

F. SUN¹
W. CAI^{1,✉}
Y. LI¹
G. DUAN¹
W.T. NICHOLS²
C. LIANG²
N. KOSHIZAKI²
Q. FANG³
I.W. BOYD³

Laser morphological manipulation of gold nanoparticles periodically arranged on solid supports

¹ Key Laboratory of Materials Physics, Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, 230031, P.R. China

² Nanoarchitectonics Research Center, National Institute of Advanced Industrial Science and Technology, Central 5, 1-1-1 Higashi Tsukuba, Ibaraki 305-8565, Japan

³ Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, UK

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ABSTRACT Laser morphological manipulation has been performed on gold nanoparticles periodically arranged on solid supports by nanosphere lithography. It is shown that third harmonic Nd:YAG pulse laser irradiation (15 mJ/cm² per pulse) leads to an evolution from the initial polycrystalline, triangular shaped particles to spherical single crystalline particles. These morphological changes are accompanied by a significant change in the optical absorption properties of the array. This study demonstrates that laser irradiation is an excellent technique to control the properties of nanostructured materials on solid supports. Further, it is suggested that the selected area treatment possible with the laser is a valuable new technique for designing functional nanomaterials for applications such as high-density data storage devices.

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1 Introduction

Nanoparticles can be periodically arranged on solid supports by nanosphere lithography [1] which is a general, simple, and low-cost method. The acquired two-dimensional nanoparticle arrays have been proposed for applications in, for example, sensors [2, 3], photonics [4, 5], magnetics [6], catalysis [7–9], data storage [10]. The intrinsic properties of such nanostructure arrays are determined by factors such as the size, shape, crystallinity, and composition of the nanoparticles as well as the geometry and interparticle spacing of the array. Recent work has shown that the optical properties of the array are particularly sensitive to the nanoparticle shape [11]. Typically morphologies are controlled during the formation process through the size of the nanospheres in the mask or by angle-controlled deposition in the nanosphere lithography [12]. There has been little work, however, on

direct morphology manipulation of the as-prepared samples. It is expected that the latter would provide a more flexible way to control the morphologies of the nanoparticle arrays and hence their properties.

In general, thermal annealing and laser irradiation are two suitable techniques to manipulate the morphologies of nanoparticles. Thermal annealing has been used to change the shapes of particles in solid matrixes or in arrays on solid supports. Numerous groups have induced a spherical particle morphology of gold [13], silver [11], nickel [9], and germanium [14] particles by heating the corresponding triangular particle arrays at elevated temperatures. This method, however, can only treat the whole sample, but cannot manipulate the particles in a selected area of the sample. In contrast, laser irradiation is able to directly manipulate the morphologies of the nanoparticles in a well-defined area of the sample. It has been shown that

metal particles and their aggregates, dispersed in colloidal solution [15–21], in a glass matrix [22, 23], or disorderly arranged on solid supports [24, 25] can be transformed into smaller or larger, and from non-spherical into spherical shapes, by laser irradiation. However, as far as we know, there have been no reports on laser-induced morphology manipulation of nanoparticle arrays on a substrate.

In this paper, we report the laser morphology manipulation of gold nanoparticle arrays formed by nanosphere lithography [11, 12] and describe their corresponding optical and structural evolution. This study demonstrates that laser irradiation is a good way of controlling the morphology of nanostructured materials and hence their properties, and also may prove to be a valuable new method for the fabrication of functional nanostructures.

2 Experiment

Gold particle arrays were fabricated by nanosphere lithography, as described elsewhere [1, 11]. Briefly, glass substrates were ultrasonically cleaned in acetone and then in ethanol for one hour. Surfactant-free colloidal polystyrene spheres (PS) were purchased from Alfa Aesar. The spheres have a diameter of 1000 nm and size distribution of less than 5%, and are dispersed in water at 2.5 wt. %. Large-scale monolayer colloidal crystals (> 1.0 cm² in diameter) were prepared on the cleaned glass substrate by spin-coating in a custom-built spin-coater. The colloidal monolayer was then lifted off and floated by immersion in wa-

✉ Fax: 86-551-5591434, E-mail: wpcai@issp.ac.cn

ter. In this way, the monolayer could be transferred onto a variety of substrates such as quartz or ITO, as previously described [26–28]. Next, substrates coated with the 2D colloidal crystals were mounted on a sample holder and transferred in an ultra-high vacuum chamber. Gold was thermally evaporated under a base pressure of 10^{-6} Pa and deposited at a rate of ~ 0.2 nm/min. A quartz crystal microbalance was used to monitor the thickness of deposited film. After deposition to a 70 nm thickness, the samples were immersed in methylene chloride under sonication to remove the nanosphere mask leaving a highly ordered array of gold particles on the surface.

