NANO LETTERS

Letter

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Electron Beam Manipulation of Nanoparticles

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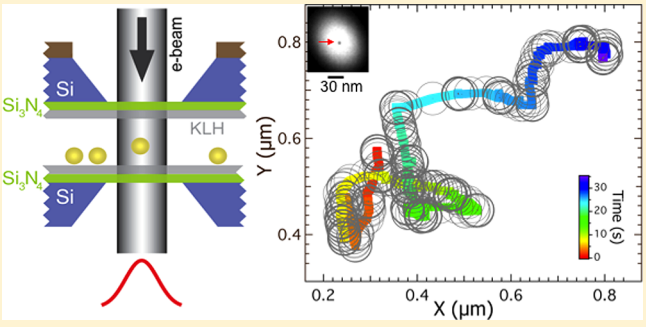
Supporting Information

ABSTRACT: We report on electron beam manipulation and simultaneous transmission electron microscopy imaging of gold nanoparticle movements in an environmental cell. Nanoparticles are trapped with the beam and move dynamically toward the location with higher electron density. Their global movements follow the beam positions. Analysis on the trajectories of nanoparticle movements inside the beam reveals a trapping force in the piconewton range at the electron density gradient of 10^3–10^4 $(e{\cdot}nm^{-2}{\cdot}s^{-1}){\cdot}nm^{-1}$. Multiple nanoparticles can also be trapped with the beam. By rapidly converging the beam, we further can "collect" nanoparticles on the membrane surface and assemble them into a cluster.



KEYWORDS: *Electron beam trap, nanoscale manipulation, liquid cell, TEM, nanoparticle interaction, directed assembly*

There have been significant interests in the manipulation of nanoscale objects driven by the desire to develop novel nanotechnological tools or devices. For example, it is often required to direct the movement of nanoparticles in order to build useful materials architectures or to fabricate functional devices using nanoparticles as building blocks. The coupling of light into a confined structure, which produces forces from an enhanced local electrical field, is often used as "optical tweezers" to trap biological materials[1−3] or particles of submicrometer sizes.[4] However, optical trapping of nanometer size objects is challenging because the forces are often too small when the sizes of the objects are reduced to the nanometer scale.[5,6] As an alternative to particle manipulation using optical forces one can envision electrons with much smaller wavelength as a potential nanoscale counterpart. Here, we show using an electron beam to trap gold nanoparticles and direct their movements over a membrane surface inside an environmental cell. Since an electron beam, such as the beam source of a transmission electron microscope (TEM) or a scanning electron microscope (SEM), can be focused into fine sizes (i.e., in subnanometer sizes) and easily operated to scan a surface up to millimeters, the ability to manipulate nanoparticles using an electron beam opens the opportunity to create a versatile tool for nanoscale science and technology.

The environmental cell used for this study contains two liquid reservoirs for liquid sample loading and an electron transparent silicon nitride window allowing the liquid sample to be examined under a TEM (details on the fabrication process are available in our previous publications[7,8]). We first render the surface of the membranes hydrophilic by glow discharge and then load a droplet of aqueous solution (∼50 nanoliters) with 1:3 dilution of the stock keyhole limpet hemocyanin (KLH) proteins (∼10 $mg{\cdot}mL^{-1}$) into one of the reservoirs and the liquid is drawn into the cell by capillary force. Subsequently, a droplet of an aqueous solution of 10 nm gold nanoparticles (used as purchased) is loaded into the cell. Previous studies have shown that nanoparticles in solution can weakly bound near the substrate surface due to a potential for attraction between the surface and the particles.[9] In this case, KLH proteins attach to the membrane surface of the environmental cell thus prevent nanoparticles from adhering to the surface. The liquid environmental cell is then sealed and loaded into a TEM. Under the TEM operated at 120 kV, we image the liquid layer sandwiched between two silicon nitride membranes. We first rapidly change the density of the electron beam casted onto the liquid film. As the consequences, the liquid film breaks and retracts which leaves gold nanoparticles loosely sitting on the wet surface. The electron beam is then focused into 50–200 nm in diameter, which roughly forms a Gaussian beam with an average electron flux of $\sim 10^5$ $e{\cdot}nm^{-2}{\cdot}s^{-1}$ (a uniform current density can be achieved at the beam center, see Figure S1, Supporting Information). The electron beam passes through the membrane window and drives the nanoparticles within the beam move between two membranes (see the schematic in Figure 1A). Movements of the nanoparticle appear to be bouncing over the membrane surface into the space filled with

