

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/6763162>

Gold Nanoparticles Propulsion from Surface Fueled by Absorption of Femtosecond Laser Pulse at Their Surface Plasmon Resonance

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · NOVEMBER 2006

Impact Factor: 12.11 · DOI: 10.1021/ja064328p · Source: PubMed

CITATIONS

32

READS

45

3 AUTHORS, INCLUDING:



Wei Qian

Georgia Institute of Technology

33 PUBLICATIONS 3,914 CITATIONS

SEE PROFILE



Mostafa A El-Sayed

Georgia Institute of Technology

675 PUBLICATIONS 53,805 CITATIONS

SEE PROFILE

Gold Nanoparticles Propulsion from Surface Fueled by Absorption of Femtosecond Laser Pulse at Their Surface Plasmon Resonance

Wenyu Huang, Wei Qian, and Mostafa A. El-Sayed*

Laser Dynamics Laboratory, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Received June 19, 2006; E-mail: mostafa.el-sayed@chemistry.gatech.edu

Many biological functions involve motion on the nanometer length scale, which are fueled by biochemical enzymatic catalysis, electrical energy derived from charge gradients, photochemical energy, such as in photosynthesis, and photomechanical energy, such as used in phototaxis. In the field of nanotechnology and in the interest of developing nanomotors, clever demonstrations of motion driven by different mechanisms have recently been demonstrated. Whitesides and co-workers¹ used gases produced in a catalyzed chemical reaction to fuel the autonomous motion. Paxton et al.² used a gold–platinum rod that moves in H_2O_2 solution. The platinum-catalyzed production of O_2 breaks the hydrogen bonding network in H_2O , creating a gradient in the liquid surface tension which induced the motion. Zettl and co-workers³ reported a nanorotor based on converting electric energy into rotational motion of a metal plate attached to a multi-walled carbon nanotube. Chien and co-workers⁴ described a high-speed rotation of nanowires suspended in water between four microelectrodes with applied ac voltages, each out of phase by 90° .

In a recent Science paper,⁵ Habenicht et al. showed that photomelting of nanoprisms on a quartz substrate with nanosecond laser pulses leads to the lifting of the sphere from the substrate with a velocity of 20 m/s. The gain from the surface energy and the change in the center of mass during the melting process fueled the nanoparticle's lift off.

In the present communication, we report on the observation that, when femtosecond laser pulses in resonance with the strong surface plasmon oscillations are used for excitation, the rates of absorption and heating become faster than the rate of melting of the nanoparticle. The nanoprism is observed to fly away while preserving its shape. SEM shows that it has a reduced bisector, and AFM study shows that its thickness is also reduced. Furthermore, it is observed that the sizes of the nanoparticles that are displaced from their original position are smaller than the space they occupied prior to their exposure to the laser pulses. Of the different mechanisms discussed, only the gold atom sublimation mechanism can account for these observations. The gold rapid sublimation could result in a rapid build up of an ultrahigh gold atomic pressure underneath the prism, which enables it to fly. Making few approximations, we calculate an average velocity of 160 m/s for the propelled nanoparticle that is irradiated under laser intensity of 5.1 mJ/cm^2 .

The nanoparticles are prepared on a quartz substrate using nanosphere lithography (NSL).^{6–8} The prepared prismatic nanoparticles have a bisector of 100 nm, a thickness of 34 nm, and a weight of 4 fg each. We placed our sample substrate horizontally with the nanoparticles on the top surface of the substrate. The laser pulse irradiated the sample from the top.

Figure 1A is an SEM image taken in the region irradiated with a laser pulse energy density of 4.1 mJ/cm^2 at 800 nm. At this laser irradiation intensity, the absorbed energy is not sufficient to lift

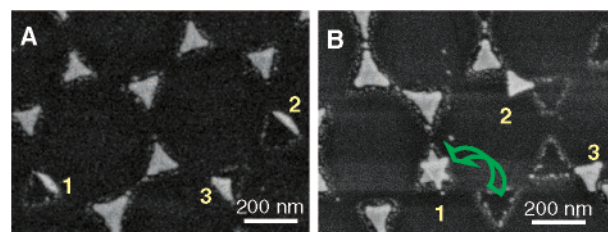


Figure 1. The dependence of the extent of the motion of the nanoprisms on the laser pulse intensity used: (A) 4.1 mJ/cm^2 ; (B) 5.1 mJ/cm^2 .

the particle from the substrate. It “stands up” on their bases. Particles 1 and 2 have enough energy to stand up perpendicular to the substrate plane, while particle 3 is tilted. These particles receive enough energy to release them from the substrate (i.e., to overcome the adhesion energy) but not to enable them to lift off from the substrate.

