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Mechanical control of the plasmon coupling with Au nanoparticle arrays fixed on the elastomeric film via chemical bond

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We have fabricated Au nanoparticle arrays on the flexible poly(dimethylsiloxane) (PDMS) film. The nanoparticles were bound to the film via a covalent bond by a ligand exchange reaction. Thanks to the strong chemical bonding, highly stable and uniformly dispersed Au nanoparticle arrays were fixed on the PDMS film. The Au nanoparticle arrays were characterized by the UV-vis, scanning electron microscope (SEM) and surface enhanced Raman scattering (SERS). The UV-vis and SEM measurements showed the uniformity of the surface-dispersed Au nanoparticles, and SERS measurement confirmed the chemistry of the PDMS film. Reflecting the high stability and the uniformity of the Au nanoparticle arrays, the plasmon wavelength of the Au nanoparticles reversely changed with modulation of the interparticle distance, which was induced by the stretching of the PDMS film. The plasmon wavelength linearly decreased from 664 to 591 nm by stretching of 60%. The plasmon wavelength shift can be explained by the change in the strength of the plasmon coupling which is mechanically controlled by the mechanical strain.

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1. Introduction

The optical response of metallic nanostructures is of fundamental scientific interest and found its potential application for a molecular sensing and optical filtering.¹⁾ For metallic nanostructures whose diameters are much smaller than the wavelength of the incident light, a localized surface plasmon (LSP) is excited in the metallic nanostructures.²⁻⁴⁾ The excitation of LSP results in a strongly enhanced electric near field localized at the particle surface. The LSP wavelength depends on the shape and size of the metallic nanostructures. In the case of Au nanoparticles, they exhibit colours ranging from red to purple according to their sizes. When the distance between nanostructures decreases, the plasmon modes of the individual nanostructures interact each other, resulting in the plasmon coupling.²⁻⁴⁾ The plasmon resonance causes a red shift of the LSP-wavelength with respect to that of the individual nanostructures. In solution, the Au nanoparticles can aggregate with the time, resulting in a red shift of the plasmon resonance, as evidence by colour change from red to purple.⁵⁻⁷⁾ This kind of colour change has been employed to detect biomolecules including DNA and protein biomarker for cancer and other diseases.^{8,9)} In addition to the shift of plasmon resonance, the plasmon coupling is the unique optical response appears in the metallic nanostructures, in which the electric field between metal nanoparticles can be increased by a factor of 1000. This strong electric field is applied to various measurement techniques including surface enhanced Raman scattering (SERS),^{10,11)} surface enhanced infrared absorption spectroscopy (SEIRAS).¹²⁾ Anker et al. reported that SERS signal can be detected from a single dye molecule using the enhanced field between Ag nanoparticles in 2008.¹³⁾

The plasmon coupling depends on the distance between nanostructures. Therefore, the controlling the distance between nanostructures is the key for governing the nano-optics. In order to control the distance between nanostructures, the nanogap electrode method based on lithographic technique is most straightforward approach. The change in extinction spectra and SERS has been reported for Au nanoparticle pairs and dimer type nanogap gold structures

fabricated with the electron beam lithographic technique.^{3,6,14)} Jain et al. showed the plasmon wavelength-shift decayed nearly exponentially with the gap distance between gold nanoparticles, and that the decay length was roughly about 0.2 in unit of particle size.⁶⁾ While the tuning of the plasmon coupling of a particle pair has become possible, the second step is tuning the gap distances and the plasmon couplings for nanoparticle assemblies. Based on this interest, nanostructures on the flexible substrate has been studied. Matthew et al. fabricated the Au nanoparticle mats on the poly(dimethylsiloxane) (PDMS) film, by transferring the monolayer of close-packed Au nanoparticles to the PDMS film.¹⁵⁾ The interparticle distances of the nanoparticle assemblies were modulated by stretching the PDMS substrate. The plasmon resonance peak in the UV-vis spectra, changes with the stretching, reflecting the change in the gap size. However, there are several issues on this Au nanoparticle mats on PDMS; low homogeneity and low resistance to chemical attack. Due to the low homogeneity of the interparticle distances, the UV-vis spectra changes with the samples, and colour is changeable depending, even, on the position in the same sample. In addition, the Au nanoparticles are fragile and easily peeled off from the PDMS film, because the Au nanoparticles are bound to PDMS via the weak physical interaction.