The gold nanoparticle array was then irradiated by laser pulses from a Nd:YAG laser operating at 1 Hz at the third harmonic wavelength of 355 nm with a nominal pulse width of 7 ns. The laser pulses were unfocused with an energy density of 15 mJ/cm^2 . Optical properties were measured using a CARY-5E spectrometer (non-polarized light). The incident light beam is perpendicular to the substrate of samples. The morphologies of the arrays were observed by field emission scanning electronic microscopy (FE-SEM, Hitachi 4800S) and atomic force microscopy (AFM). The microstructures of the arrays were examined on a TEM (JEM-200CX) by scraping the particles from the substrates and transferring them to a carbon-coated copper TEM grid.

3 Results

Figure 1 shows an as-prepared Au nanoparticle array on an ITO substrate. As can be seen, the particles are hexagonally arranged with a $P6mm$ symmetry and have triangular cross-section with a height of about 70 nm. Figure 2 shows the morphological evolution versus the number of laser pulses. After about 40 laser pulses, the three sharp corners of each particle become separated from the main body of the particle and three nanogaps of about 30 nm are formed in each particle, as demonstrated in Fig. 2a. This morphology is particularly intriguing because it might be possible for such an array to be used as a substrate for molecular switching devices [29]. As the number of laser pulses is increased to 100,

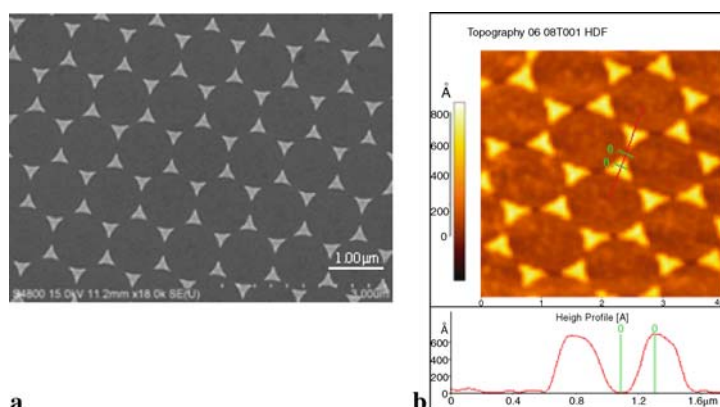


FIGURE 1 FE-SEM (a) and AFM (b) images of a gold particle array fabricated with 1000 nm diameter polystyrene sphere colloidal monolayer before laser irradiation

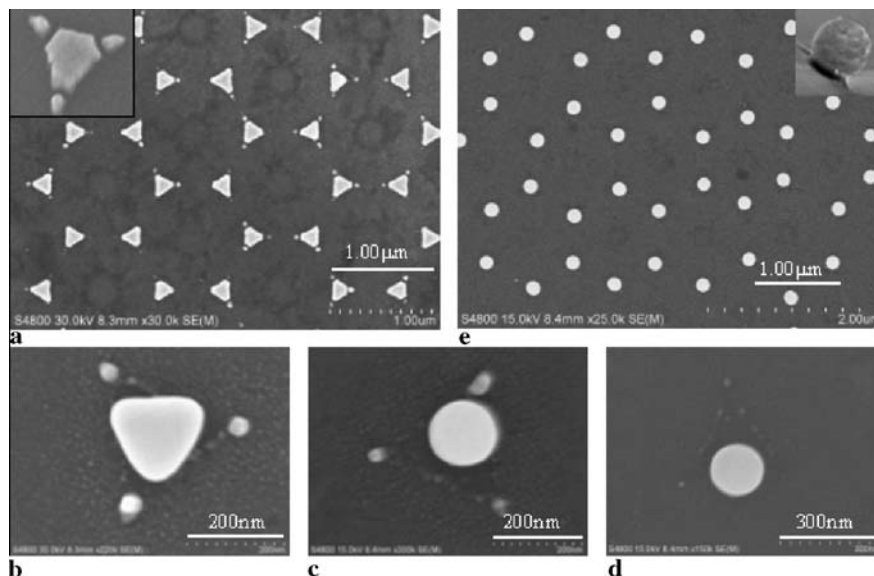


FIGURE 2 Morphology of gold particle arrays on ITO substrates after 355 nm laser irradiation (15 mJ/cm^2 per pulse) for different numbers of pulses. (a): 40 times; (b): 60 times; (c): 80 times; (d): 100 times and (e): 500 times

