1 Introduction

Plasmonics integrates electromagnetic waves with metal nanostructures, allowing the manipulation of electromagnetic waves at the nanometer scale [1,2]. This provides the possibility for all-optical, ultra-high-speed computing or even the creation of networks and grids with much faster speeds and lower energy losses compared to current microelectronic circuits [3–10]. It also provides a means to circumvent optical diffraction limits—which restrict the image resolution of the microscope—via the use of various metamaterials such as the superlens [11,12], hyperlens [13,14], and their derivatives [15,16]. Active metamaterials consisting of both metal structures and an active medium such as liquid crystals [17–24] or bistable molecules [25–34] have also been demonstrated as effective nanoscale optical modulators. Advanced fabrication techniques have equipped researchers with a powerful toolkit to further explore plasmonic phenomena [35–39].

Localized surface plasmon resonance (LSPR) [40,41] is an important branch of plasmonics, linking metal nanoparticles with extraordinary optical responses. LSPR occurs when the oscillating frequency of incident light matches with the intrinsic electron resonance on the surface of a noble metal nanoparticle. Enhanced electron oscillations at the resonance frequency cause increased optical absorption, thus LSPR is characterized by peaks in the absorption spectrum. The factors affecting LSPR include the size and shape of particles/holes [42,43], the distance between adjacent particles/holes, the thickness of the fabricated structures, and the environment surrounding the structures [44–50]. Specific LSPR peaks can be obtained by engineering the metal nanostructures into different sizes and arrangements [51]. However, for each desired LSPR, a different corresponding geometry must be designed and fabricated. Active plasmonics that can actively tune the LSPR after fabrication via flexible approaches utilizing either mechanical stretching or thermal expansion to alter the nanostructure substrate possesses a highly desirable feature preferred in applications such as plasmonic switches or biosensing [52–54].

Here, we describe a method to fabricate Au nanodisks onto an elastic PDMS substrate. Due to the weak bonding between Au and PDMS, the nanostructures were fabricated onto an intermediate layer for sufficient adhesion. In addition, by mechanically stretching the PDMS substrate, above which sit the Au-patterned nanostructures, we observed a real-time tuning of the plasmonic resonance due to the varying distance between adjacent nanodisks. Our design utilizes low-cost nanofabrication techniques and can find application in plasmonic sensing [55], optical imaging, optical memory elements, and energy harvesting [56].

2 Experimental Details

A schematic of the working mechanism is shown in Fig. 1. In order to dynamically tune the LSPR of an Au nanostructure array, we fabricated the array on the resilient, mechanically limber substrate: PDMS. However, the deposition of Au directly on PDMS is not favorable as the two only weakly interact. To overcome this challenge, we used a monolayer self-assembly process based on a standard Langmuir–Blodgett [57] followed by standard etching and film deposition procedures.