To overcome these problems, we focused on the chemical approach to fabricate the stable Au nanoparticle arrays on the flexible substrate. The Au nanoparticles were covalently attached to substrate by the chemical reaction. This chemical approach has been already reported for the solid substrate, such as glass, indium tin oxide (ITO), SiO₂/Si substrates.¹⁶⁾ However, there are little studies with the flexible substrates. In this study, the Au nanoparticles were chemically bounded to the PDMS substrate functionalized with 3-mercaptopropyltrimethoxysilane via chemical bonding. The Au nanoparticles were attached to the PDMS by ligand exchange reaction. The gold nanoparticles fixed on the chemically functionalized PDMS (f-PDMS-Au) was very stable and uniform. Stretching the f-PDMS-Au proves active and reversible tuning of their plasmonic properties. The stretching induced blue shift of the plasmonic resonance.

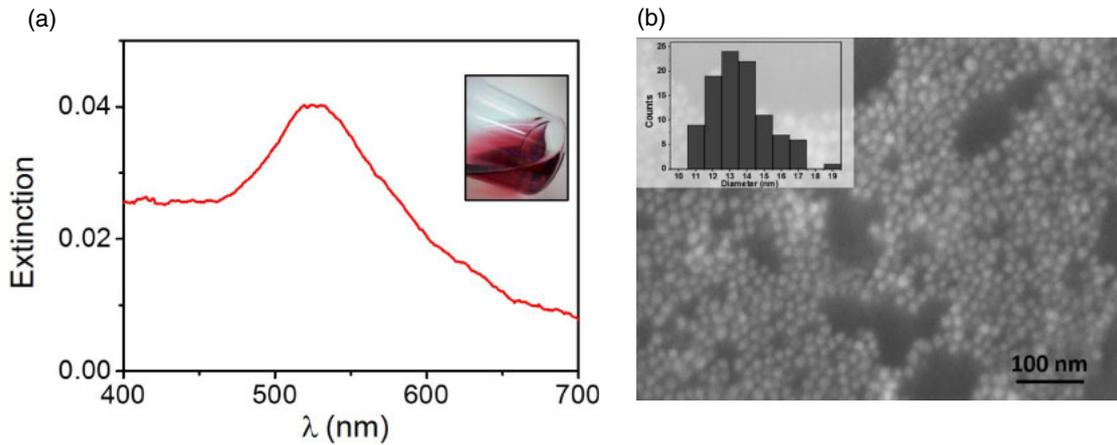


Fig. 3. (Color online) (a) Extinction spectrum of gold nanoparticles solution, Inset: Photo image of Au nanoparticles solution. (b) SEM image of Au nanoparticles deposited on conductive ITO substrate. Inset: Distribution of particle diameters obtained from 100 nanoparticles.

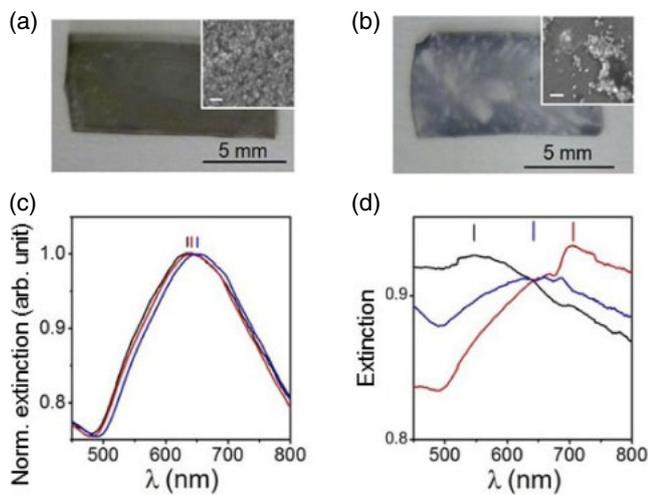


Fig. 4. (Color online) Pictures of f-PDMS-Au (a) and n-PDMS-Au (b), inset: SEM images of both substrate. The white scale bar: 200 nm. (c, d) Comparison of UV-vis spectra of different area of the identical sample obtained with f-PDMS-Au (c) and n-PDMS-Au (d). UV-vis spectra of (c) are normalized to a maximum value of each spectrum.

tively.²⁰ In our sample, the value of the absorbance ratio (A_{spr}/A_{450}) was 1.57, which corresponded to the nanoparticle size of 12 nm. The nanoparticle's size was also evaluated by SEM [Fig. 3(b)]. The inset of Fig. 3(b) shows the distribution of the particle size obtained from 100 nanoparticles. The average diameter was 14 nm, which agreed with the value obtained by UV-vis. The distribution was narrow, indicating that the nanoparticles were monodisperse.