When the laser intensity is 5.1 mJ/cm^2 at 800 nm, particle 1 in Figure 1B lifts away from its original position, flies a certain distance, and lands on top of another nanoparticle (indicated by the green arrow in Figure 1B). The original position of particle 1 is shown by the dark image decorated by bright small gold clusters. These clusters are formed during the gold deposition step of the NSL technique by scattered gold atoms. From Figure 1B, it is clear that the displaced particles (1, 2, and 3) are smaller in size than the space they occupied before their movement. This could be due to atomic sublimation or partial soft melting of the nanoprism.⁹ The former would decrease the thickness of the particle, while the latter mechanism would increase the particle thickness and decrease the bisector.

Figure 2A shows that a standing prism has a height which is very comparable to the particle bisector. Figure 2B shows that a displaced particle has a smaller thickness than the one that did not leave its position. The AFM measurement of the nonirradiated nanoparticles shows an average thickness of $34.1 \pm 1.1 \text{ nm}$, while the average thickness of the displaced nanoparticles is $30.8 \pm 0.6 \text{ nm}$. These results suggest that displaced particles could involve a mechanism based on rapid atomic sublimation.

There are a number of nonradiative relaxation processes that take place following the surface plasmon excitation of nanoparticles. Following electron–electron relaxation processes, which occur on the femtosecond time scale, electron–phonon processes occur on the 1 ps range in gold nanoparticles.¹⁰ Phonon–phonon processes occur on the hundreds of picosecond time scale.¹¹ As the energy deposition rate increases above the phonon–phonon relaxation rate, melting into spheres could take place. Gold nanorods melt in colloidal solution into spheres at $10 \mu\text{J}$ pulse energies in tens of picosecond.¹²

The most distinct difference between nonresonant nanosecond⁵ and our resonant femtosecond laser irradiation experiments is the rate of energy deposition to the nanoprisms. With nanosecond laser

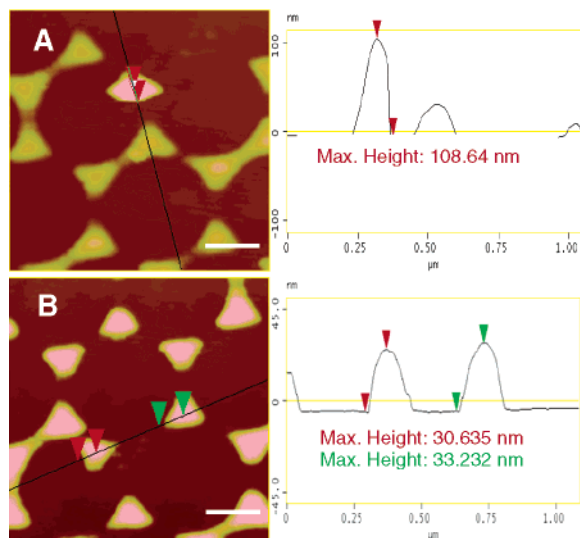


Figure 2. (A) An AFM image of a standing nanoparticle. The height of the standing particle is found to be very close to the value of its bisector. (B) The AFM image of a displaced nanoparticle. Its thickness (indicated by the red cursor) is smaller than the undisplaced one (indicated by the green cursor). The scale bars represent 200 nm.

irradiation, the optical excitation rate was such to allow sufficient time for the lattice to melt. With the femtosecond laser excitation, the melting channel is bypassed and higher energy channel takes over, like multiphoton ionization, evaporation of absorbed water in the prism or the quartz, or gold atom sublimation. Detailed work is now going on to distinguish between these processes as mechanisms for ejecting the nanoprism from the substrate surface. If atomic gold sublimation is indeed the mechanism,¹³ the rapid build up of the pressure underneath the nanoparticle could give the nanoparticle a sudden impulse sufficient for it to break away from the substrate and fly.

To examine gold atomic sublimation mechanism, we calculated the decrease in the nanoprism thickness by atomic sublimation. We observed that, at the observed flying energies, the pulse rate did not change the damage pattern of the nanoprisms on the substrate. This suggests that it is the energy spatial distribution of the first laser pulse that governs the damage pattern on the substrate. From the absorption spectrum and the special energy density distribution of the laser pulse, we calculate that one flying nanoparticle can absorb 7.37×10^{-13} J of energy from 1 fs laser pulse. This energy is sufficient to sublime 1.8×10^{-18} moles of gold atoms, which correspond to a thickness loss of 2.9 nm for the studied nanoparticle (see Supporting Information). This calculated thickness loss is, within experimental error, comparable to the thickness difference observed in the AFM measurement between the displaced and the undisplaced nanoparticles. This agreement could be taken as a support of the gold atomic sublimation mechanism for the flying. However, it is also possible that water desorption or electrostatic forces resulting from multiphoton ionization could be the mechanism of flying.