The PDMS substrate was prepared as follows: First, a silicon wafer with smooth surfaces was cleaned and coated with 1H, 1H, 2H, 2H-perfluorooctyltrichlorosilane (Sigma-Aldrich) to reduce the surface energy. This treatment protects the PDMS from deformation during the detachment process and significantly reduces the surface roughness. Next, Sylgard® 184 Silicone Elastomer base and curing agent (Dow Corning, Midland, MI) were mixed in a 10:1 weight ratio and applied to the pretreated silicon wafer. The mixture was then cured at 70°C for 20 min. Once cured, it was cut and peeled from the silicon wafer. Finally, a zapping...
process was initiated to create charges on the PDMS surfaces to increase the bonding between PDMS and dielectric materials. Polystyrene (PS) nanospheres with a mean diameter of 1.05 \( \mu \text{m} \) were obtained in solution (10 wt. %; Bangs Laboratories, Inc.) and diluted to 1 wt. % with ethanol. The diluted suspension was pulled into a precleaned Langmuir–Blodgett deposition trough (KSV NIMA) filled with deionized water. Upon the addition of several microliters of sodium dodecyl sulfate, the PS nanospheres were dispersed on the water surface (Fig. 2(a)). The barriers of the trough were brought close together to form a monolayer of PS nanospheres (Fig. 2(b)). The PDMS slab was then placed onto the patterned monolayer to directly transfer the PS nanosphere array from the liquid surface to the pretreated PDMS surface (Figs. 2(c) and 2(d)). A plasma etching process was applied to flatten and separate the transferred PS nanospheres. As shown in Fig. 2(g), the diameter of the PS nanospheres shrinks from 1.05 \( \mu \text{m} \) to 800 nm after etching, leaving the spacing between adjacent nanospheres around 250 nm. Finally, a 2-nm-thick adhesion layer of Cr and a 40-nm-thick layer of Au were sputtered onto the reshaped nanospheres to form the Au nanostructure arrays. Figure 2(h) shows the SEM image of the sample after Cr/Au deposition. The hexagonal array has a period of 1.05 \( \mu \text{m} \) and a spacing of \( \sim 165 \text{ nm} \). The observed structures are nanonipple-like structures rather than in perfect disk shapes because the beads supporters would not provide a flat surface for the deposition after etching. However, it does not affect our concept of plasmonic tuning via PDMS substrate stretching, and the shape effect on plasmonic resonance is not the focus of our work. Thus, we approximated the nanonipples to nanodisks for the simplicity of simulation and analysis, and our approximation has been confirmed and supported in both simulation and experiment.

The experimental setup is schematically illustrated in Fig. 1. The dimension of sample we used in the experiment is around 1 cm by 1 cm, cutting from a large sample area. The sample was affixed to a caliper with a stretching range of 0 to 2000 \( \mu \text{m} \) and a precision of 10 \( \mu \text{m} \). An ultraviolet-visible-infrared spectrometer (Ocean Optics Co., HR4000) was operated in reflection mode to measure the reflectance spectrum of the Au nanostructure arrays. Both the source and detector optical fibers were mounted normal to the sample. The dynamic tuning of LSPRs from Au nanostructure arrays was then monitored over a spectral range of 400–900 nm upon sample stretching.

**Fig. 1** Schematic of the experimental setup. The active tuning of LSPR of the Au nanodisk arrays is achieved by mechanically stretching the sample.
Fig. 3  (a) Microscopic image of Au nanodisk array immobilized on a PDMS substrate. Three axes of the hexagonal array are marked for measuring the geometry change upon stretching. (b)–(d) The measured change in array period along three axes.

Fig. 4  (a) Measured and (b) FDTD-simulated LSPR reflectance spectrum of the Au nanodisk arrays immobilized on a PDMS substrate in relaxed state.
3 Results and Discussion

Figure 3(a) shows original microscopic images of a relaxed Au nanodisk array, and a processed image to mark the lattice boundaries of adjacent nanodisks. The arrowed lines denote the three axes of the hexagonally arranged array, and the horizontal line indicates the stretch direction. The maximum stretch is 2000 μm, and the change in period along three axes of the hexagonal array is plotted in Figs. 3(b)–3(d), respectively. The change in period was measured from captured microscopic images and its value was averaged over several locations. We note that only the distance between adjacent nanodisks changed during the stretching process and the shape of the nanodisks maintained the same as in their relaxed state. This is caused by the intermediate PS sphere layer separating the gold nanostructures and the PDMS substrate. The gold nanostructures are stick to the PS spheres rather than attaching to the PDMS layer directly; thus, the gold structures will not change their shapes unless the stretching force from PDMS substrate is strong enough to tear the PS spheres, which is unlikely to happen in our case.

