Flexible Plasmonic Tapes with Nanohole and Nanoparticle Arrays for Refractometric and Strain Sensing

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Abstract

Realization of plasmonic nanostructures on flexible and stretchable substrates have attracted considerable attention because such integration provides novel functionalities for sensing applications. Here we present a plasmonic tape by achieving metal nanostructures on the transparent tape with a simple transfer technique. Examples include the tapes with nanohole and nanoparticle arrays for refractive index and strain sensing, respectively. These continuing and discrete structures on tapes feature characteristic plasmonic resonances and excellent flexibility. The tape with the nanohole array shows higher sensitivity in the refractive index sensing than that on the rigid substrate. The nanoparticle array used in strain sensing discloses two plasmonic modes with different responses. This plasmonic tape offers a flexible platform for plasmonic sensing and may open application possibilities in scenarios inaccessible by conventional plasmonic sensors.

Introduction

Recent advances of flexible electronic sensors have created new pathways to access unconventional interfaces and innovative functions for the next generation of soft electronic systems.[1-2] Similarly, the concept of flexible plasmonics has arisen from the realization of active optical metamaterials on nonplanar, stretchable, and/or flexible substrates.[3] These new designs have broaden the scope of plasmonics and its sensing application. Metal nanostructures have played a key role in the field of plasmonics due to their excellent ability to concentrate light at the nanoscale. On the stretchable substrates, their plasmonic properties can be tuned through mechanical manipulation.[4-7] These flexible systems can

adhere to curved surfaces, allowing applications such as strain sensors, biosensing, flat lens and color generation.[8-16]

The realization of plasmonic nanostructures on flexible substrates in a controlled manner is critical to their availability of sensing. Most of existing methods combine on-rigid patterning techniques (e.g. e-beam lithography) with a transfer procedure to integrate metal nanostructures on final substrates.[8, 17-18] They require either a complex process, or a special treatment of the substrate for better adhesion.[19] In contrast, stencil lithography utilizes a stencil as a shadow-mask to directly create nanopatterns on a wide range of flexible substrates.[12, 20] However, the physical contact with the substrates during metal deposition may result in the failure of the fragile stencil. Due to the weak adhesion, the patterned structures may break away from the substrate when it is under strain in some sensing environment. A versatile and low-cost method is still in demand to realize flexible and reliable plasmonic devices for their widespread sensing application.

Herein we develop a plasmonic tape that combines metal nanostructure arrays on a transparent tape using a simple transfer procedure. No surface treatment of either templates or substrates is needed in the transfer procedure due to strong adhesion from the tape adhesive in comparison with the previous method.[6] The obtained plasmonic structures maintain their original pattern and good adhesion on the tape. We select structure arrays rather than a randomly arranged nanostructures[9-10] or single nanoantennas[11] since structure arrays exhibit robustness and performance consistency, which are of critical importance for applied nano materials. As examples, the tapes with nanohole and nanoparticle arrays are demonstrated as refractive index and strain sensors, respectively. They feature characteristic plasmonic properties and comparative performances as those on rigid substrates. For our plasmonic tapes, the sticky adhesive can not only reliably attach the nanostructures, but also adheres to the analyte surfaces in practical applications. This flexible platform promises new applications of plasmonic probes in sensing environmental changes that are otherwise inaccessible. Further, our plasmonic tape and related method provide a unique avenue to flexible plasmonics in terms of versatile manufacture and practical use.

Results and Discussion

The schematic in Fig. 1a depicts the patterning of metal nanostructures on the transparent tape. Our method is based on the template transfer technique that uses a pre-patterned Si wafer with nanostructures as the template to form gold nanostructures.[21-22] The procedure starts with gold deposition on the Si template either using electron-beam or thermal evaporation. These physical vapour deposition techniques are highly anisotropic, e.g. only in the vertical direction, where the metal does not adhere to the side walls of the Si nanostructures. On condition that the height of the Si nanostructure is larger than the thickness of gold, our technique ensures the disconnection between the deposited metal on top of the patterned Si wafer and that deposited in the dented area. Thus, gold nanostructures with the same geometry in the horizontal plane are naturally replicated during gold deposition. Afterwards, a piece of Scotch transparent tape is attached to the template. Peeling the tape from the template results in the transfer of the gold nanostructure due to the larger adhesion from the adhesive on the tape than that from the

Si template. As shown in Fig. 1b, gold nanoparticle arrays with different periods on the tape show diverse colours due to strong diffraction.