Irrespective of the mechanism responsible for flying, it is possible to calculate the initial speed of the flying nanoprism that is irradiated under laser intensity of 5.1 mJ/cm^2 with the assumption that the difference between the absorbed energy by any of the standing nanoparticle (that is irradiated under laser intensity of 4.1 mJ/cm^2 and does not fly) shown as particle 1 and 2 in Figure 1A and the one that is able to fly (particle 1 in Figure 1B) is the kinetic energy given to the flying nanoparticle. The energy difference is measured to be $51 \pm 15 \text{ fJ/particle}$ (see Supporting Information). Thus, the

initial flying speed of particle 1 in Figure 1B can be $\sim 160 \text{ m/s}$ ($\sim 360 \text{ miles/h}$).

In summary, the mechanism of the lift of the photoenergized gold nanoprisms from a quartz substrate and their final shape depend on the rate of energy deposition and the wavelength of incident laser. If the rate is relatively slow to allow the nanoprism to melt into spheres (e.g., in the nanosecond pulsed laser nonresonant excitation), the surface energy associated with the shape change and the change in center of gravity lead to the lift off. If the rate of energy deposition is fast (e.g., in the femtosecond pulsed laser resonant excitation), energy channels higher than the melting one can be reached by nonlinear absorption processes resulting in multiphoton ionization or dissociation (sublimation), or inducing water desorption. Rapid heating and evaporation of absorbed water within the prism or in the attached quartz could take place. Of all these mechanisms, only the atomic gold sublimation mechanism could account for the observed reduction in the nanoprism size. The rapid build up of the gold pressure underneath the particle could propel the femtogram nanoprism to fly with a velocity $> 360 \text{ miles/h}$. While the gold sublimation process accounts for the reduction of the nanoprism size, it is still possible that the flying mechanism and the size reduction mechanism involve different processes. Studies to distinguish between the different mechanisms are now in progress.

The observed trajectory of the flying nanoprisms must depend on the anisotropy of the interaction between the nanoprism and the quartz at the interface. This depends on the interfacial structure between the gold nanoprism and the substrate. Particle 1 in Figure 1B must have undergone a large number of rotations and/or jumped to a high level in its flying trajectory as the apparent displaced distance is only $\sim 200 \text{ nm}$, which is too small for an initial velocity of 160 m/s . We are currently carrying out a study to understand the details of this anisotropy, hoping to be able to control the trajectory of the motion.

Acknowledgment. The authors thank Mr. Christopher Tabor for his careful reading of the manuscript. This work is supported by the Division of Material Research of the National Science Foundation (Grant No. 0138391).

Supporting Information Available: Nanoprism array preparation, femtosecond laser irradiation setup, jumping speed measurement, and sublimation thickness calculation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Ismagilov, R. F.; Schwartz, A.; Bowden, N.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 652–654.
- (2) Paxton, W. F.; Kistler, K. C.; Olmeda, C. C.; Sen, A.; St. Angelo, S. K.; Cao, Y. Y.; Mallouk, T. E.; Lammert, P. E.; Crespi, V. H. *J. Am. Chem. Soc.* **2004**, *126*, 13424–13431.
- (3) Fennimore, A. M.; Yuzvinsky, T. D.; Han, W. Q.; Fuhrer, M. S.; Cumings, J.; Zettl, A. *Nature (London)* **2003**, *424*, 408–410.
- (4) Fan, D. L.; Zhu, F. Q.; Cammarata, R. C.; Chien, C. L. *Phys. Rev. Lett.* **2005**, *94*, 247208.
- (5) Habenicht, A.; Olapinski, M.; Burmeister, F.; Leiderer, P.; Boneberg, J. *Science* **2005**, *309*, 2043–2045.
- (6) Huang, W. Y.; Qian, W.; El-Sayed, M. A. *Nano Lett.* **2004**, *4*, 1741–1747.
- (7) Hulteen, J. C.; Van Duyne, R. P. *J. Vac. Sci. Technol. A* **1995**, *13*, 1553–1558.
- (8) Wang, X. D.; Summers, C. J.; Wang, Z. L. *Nano Lett.* **2004**, *4*, 423–426.
- (9) Huang, W. Y.; Qian, W.; El-Sayed, M. A. *J. Appl. Phys.* **2005**, *98*, 114301.
- (10) Link, S.; El-Sayed, M. A. *Annu. Rev. Phys. Chem.* **2003**, *54*, 331–366.
- (11) Link, S.; Hathcock, D. J.; Nikoobakht, B.; El-Sayed, M. A. *Adv. Mater.* **2003**, *15*, 393–396.
- (12) Link, S.; Burda, C.; Nikoobakht, B.; El-Sayed, M. A. *Chem. Phys. Lett.* **1999**, *315*, 12–18.
- (13) Gamaly, E. G.; Rode, A. V.; Luther-Davies, B.; Tikhonchuk, V. T. *Phys. Plasmas* **2002**, *9*, 949–957.

JA064328P