Received: July 27, 2012
Revised: October 2, 2012
Published: October 4, 2012

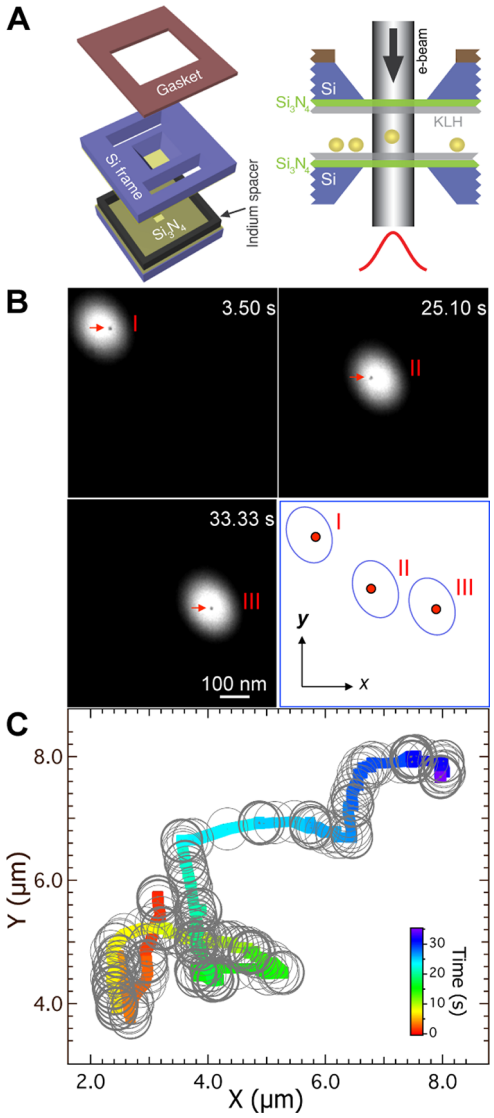


Figure 1. Manipulation of gold nanoparticle movements in a liquid cell using an electron beam. (A) Schematic of experimental set up, where an electron beam passes through the silicon nitride window and traps gold nanoparticles inside the beam. (B) Sequential images showing the global movement of a gold nanoparticle follows the movement of the beam. The location of the gold nanoparticle inside the beam is highlighted by arrows. The displacements of the beam and the nanoparticle are shown in the bottom right by overlapping their positions in one picture. (C) Trajectories of the electron beam movement and the global movement of the gold nanoparticle.

water vapor inside the environmental cell. We record the movements of gold nanoparticles inside the cell at a rate of 30 frames per second and track the trajectories of their two-dimensional movements inside the electron beam.

We control the movements of the electron beam at approximately 10 nm per second (faster or slower movement of the beam is possible). Then, the gold nanoparticle trapped inside the beam is dragged along with the beam while moving chaotically inside the beam (Movie S1, Supporting Information). Gold nanoparticles are mostly close to one of the two membranes at the window. Figure 1B shows the sequential images of a gold nanoparticle trapped inside the beam and its global movements following the movements of the beam. Although the positions of the gold nanoparticle inside the beam vary with time, the average displacement of the nanoparticle follows the electron beam position (Figure 1C).