the nanoparticles at the corners become smaller and almost disappear, while the main body of the particle evolves from a polyhedron to a rounded and finally to a nearly fully circular shape, as illustrated in Fig. 2b–d (from top view). This demonstrates that the morphology of the nanostructured arrays can be manipulated by laser radiation through appropriate selection of the number of pulses. Applying more than 100 laser pulses did not induce any further changes but complete disappearance of the nanoparticles at the corners and the edge sides of the original particles. Figure 2e shows a sample having been irradiated by more than 500 pulses, and its morphology is similar to that of the sample irradiated for about 100 pulses indicating that the particle has reached its equilibrium shape after 100 pulses. Further, tilted

observation has shown that the final particles are nearly spherically shaped, as demonstrated in the inset of Fig. 2e, which is also consistent with Kawasaki et al.'s reports [30]. Similar morphological evolutions were also observed for gold particles on quartz substrates irradiated with 355 and 532 nm laser wavelength pulses, respectively, suggesting a generality to this technique. Finally, it is noted that many of the particles seem to move slightly during irradiation, or the final spherical particles are not exactly located at the centers of the triangles (see Fig. 2c and d).

Transmission electron microscopy (TEM) examination has shown that the individual gold particles in the array are polycrystalline prior to irradiation. Laser irradiation, however, leads to transformation from polycrystalline

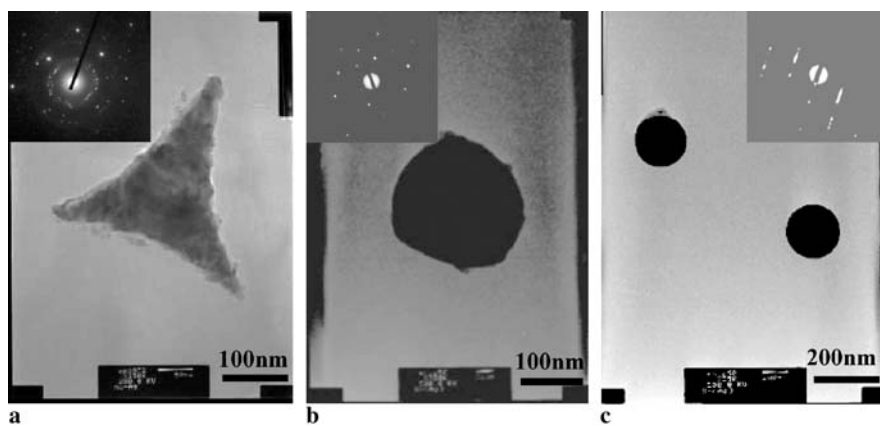


FIGURE 3 TEM images of single gold particles. (a): as-prepared triangular gold particle. (b) and (c): after irradiation, by 100 and 500 laser pulses, respectively. The insets show the corresponding selected-area electron diffraction patterns

to a single crystal structure, as illustrated by selected area diffraction patterns of the single particles scraped from the substrates shown in Fig. 3. It means that laser irradiation not only modify the morphology but also the structure of the particles, indicating that some new properties sensitive to the structure will appear.

Changes in the optical absorption spectra which accompany the particle shape changes for the gold particle arrays on quartz substrates were measured versus the number of laser pulses as shown in Fig. 4. The as-prepared samples show a very broad absorbance peak centered around 680 nm together with a shoulder extending well into the near infrared region, which indicates that the peak is composed of at least two peaks. The peak at 680 nm decreases and disappears as the laser irradiation is in-

creased up to 100 pulses. In addition, after irradiation by about 60 pulses, another peak emerges around 550 nm. After about 100 pulses, the peak shifts to 530 nm. This peak shows very little dependence on the number of laser pulses beyond 100 laser pulses in agreement with the lack of morphology change.