Figure 4(a) shows a picture of the f-PDMS-Au. The f-PDMS-Au has a shiny mirror-like metallic sheen, which was very different from the red Au nanoparticle solution. It is noteworthy that the colour was uniform, and SEM image (inset of Fig. 4) supported that Au nanoparticles distributed homogeneously. Figure 4(c) shows the UV-vis spectra of the same sample with different positions. The resonant wavelength was 650 nm, and the fluctuation of the resonant wavelength was as small as 6 nm. The resonant wavelength of nanoparticle arrays was obtained by fitting the spectrum with the Gaussian function in the present study. For comparison, we also prepared the Au nano particles on the PDMS film without the chemical modification, following the previously reported

study.¹⁵ Monolayers of close-packed Au nanoparticles were first self-assembled at a hexane/water interface by adding the 1-dodecanethiol. Then the Au nanoparticles were transferred to the non-functionalized PDMS film (n-PDMS-Au). The obtained sample was inhomogeneous [Fig. 4(b)]. We can see small blue areas, corresponding to the presence of nanoparticles, and the transparent areas, corresponding to the lacking of nanoparticles. The discontinuous coating of nanoparticles was confirmed by SEM [inset in Fig. 4(a)], showing the random distribution of nanoparticles on the surface. The extinction spectra fluctuated with the position, reflecting the inhomogeneity of the sample [Fig. 4(d)]. The fluctuation of the resonant wavelength increased from 6 to 72 nm.

We have successfully prepared the uniform and stable Au nanoparticle arrays on the flexible PDMS film via a strong covalent bond. The presence of a strong interaction guarantees the stability of the system, compared with the n-PDMS-Au. In the preparation of the f-PDMS-Au, the PDMS film was washed, and thus, the Au nanoparticles not covalently bonded to the surface, was removed from the surface. Consequently, the PDMS was covered with the monolayer of Au nanoparticles, while the additional multilayer of Au nanoparticles were not formed on the PDMS. The uniformity of the sample can be controlled by the first step with silane derivatization of the PSMS surface, the proper concentration of silane, the correct temperature and time allowed to synthesize a sample with a very thin layer of silane without aggregation that is the base for the second step with gold nanoparticles.

We then investigated the change in the optical properties of the film by the mechanical stretching. The UV-vis spectra of the f-PDMS-Au show a blue-shift with stretching. Figure 5(a) shows examples of the UV-vis spectra during the stretching process. Figure 5(b) shows the wavelength of the peak in the spectra (λ_{max}) as a function of stretching. During the stretching process, λ_{max} moved from 623 to 575 nm, and returned to 624 nm by relaxing the mechanical strain. Figure 5(c) is the average peak position as a function of the stretching obtained from three samples. λ_{max} shifted from 664 to 591 nm by stretching of 60%. Similar trend was reported by Millyard et al. using the n-PDMS-Au. They reported the plasmon shift of 40 nm for that sample with a maximum stretch of 35%.¹⁵

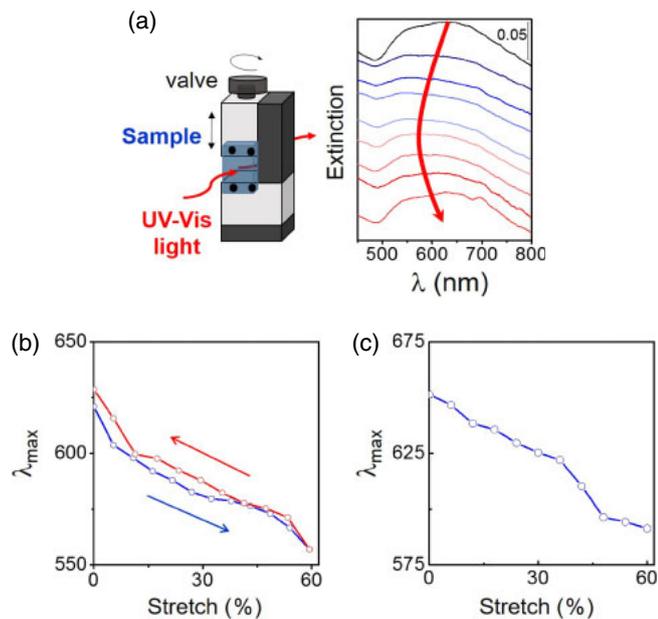


Fig. 5. (Color online) (a) UV-vis spectra of f-PDMS-Au obtained under increasing and then decreasing the mechanical strain together with the experimental set-up. (b) Example of shift of λ_{\max} as a function of stretching (blue) and relaxing process (red). (c) Average of shift of λ_{\max} as a function of stretching. Data are obtained from three different samples.