We park the electron beam on the window for an extended period of time, so that motion of the gold nanoparticle trapped inside the beam can reach quasi equilibrium. We plot the two-dimensional movements of the nanoparticle within the beam in Figure 2, parts A and B (also see Movie S2, Supporting

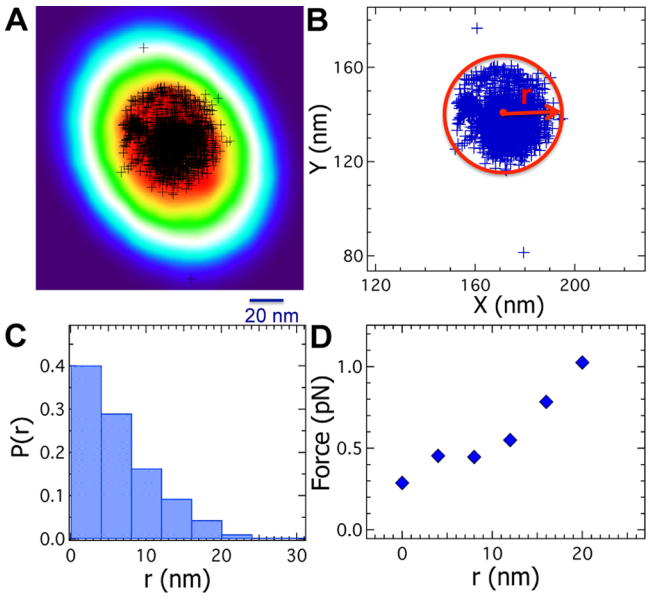


Figure 2. Estimation of the trapping force. (A) Two-dimensional projection of the gold nanoparticles inside the beam over an extended period of time. Positions of the gold nanoparticles are highlighted in black cross. Color gradient map shows the intensity of the beam. (B) Statistic distribution of the gold nanoparticle movements corresponding to part A. (C) Probability distribution of the displacements of the gold nanoparticle relative to the beam center. (D) Trapping force as a function of the displacement from the beam center.

Information). From experimental results shown in Figure 2B, we calculate the probable distribution of the nanoparticle displacement and the results are plotted in Figure 2C. It shows that nanoparticles are moving toward the beam center. Since motion of the nanoparticle is consistent along the trajectories of the nanoparticle movements and the movements reach a quasi equilibrium, Boltzmann's distribution function is applied as a simple estimate of the trapping force responsible for the lateral movements of the nanoparticle toward beam center. Considering movement of the nanoparticles is not completely Brownian (i.e., Brownian motion from collisions with the water molecules) and can be affected by the electron beam, we have estimated the electron beam scattering effects on the nanoparticle movements. The results show that electron beam can indeed contribute by direct momentum transfer to the nanoparticle movements especially the vigorous bouncing motion of the nanoparticle in the vertical direction. However, forces resulting from the electron beam scattering turn out to be small and negligible (i.e., 10^{-3} pN at the maximum momentum transfer; see Supporting Information). At the quasiequilibrium condition, the probability distribution $P(x,y)$ of the nanoparticle movements can be expressed as

$$P(x, y) = A_0 e^{-\phi(x,y)/k_B T} \quad (1)$$

dx.doi.org/10.1021/nl302788g | Nano Lett. 2012, 12, 5644−5648

where $\phi(x,y)$ is the potential energy, k_B is Boltzmann's constant, T is temperature, and A_0 is a constant. Therefore, $\phi(x,y)$ can be written as

$$\phi(x, y) = -k_B T \ln[P(x, y)/A_0] = -k_B T[\ln P(x, y) - \ln A_0] \quad (2)$$

The spatial derivative of the potential energy gives the trapping force $\vec{F}(r)$:

$$\vec{F} = -\frac{d\phi}{dr}\hat{r} = k_B T \frac{1}{P(r)}\frac{dP(r)}{dr}\hat{r} \quad (3)$$

where $d\hat{r} = d\hat{x} + d\hat{y}$. Using eq 3, we have estimated the trapping force as a function of the displacement, see Figure 2D.

It is noted that the trapping force is dependent on the beam configuration. Trapping is less stable in the center of the beam where the electron flux gradient is the least, while the particle experiences strong pulling toward the center in the outer region with stronger force at the edge where there is a higher gradient of the beam. Figure S1, Supporting Information, shows the configuration of the beam for trapping of nanoparticles, where the beam is more uniform at the center and it is roughly Gaussian at the outer region. A trapping force in the piconewton range is achieved at the current beam condition.