4 Discussion

Now let us take a brief discussion. Although complete understanding of the mechanism for the laser induced morphology evolution needs more and deeper work, here we can explain the results above based on the particle-laser interaction. The particle arrays in this study were prepared by physical vapor deposition on the PS monolayer. It is well known that such vapor deposition usually leads to the

formation of triangular noncompact particles (with a porosity) consisting of ultra-fine nanoparticles or grains, which exhibit polycrystalline electronic diffraction, as seen in Fig. 3a. Obviously, laser irradiation will heat and sinter the triangular particles. After laser irradiation for a short time (e.g., 40 pulses), the main body of a triangular particle will become compact due to heating-induced sintering of ultra-fine nanoparticles. Such compactness will result in contraction of the triangular particles, and the contraction will induce formation of nanogaps, nanoparticles at the corners and the edge sides of the triangular particles, because of the edge effect and the interaction between the particles and the substrate (see Fig. 2). With increase of laser irradiation time, the compact particle will be spheroidized by surface atomic diffusion and the grains in the particles will grow due to heating [31], leading to final spherical particles with single crystal structure in TEM observation, while the small nanoparticles at the corners and edges will get smaller and smaller by local-evaporation and/or ripening process [31], and finally disappear, as seen in Figs. 2 and 3. In addition, since the nanogaps were not always formed at the symmetrical sites of a triangle during initial irradiation, some of the final spherical particles slightly deviate from the centers of the triangles (see Fig. 2e).

According to Jin et al.'s and Kottmann et al.'s work [32–34] and Mie theory [35], the triangularly shaped gold particles should exhibit surface plasmon resonance (SPR) containing one out-plane resonance and two in-plane resonances. The out-plane resonance should be at a shorter wavelength that is too weak to be discerned. One of the in-plane resonances should be around 530 nm and another at a longer wavelength (depending on a morphology factor). In contrast, spherical particles have only a single SPR band at 530 nm. In the spectra shown in Fig. 4, the broad absorption band around 680 nm for the sample before irradiation can be attributed to the superposition of the two bands of the triangular shaped particles. Subsequent irradiation induces a spheroidization of the particles, leading to a decrease and eventual disappearance of the shape-

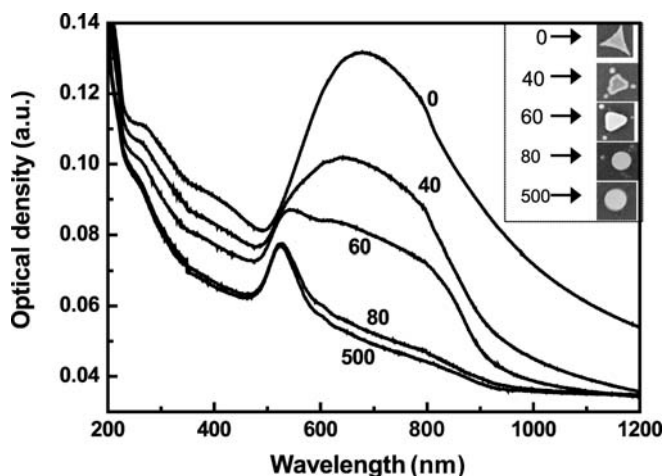


FIGURE 4 Evolution of the optical spectra of gold particle arrays on quartz versus laser irradiation with the indicated number of laser pulses. Inset: the corresponding morphology of individual dots at each pulse number

dependent band around 680 nm, leaving to only the single SPR band at 530 nm corresponding to a spherical particle. The variations of spectra can reflect the morphological changes of the particle arrays and, further, the related information of the laser, which shows the potential application of such method in the fabrications of data storage devices.

5 Conclusions

Morphology manipulation of gold nanoparticle arrays formed by nanosphere lithography was performed by laser irradiation. Laser pulses induced a morphology evolution from triangularly to nearly spherically shaped particles and a structural evolution from poly to single crystal. The corresponding optical absorption spectra were found to also change significantly with particle shape, and thus this material could be used for super-density optical data permanent storage. This study provides not only a good way to control the morphology of nanostructured materials and hence their properties, but also introduces a new tool for the fabrication of specific future nano-devices by area-selective treatment.