The shift of λ_{\max} can be explained by the change in the strength of the strength of the plasmon coupling. When the light is irradiated to the Au nanoparticles, the localized surface plasmon is excited. The excitation of plasmon results in a near field localized at the particle surface. When two nanoparticles are placed next to each other, the near field on one particle interacts with that on an adjacent particle in close proximity, coupling the plasmon oscillation together. The energy of the hybridized plasmon mode is lower (red shift) with respect to that of the plasmon modes of the individual nanoparticles.^{2-4,21)} The near field decays over a length that is roughly equal to the size of nanoparticle. In the dipole coupling model,²²⁾ the dipolar near field decays as the cube of the inverse distance. Therefore, the plasmon coupling strength becomes a function of d^{-3} . Since the plasmon shift reflects the strength of the interparticle electromagnetic coupling, the plasmon shift decays as the cube of the inverse distance.⁶⁾ Jain et al. experimentally showed the plasmon shift for the gold nanodiscs pairs fabricated with the lithographic technique on quartz slide. The plot of the plasmon shift versus the gap distance between nanoparticles followed nearly exponential decay. The decay length was roughly 0.2 times the nanoparticle size.⁶⁾ Yokota et al. showed the plasmon shift from 650 to 790 nm by changing the distance between Au nanostructures from 100 to 5 nm.¹⁴⁾

In the present study, the plasmon wavelength was 520 nm for individual nanoparticles, while it was 650 nm for f-PDMS-Au before stretching (red shift of 130 nm). The plasmon was red shifted with respect to the individual particles. By stretching the f-PDMS-Au, the plasmon wavelength linearly decreased with stretching (blue shift) by 80 nm. The shift of 80 nm was smaller than 130 nm, and plasmon shift linearly changed with the stretching, indicating that we only observed the part on the decay curve for the plasmon shift as a function of the gap distance. Here, we

assume that the Au nanoparticles are aligned parallel to the stretch direction, where the particle size and gap size are d and g , respectively. The particle size does not change with the stretching. So, when the film is stretched by 60%, $d + g + \Delta g = 1.6(d + g)$, where Δg is the increase in the gap size. $\Delta g = 0.6(d + g)$. The Δg increases with d , and is larger than $0.6d$. In this study, d was 14 nm, and thus, Δg was larger than 8.4 nm, which is compatible to the particle size. If the film was uniformly stretched, the plasmon coupling strength should be drastically reduced, and plasmon wavelength should be close to that for individual nanoparticles. The gap distance was not changed as expected. The large discrepancy and broadening of the spectrum can be explained by several possible reasons. The inhomogeneous stretching of the film, misalignment of the gap direction with the stretching direction, ignorance of the higher order plasmon coupling (quadrupolar plasmon) quantum effect,²³⁾ and far-field interaction.²⁴⁻²⁶⁾ The effect of the far-field interaction is clearly observed when the interparticle distance approaches the plasmon resonance wavelength. The plasmon resonance is red shifted due to the dipolar coupling.

4. Conclusions

We reported stable and quick derivatization method to synthesize a system composed by PDMS decorated with gold nanoparticles, which were bonded to the PDMS via covalent bond. The analysis (Raman scattering, TEM, and UV-vis) demonstrated the success in chemical derivatization and the homogeneity of the sample. We succeeded to study the reversibility of tunable plasmonic properties by stretching and relaxing the substrate composed. Stretching the elastomeric PDMS film caused the interparticle distance change, consequently optical properties change. The plasmon wavelength linearly decreased from 664 to 591 nm by stretching of 60%.