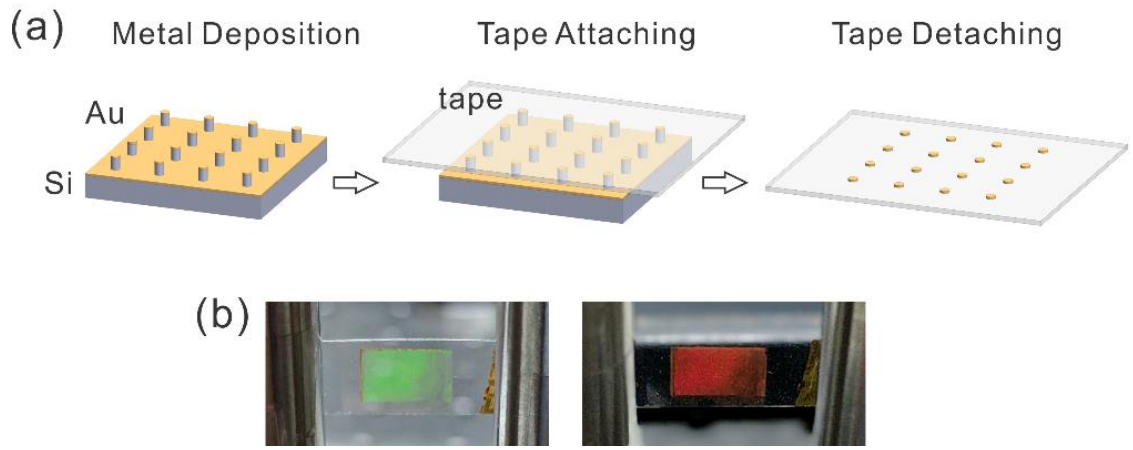

Figure 1. (a) Schematic of fabrication procedure for plasmonic tapes. (b) Gold nanoparticle hexagonal arrays (left, period, P = 600 nm period; right, P = 700 nm) on the transparent tapes display vivid colours.

Both continuing and discontinuing structures can be reliably transferred to the transparent tape by this technique. As examples, a gold nanoparticle and nanohole array on the tapes are demonstrated in scanning electron microscopy (SEM) images shown in Fig. 2a and b, respectively. These arrays copy the pattern of the structures on their corresponding templates. To investigate the structural integrity of transferred arrays, their SEM images are randomly selected at different spots over a large area (25×25 μm) as two examples shown in Fig. 2. The red circles in Fig.2a indicate the vacancies (14 in left; 27 in right) in the arrays both consisting of about 1400 nanoparticles. By visually spotting the vacancy of missing particles in the recorded images, it is confirmed that more than 97% of nanoparticles have been successfully transferred onto the tape. All the single defects have less than 3×3 nanoparticle missing in the transferred structures. Notice that a few nanoparticles slightly deviate from the original position due to the tape stretching. In comparison, the nanohole array on the tape precisely maintains its arrangement and integrity without cracking. The fine grain of gold on the nanohole array film can be viewed owing to its smooth surface, which can facilitate the propagation of surface plasmons.[23] Note the grain-like features between the nanoparticles are the adhesive on the tape.

