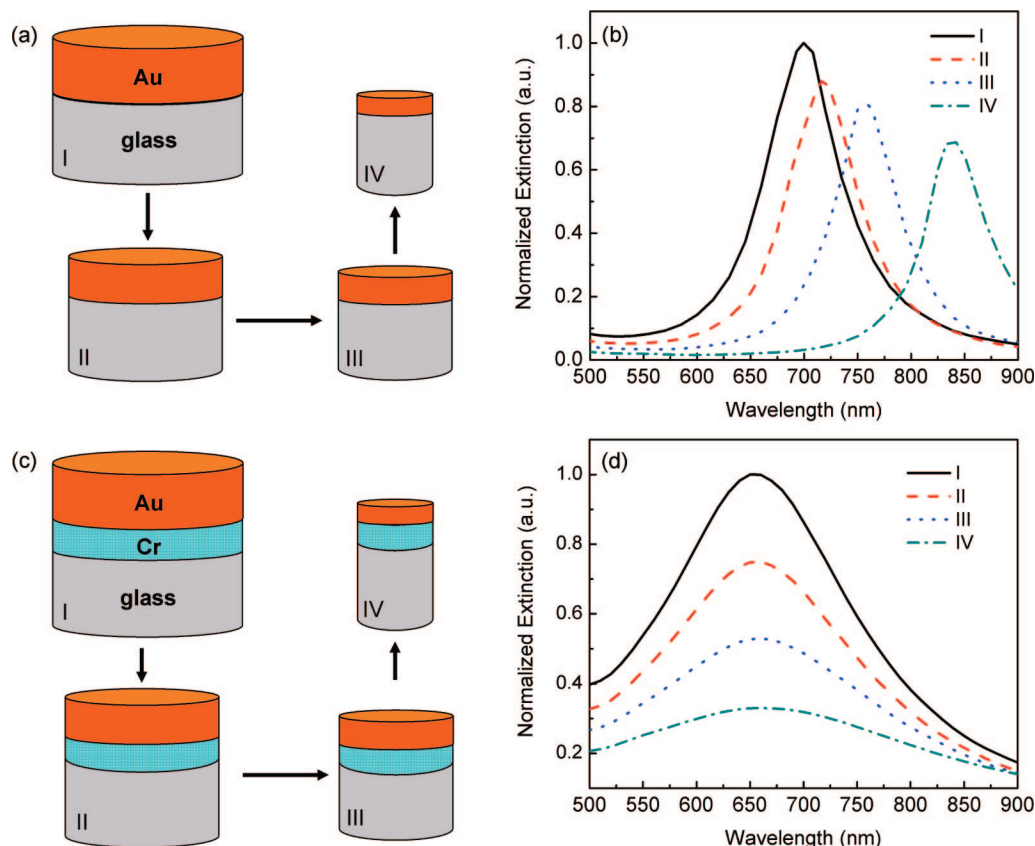


Figure 5. (a) Schematic of two-layer (without Cr) Au nanodisk models employed for DDA calculations. (b) Corresponding DDA-calculated extinction spectra of the models described in part a. (c) Schematic of three-layer Au nanodisk models (with a Cr layer of 4 nm in height) employed for DDA calculations. (d) Corresponding DDA-calculated extinction spectra of the models described in part c.

represents each nanoparticle by a single dipole, while in DDA one represents each nanoparticle by a cubic lattice of dipoles (which are subject to polarization). We calculated the extinction spectra of both a single Au oblate spheroid and a hexagonal array of 210 Au oblate spheroids (of dimensions similar to those of the Au layer in the three-layer disk but without the Cr or the glass substrate layers). Both results showed that the LSPR peak wavelength redshifted and the bandwidth narrowed with chemical etching (data not shown). These results also indicated that the coupling effect among the Au nanodisks in the hexagonal array of an array period of 320 nm did not significantly change the LSPR behavior. Therefore, the observed redshifting and broadening of the LSPR spectra were primarily caused by the morphology change of the nanodisks during the etching process, as well as the presence of the thin Cr adhesion layer.

4. Conclusion

We performed chemical etching of Au nanostructure arrays to tune their LSPR. Au nanostructure arrays were fabricated by a hybrid NSL/RIE technique and underwent isotropic etching in typical Au etchant solutions. The etching time controlled the morphology of the Au nanostructure arrays that was readily monitored by means of the LSPR signal. Continuous redshifting of the LSPR wavelength was realized by chemical etching of Au nanodisk arrays, while blueshifting was realized by chemical etching of Au nanosphere arrays. Further, theoretical calculations were performed to elucidate the etching process and the LSPR behavior of the Au nanodisk arrays. The chemical etching technique featured a simple experimental setup and allowed for fine adjustment of the LSPR peak position in aqueous solution. The technique will serve as a platform for studying plasmon-

exciton coupling effects,^{56,57} optimizing SERS,³¹ and engineering LSPR chemical/biological sensors.^{17,58}

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