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- 1) T. P. Otanicar, D. Dejamette, Y. Hewakuruppu, and R. A. Taylor, *Adv. Opt. Photonics* **8**, 541 (2016).
- 2) S. A. Maier, M. L. Brongersma, P. G. Kik, and H. A. Atwater, *Phys. Rev. B* **65**, 193408 (2002).
- 3) W. Rechberger, A. Hohenau, A. Leitner, J. R. Krenn, B. Lamprecht, and F. R. Aussenegg, *Opt. Commun.* **220**, 137 (2003).
- 4) A. García-Martín, D. R. Ward, D. Natelson, and J. C. Cuevas, *Phys. Rev. B* **83**, 193404 (2011).
- 5) P. Nordlander, C. Oubre, E. Prodan, K. Li, and M. I. Stockman, *Nano Lett.* **4**, 899 (2004).
- 6) P. K. Jain, W. Y. Huang, and M. A. El-Sayed, *Nano Lett.* **7**, 2080 (2007).
- 7) Y. Tsuboi, R. Shimizu, T. Shoji, and N. Kitamura, *J. Am. Chem. Soc.* **131**, 12623 (2009).
- 8) O. Zagorodko, J. Spadavecchia, A. Y. Serrano, I. Larroulet, A. Pesquera, A. Zurutuza, R. Boukherroub, and S. Szunerits, *Anal. Chem.* **86**, 11211 (2014).
- 9) Y. Hong, M. Ku, E. Lee, J.-S. Suh, Y.-M. Huh, D. S. Yoon, and J. Yang, *J. Biomed. Opt.* **19**, 051202 (2013).
- 10) A. Barhoumi, D. Zhang, F. Tam, and N. J. Halas, *J. Am. Chem. Soc.* **130**, 5523 (2008).
- 11) S. E. J. Bell and N. M. S. Sirimuthu, *J. Am. Chem. Soc.* **128**, 15580 (2006).
- 12) L. V. Brown, K. Zhao, N. King, H. Sobhani, P. Nordlander, and N. J. Halas, *J. Am. Chem. Soc.* **135**, 3688 (2013).

- 13) J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao, and R. P. Van Duyne, *Nat. Mater.* **7**, 442 (2008).
- 14) Y. Yokota, K. Ueno, and H. Misawa, *Chem. Commun.* **47**, 3505 (2011).
- 15) M. G. Millyard, F. Min Huang, R. White, E. Spigone, J. Kivioja, and J. J. Baumberg, *Appl. Phys. Lett.* **100**, 073101 (2012).
- 16) K. Isozaki, T. Ochiai, T. Taguchi, K. Nittoh, and K. Miki, *Appl. Phys. Lett.* **97**, 221101 (2010).
- 17) G. D. Sui, J. Y. Wang, C. C. Lee, W. X. Lu, S. P. Lee, J. V. Leyton, A. M. Wu, and H. R. Tseng, *Anal. Chem.* **78**, 5543 (2006).
- 18) L. Jayes, A. P. Hard, C. Sene, S. F. Parker, and U. A. Jayasooriya, *Anal. Chem.* **75**, 742 (2003).
- 19) D. K. Cai, A. Neyer, R. Kuckuk, and H. M. Heise, *J. Mol. Struct.* **976**, 274 (2010).
- 20) W. Haiss, N. T. K. Thanh, J. Aveyard, and D. G. Fernig, *Anal. Chem.* **79**, 4215 (2007).
- 21) H. Xu, J. Aizpurua, M. Kall, and P. Apell, *Phys. Rev. E* **62**, 4318 (2000).
- 22) P. L. Stiles, J. A. Dieringer, N. C. Shah, and R. R. Van Duyne, *Annu. Rev. Anal. Chem.* **1**, 601 (2008).
- 23) K. J. Savage, M. M. Hawkeye, R. Esteban, A. G. Borisov, J. Aizpurua, and J. J. Baumberg, *Nature* **491**, 574 (2012).
- 24) B. Lamprecht, G. Schider, R. T. Lechner, H. Ditlbacher, J. R. Krenn, A. Leitner, and F. R. Aussenegg, *Phys. Rev. Lett.* **84**, 4721 (2000).
- 25) N. Féridj, G. Laurent, J. Aubard, G. Lévi, A. Hohenau, J. R. Krenn, and F. R. Aussenegg, *J. Chem. Phys.* **123**, 221103 (2005).
- 26) S. Gwo, H. Y. Chen, M. H. Lin, L. Y. Sun, and X. Q. Li, *Chem. Soc. Rev.* **45**, 5672 (2016).