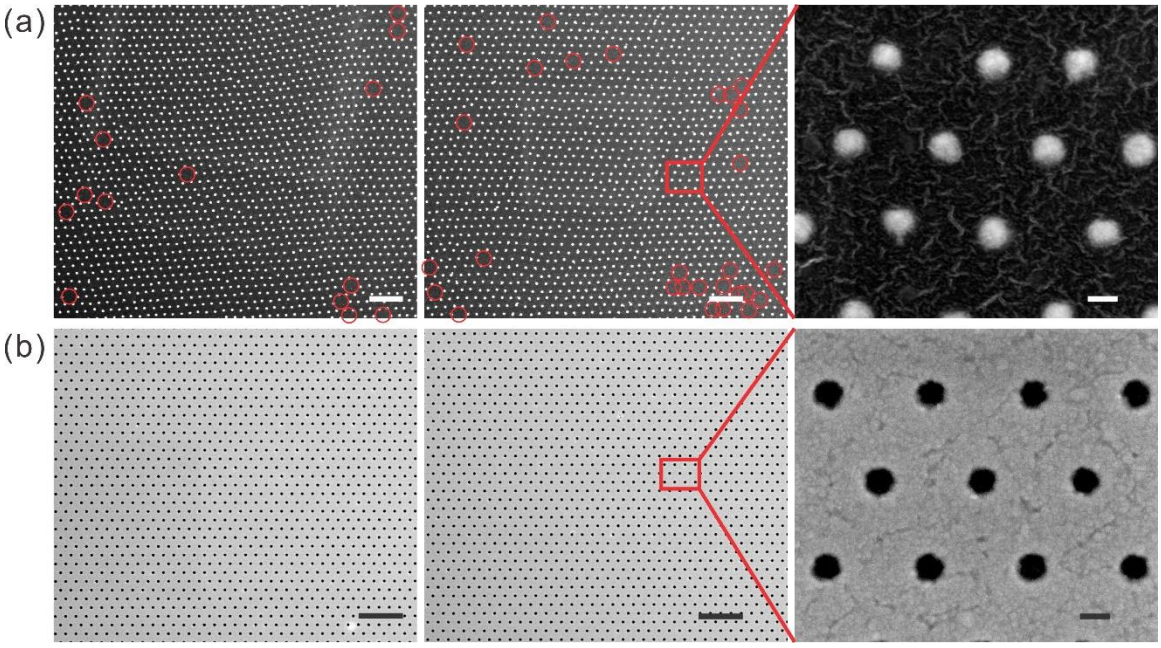

Figure 2. Typical SEM images of (a) nanoparticle arrays (diameter, D = 200 nm; P = 600 nm) and (b) nanohole arrays (D = 200 nm, P = 700 nm) on the transparent tape at two different areas, respectively. The red circles in (a) indicate the vacancies in the nanoparticle arrays. Scale bars, 3 μm (left and middle) and 200 nm (right) in (a) and (b).

These plasmonic tapes preserve the characteristic optical properties of the attached metal nanostructures as those on rigid substrates. For instance, the nanohole hexagonal array with 700 nm period on the tape show very similar transmission spectra features as those in our previous work.[22] The resonances on the top surface of nanohole array result in multiple peaks between 500 nm and 600 nm, while the 700 nm and 1000 nm resonances are related to the tape substrate. For the nanohole array of 600 nm period, the transmission peaks appear at different wavelengths from those of the 700 nm period array on the tape, due to the shift of plasmonic resonances as shown in Fig. 2a.

The plasmonic tape is characterized as a refractive index probe using different concentrations of NaCl solutions. When the tape is exposed to the solutions, narrow peaks and troughs are observed between 800 nm and 925 nm in the transmission spectra (Fig. 3b). These maxima and minima proportionally shift to longer wavelengths as the surrounding refractive index increases. The refractive index sensitivities (defined by the slope of resonance wavelength as a function of the refractive index) are calculated by linearly fitting three peak shifts (inset in Fig. 3b). The highest sensitivity of this plasmonic tape surprisingly reaches 706 nm/RIU (refractive index unit), exceeding that of 595 nm/RIU from the same structure on a multi-mode optical fiber.[21] The probable reason is that the permeation of NaCl solutions into the adhesive layer through gold nanoholes leads to such a large resonance shift.[24] The overall performance of a plasmonic sensor is dominated by both the sensitivity of the resonance and its spectral line width. The full width at half-maximum (FWHM) of the resonance with 706 nm/RIU sensitivity is narrowed down to 13.5 nm. Such a narrow line width indicates the long lifetime of the resonance and high structure quality of

the nanohole array on this flexible tape. Accordingly, the figure of merit (FOM) defined as the refractive index sensitivity divided by the corresponding FWHM, achieves 52 which is comparable to the previously reported value for the same gold nanohole array on optical fibers.[21]