Upon being stretched, axes 2 and 3 are elongated, while axis 1 is condensed. It can be seen from Fig. 3 that the relation between the stretch amplitude and period shift is nearly linear along all axes. The maximum rate of change of the period along axes 2 and 3 is ~4.3%, and ~1.6% for axis 1. Poisson’s ratio (υ) was calculated from the geometric relation between the axes (0.45), which accurately matches the intrinsic material property of PDMS (υ = 0.5). Finally, the angle between axes 1 and 2 increases from 60 deg to 62 deg upon maximum stretching, while the angle between axes 2 and 3 decreases to 56 deg.

The LSPR properties of the Au nanodisk arrays, which were immobilized onto the PDMS substrate, were studied by taking the arrays’ reflectance spectrum. Figure 4(a) shows the measured reflectance spectrum of the relaxed Au nanodisk arrays. To further understand the spectrum, a numerical calculation was conducted using commercial software (NUMERICAL FDTD) [58] to simulate a perfect hexagonal array of Au nanodisks standing on a dielectric substrate. The period, the diameter, and the thickness of the Au nanodisks were 1050 nm, 800 nm, and 40 nm, respectively. The dielectric constant of Au was obtained from a fit to the Johnson–Christy data [59]. An unpolarized, broadband light source was set normal to the substrate and the reflectance spectrum is shown in Fig. 4(b) (modeled without Cr adhesion layer).

The reflectance minimum is related to intrinsic absorption and transmission of the incident light by the Au, while the peak indicates minimal coupling between the incident light and the localized surface plasmons. The experiment result closely matched the simulation and confirmed that the tightly packed Au nanoparticle arrays have been formed as expected.

Figure 5(a) shows the reflectance spectra of Au nanodisk arrays on a PDMS substrate undergoing various levels of stretching. The stretching neither broadened nor decreased the intensity of the LSPR spectra. There is no obvious shift in the spectral dip since it represents the intrinsic transmission and absorption of Au and is not dependent on geometry. The reflectance peak, however, exhibits a clear blueshift proportional to the amount of stretch, which is consistent with the observation in Ref. [60]. The reflectance peak shift versus stretch magnitude is plotted in Fig. 5(b); the plot shows a maximum peak shift of 30 nm (from 752 nm in the relaxed state to 722 nm at maximum stretch). The peak shift is reversible, i.e., the peak wavelength moves back to 752 nm when the sample is released, and the tuning of the peak wavelength becomes uniform across the sample. This kind of phenomenon enables the nanodisk array “glued” on a PDMS substrate be used as an ultrasensitive optical tool to monitor small changes of the external tension force applied.

The blueshift of the reflectance peak wavelength is the result of the change in Au nanodisk array geometry. LSPR in nanoparticle arrays is highly dependent on coupling between adjacent particles, which in-turn strongly depends on the interparticle distance. The sample was stretched in only one direction, but due to Poisson’s effect the size in the relaxed direction was decreased while the period in the other two directions was increased. The spacing of the Au nanodisk arrays was not homogeneously changed; however, the effective interparticle distance increased as the sample was stretched, leading to less influence from electron coupling between adjacent Au nanodisks as well as a blueshift in the reflectance peak.

4 Conclusions

We have developed a simple, inexpensive method to fabricate patterned Au nanostructures on a PDMS substrate. The plasmonic resonance of the Au nanostructures can be actively controlled by stretching the PDMS substrate. The stretching increases the distance between adjacent Au nanostructures, leading to a shift in their plasmonic resonance. The shift is repeatable, reversible, and has potential applications in LSPR sensing, Raman sensing, and coupled resonance studies.

Acknowledgment

Yanhuai Zhao and Thomas Walker contributed equally to this work. The authors want to thank Dr. Shikuan Yang and Dr. Cheng-long Zhao for helpful discussion. This research was supported by NIH Director’s New Innovator Award (1DP2OD007209–01), the National Science Foundation (0824183 and 0801922), U.S. Department of Agriculture (USDA/NRI), Air Force Office of Scientific
Research, and the Penn State Center for Nanoscale Science (MRS). Components of this work were conducted at the Penn State node of the NSF-funded National Nanotechnology Infrastructure Network.

References