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REFERENCES

- J.C. Hultheen, R.P. Van Duyne, *J. Vac. Sci. Technol. A* **13**, 1553 (1995)
- A.J. Haes, W. Paige Hall, L. Chang, W.L. Klein, R.P. Van Duyne, *Nano Lett.* **4**, 1039 (2004)
- A.J. Haes, S.L. Zou, G.C. Schatz, R.P. Van Duyne, *J. Phys. Chem. B* **108**, 6961 (2004)
- C.L. Haynes, A.D. McFarland, L.L. Zhao, R.P. Van Duyne, G.C. Schatz, L. Gunnarsson, J. Prikulis, B. Kasemo, M. Kall, *J. Phys. Chem. B* **107**, 7337 (2003)
- C.L. Haynes, R.P. Van Duyne, *Nano Lett.* **3**, 939 (2003)
- R.M. Winze, M. Kleiber, N. Dix, R. Wiesenanger, *Appl. Phys. A* **63**, 617 (1996)
- Y. Tu, Z.P. Huang, D.Z. Wang, J.G. Wen, Z.F. Ren, *Appl. Phys. Lett.* **80**, 4018 (2002)
- X.D. Wang, C.J. Summers, Z.L. Wang, *Nano Lett.* **4**, 423 (2004)
- K. Kempa, B. Kimball, J. Rybczynski, Z.P. Huang, P.F. Wu, D. Steeves, M. Sennett, M. Giersig, D.V.G.L.N. Rao, D.L. Carnahan, D.Z. Wang, J.Y. Lao, W.Z. Li, Z.F. Ren, *Nano Lett.* **3**, 13 (2003)
- J. Sort, H. Glacynska, U. Ebels, B. Dieny, M. Giersig, J. Rybczynski, *J. Appl. Phys.* **95**, 7516 (2004)
- C.L. Haynes, R.P. Van Duyne, *J. Phys. Chem. B* **105**, 5599 (2001)
- C.L. Haynes, A.D. McFarland, M.T. Smith, J.C. Hultheen, R.P. Van Duyne, *J. Phys. Chem. B* **106**, 1898 (2002)
- F. Burmeister, C. Schafle, P. Leiderer, *Langmuir* **13**, 2983 (1997)
- N. Li, M. Zinke-Allmann, *Jpn. J. Appl. Phys.* **41**, 4626 (2002)
- H. Kurita, A. Takami, S. Koda, *Appl. Phys. Lett.* **72**, 789 (1998)
- J.H. Hodak, A. Henglein, M. Giersig, G.V. Hartland, *J. Phys. Chem. B* **104**, 11 708 (2000)
- S. Link, C. Burda, B. Nikoobakht, M.A. El-Sayed, *J. Phys. Chem. B* **104**, 6152 (2000)
- S. Link, Z.L. Wang, M.A. El-Sayed, *J. Phys. Chem. B* **104**, 7867 (2000)
- H. Fujiwara, S. Yanagida, P.V. Kamat, *J. Phys. Chem. B* **103**, 2589 (1999)
- Y. Takeuchi, T. Ida, K. Kimura, *J. Phys. Chem. B* **101**, 1322 (1997)
- F. Mafune, J.Y. Kohno, Y. Takeda, T. Kondow, *J. Phys. Chem. B* **106**, 8555 (2002)
- A.L. Stepanov, D.E. Hole, A.A. Bukharaev, P.D. Townsend, N.I. Nurgazizov, *Appl. Surf. Sci.* **136**, 298 (1998)
- M. Kaempfe, T. Rainer, K.-J. Berg, G. Seifert, H. Graener, *Appl. Phys. Lett.* **74**, 1200 (1999)
- J. Bosbach, D. Martin, F. Stietz, T. Wenzel, F. Träger, *Eur. Phys. J. D* **9**, 613 (1999)
- T. Wenzel, J. Bosbach, A. Goldmann, F. Stietz, F. Träger, *Appl. Phys. B* **69**, 513 (1999)
- F. Burmeister, C. Schafle, B. Keilhofer, C. Bechinger, J. Boneberg, P. Leiderer, *Adv. Mater.* **10**, 495 (1998)
- F.Q. Sun, W.P. Cai, Y. Li, B.Q. Cao, Y. Lei, L.D. Zhang, *Adv. Funct. Mater.* **14**, 283 (2004)
- F.Q. Sun, W.P. Cai, Y. Li, B.Q. Cao, F. Lu, G.T. Duan, L.D. Zhang, *Adv. Mater.* **16**, 1116 (2004)
- J. Lahann, S. Mitragotri, T.N. Tran, H. Kaido, J. Sundaram, I.S. Choi, S. Hoffer, G.A. Somorjai, R. Langer, *Science* **299**, 371 (2003)
- M. Kawasaki, M. Hori, *J. Phys. Chem. B* **107**, 6760 (2003)
- J.D. Verhoeven, *Fundamentals of Physical Metallurgy* (Wiley, New York, 1975)
- R.C. Jin, Y.W. Cao, C.A. Mirkin, K.L. Kelly, G.C. Schatz, J.G. Zheng, *Science* **294**, 1901 (2001)
- J.P. Kottmann, O.J.F. Martin, *Appl. Phys. B* **73**, 299 (2001)
- J.P. Kottmann, O.J.F. Martin, *Opt. Express* **6**, 213 (2000)
- U. Kreibitz, M. Vollmer, *Optical Properties of Metal Clusters* (Springer, Berlin, 1995)