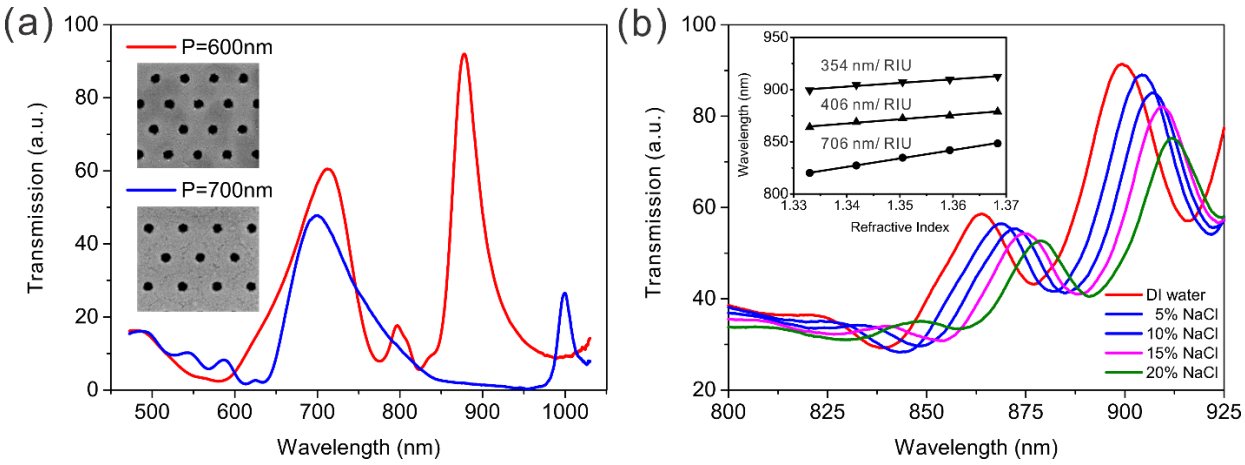

Figure 3. (a) Transmision spectra of plasmonic tapes with nanohole arrays (P = 600 nm and 700 nm). Insets, the corresponding SEM images. (b) Refractive index sensitivity measurement with water and NaCl solutions of different concentrations. Inset: linear fitting the peak shifts around 830 nm, 860 nm, and 900 nm for respective sensitivity calculation.

As plamonic tapes are stretchable, they have the potential for use in strain sensing. When the plamonic tape is stretched, the distances between the nanoparticles are changed as shown in Fig. 4a. As a result, their resonance coupling varies, leading to the spectral shift. Two resonance minimums appear in the transmision spectrum of a nanoparticle array with 600 nm period on the tape. Notice that these two resonances reveal different shifting behaviours (Fig. 4b). The resonance at the shorter wavelength become more sensitive as the tape strain ε increases (inset in Fig. 4b). In contrast, the shifting of the resonance at the longer wavelength gradually saturates over 20% ε. Moreover, the short-wavelength resonance keeps the same strength during strain, whereas the long-wavelength one remarkablely decays. Note that the tape backing film (unplasticized polyvinyl chloride, UPVC) is subject to fail when the strain goes beyond 45%. Thus, we limit our analysis to the low strain range. In addition, the stretching is irreversible for this UPVC tape. However elastomeric tape can be used for applications that require high-strain repeatable stretching.

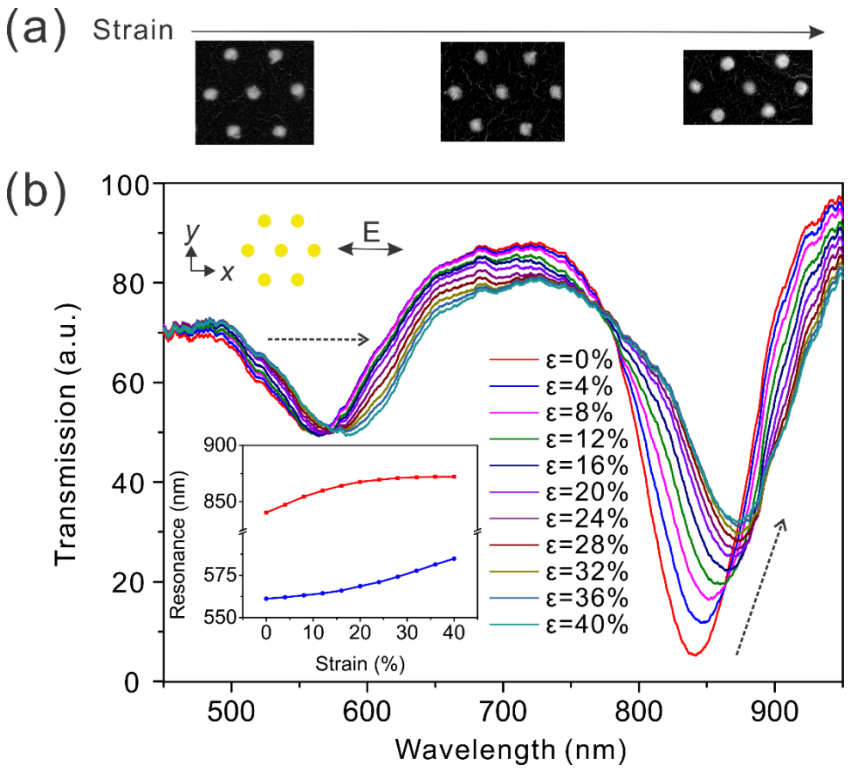

Figure 4. (a) Typical SEM images of a nanoparticle array (P = 600 nm, D = 200 nm) on the tape under strain along one translation axis of the nanoparticle array. (b) Sensing the tape strain ε by the nanoparticle array in (a) with the polarization and stretching direction aligned. Inset: resonance wavelengths measured for strain sensitivity calculation.

To understand the possible reason behind these spectral features, we performed finite-difference timedomain (FDTD) simulations. As shown in Fig.5, the two resonances are related to two different modes respectively: a top mode along the top edge of nanoparticles at 558 nm, and a bottom mode around the bottom edge at 838 nm. By stretching the tape, the nanoparticles in the hexagnal array split farther from each other along the stretching direction, and meanwhile get closer in the direction orthogonal to polarization due to the tape strain. The splitting between particles redshifts the resonance, and vice versa. Beyond 15% ε, the tape starts to undergo dramatic thinning instead of strain in the direction orthogonal to polarization. Thus the particle splitting (positive for resonance shifting) dominates and speeds up the shifting.

Besides the distance change between nanoparticles, the tape stretching also results in their partial detactment from the adhesive over 20% ε. This significantly reduces the refractive index around the bottom edge of nanoparticles, thereby offseting the strain-induced redshift of the bottom-mode resonance. The bottom-mode transmission decay is also due to this refractive index decrease. Under the working condition of less than 15% ε, the sensitivity of top-mode and bottom-mode resonance is calculated to be 37 nm/ε and 137 nm/ε respectively (inset in Fig 4.). This high sensitivity is comparable to those of the randomly arranged nanorods (~120 nm/ε)[9] and nanoparticles (~200 nm/ε)[10], or bow tie nanoantennas (~80 nm/ε)[11] on polydimethylsiloxane (PDMS) substrates.

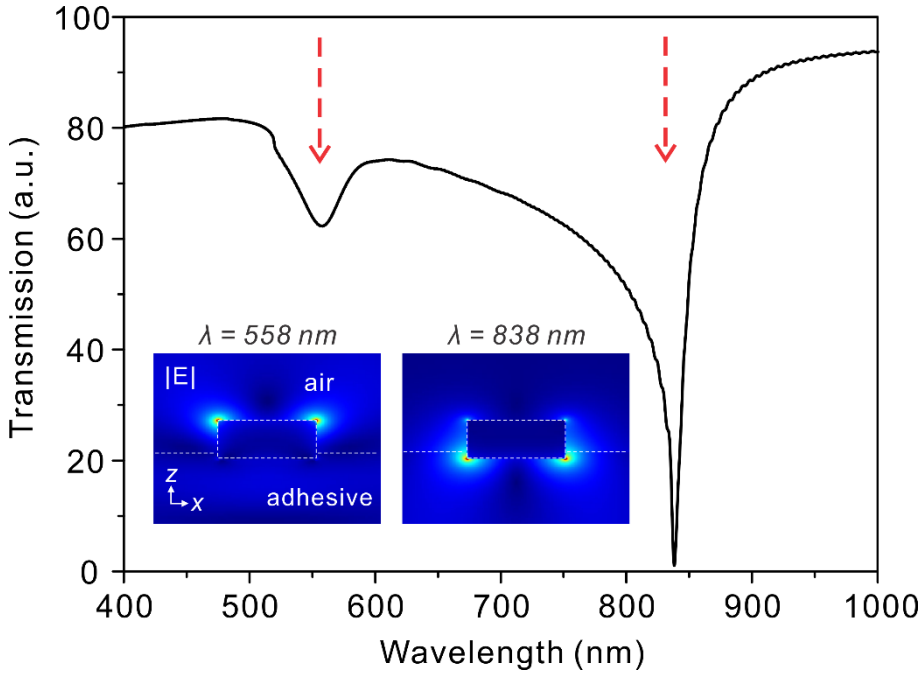

Figure 5. Simulated transmission of the gold nanoparticle array with 600 nm period on adhesive of refractive index 1.61. Inset: electric field distributions (|E|) for the top mode at 558 nm and the bottom mode at 838 nm in the x–z plane, respectively.

Conclusions

In conclusion, we have realized a plasmonic tape by using a single-step template transfer procedure. The presented low-cost and efficient fabrication method could be essential for emerging sensing technologies based on flexible plasmonics. The obtained plasmonic tapes reveal tunable plasmonic properties and excellent flexibility. The nanohole array on the tape exhibits higher refractive index sensitivity than the same structures on the rigid substrate. The used nanoparticle array reveals two plasmonic modes with different responses in strain sensing. This simple platform of plasmonic tape will open up new horizons in flexible plasmonics and inspire innovative plasmonic structures for applications in various fields.

Experimental Section

Transferring nanostructure arrays to tapes

The used Scotch® Transparent Film Tape (3M) has a pressure sensitive acrylic adhesive, backing a UPVC film with 45 % elongation at break. A pre-patterned Si template (LightSmyth Technologies) with nanostructures was first cleaned in piranha solution (98% H_2SO_4: 30% H_2O_2 = 3:1, v/v) and dried using N_2 gas. A custom thermal evaporator was used to deposit 100-nm-thick gold onto the Si template without the adhesion layer. The deposition rate of 1 Å/s was maintained at ~5 × 10^{-6} Torr. A section of the tape was then attached on the gold and gently squeezed the backing film back and forth by using a glass rod, until there was no observable gap underneath. As the adhesive on the tape is a 20 µm acrylics elastomer, it is easy to make conformal contact with the nanostructures on the flat Si template. Peeling the tape from the template resulted in the transfer of the nanostructure arrays.

Refractive index sensing

Two optical fibers were deployed perpendicular to the nanohole array on either side of the plasmonic tape for transmission measurement. One optical fiber was used to deliver incident light from a white light source (HL-2000, Ocean Optics) to the tape and the other fiber was employed to collect transmission signals to a spectrometer (QE Pro, Ocean Optics). Refractive index solutions were prepared by adding NaCl into deionized water to obtain various concentrations (5%, 10%, 15% and 20%) with different refractive index (1.3418, 1.3505, 1.3594, and 1.3684, respectively). NaCl solutions were dropped onto the nanohole array and transmission spectra were recorded until the solution touched the nearby optical fiber endface.

Strain sensing

Either blank end of the plasmonic tape with the nanoparticle array was wrapped around a post fixed on a secured translational stage. Two optical fibers were deployed as those in the refractive index sensing. The transmission spectra of the nanoparticle array were recorded during the stretching of this plasmonic tape by separating two posts using the translational stages.

FDTD simulation of nanoparticle array

3D FDTD simulations were performed using a commercial software, FDTD Solutions (Lumerical Inc.). The gold nanoparticles (P = 600nm, D = 200nm; height, H = 100 nm) were buried 20 nm in the substrate. A uniform mesh size of 2 nm (x, y and z directions) was used. We set perfectly matched layer boundary conditions for the z direction, and periodic boundary conditions for x and y directions of the simulation region. Two electric-field monitors were used to record the field distributions at 558 nm and 838 nm, respectively.

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