We have considered the mechanisms of the electron beam trapping. Forces from our observations might be possible when a negative pressure within the illuminated area is created from the interaction of the electron beam with the wet surface. For example, a negative pressure can result from water being vaporized more rapidly under the beam than the surrounding area. We have observed that the water pattern on the illuminated membrane surface changes under the beam and it is different from those areas without the long exposure (Figure S2, Supporting Information). Considering previous reports that nanoparticles move under the electron beam where it is unlikely a negative pressure is involved,[10,11] we have also considered other factors, such as electron beam scattering, static charge-electron beam interaction, thermophoresis,[12,13] etc. (Supporting Information). According to our estimation, the contributions from these individual factors are orders of magnitude smaller than the experimentally observed force, or they can have the opposite sign to the observed force (e.g., thermophoresis effect). More generic electron beam and matter interactions need to be further explored.

In addition to trapping of a single nanoparticle, multiple gold nanoparticles can also be trapped inside an electron beam and their ensemble displacement follows the movement of the beam. Figure 3A shows a pair of gold nanoparticles and a group of three nanoparticles trapped inside the beam. Their relative positions inside the beam frequently change (also see Movies S3 and S4, Supporting Information). We track the positions of each individual nanoparticle. If we treat one nanoparticle as the center, the relative displacement of other particle can be plotted. Figure 3B shows the center-to-center distance between two nanoparticles in a nanoparticle pair as a function of time. The statistical distribution of the interparticle displacement projected in the viewing plane is plotted in Figure 3C. At the quasi equilibrium condition, forces between the two nanoparticles can be estimated using eq 3. Such estimate gives an attractive force of sub-pN range when the two nanoparticles are close each other (i.e., 1−12 nm) (Figure 3D).

Interaction between nanoparticles can be complex and diverse, for example, it may include van der Waals' forces,

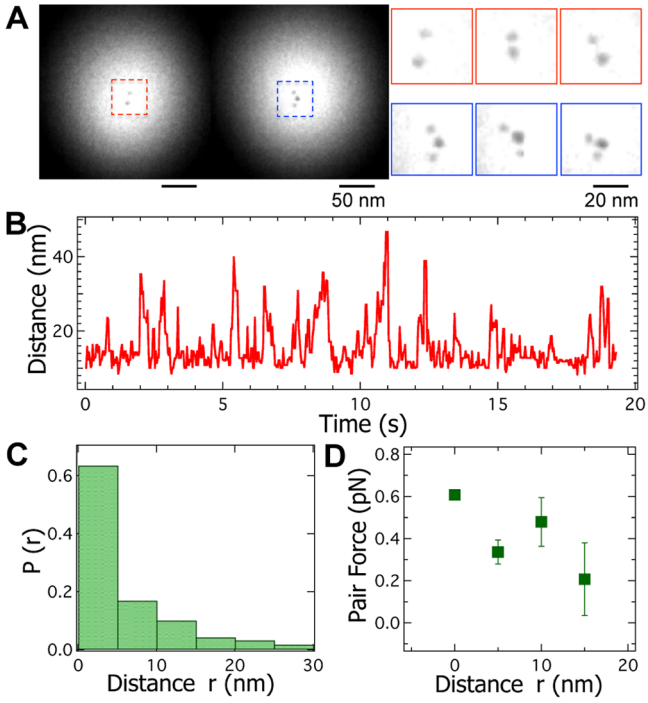


Figure 3. Trapping of multiple gold nanoparticles using the electron beam. (A) TEM images show two or three gold nanoparticles are trapped inside the beam. The magnified sequential images indicate the relative positions of the gold nanoparticles inside the beam. (B) The center-to-center distance between the two nanoparticles in part A left as a function of time. (C) Statistic distribution of the displacements between the two nanoparticles (interparticle distance) corresponding to part B. (D) Forces between the two nanoparticles as a function of the interparticle distance. Calculation error bars corresponding to the limited number of sampling are shown in the plot.

hydrophobic attractions, and charge−charge interactions, dipolar interactions, etc.[14−17] And, the electrostatic dipolar interactions have been observed among other metallic nanoparticles.[18] We noted that although there is an attractive force between gold nanoparticles, nanoparticles are bouncing vigorously and are not aggregated during an extended period of time. It is likely that the strong scattering effect from the electron beam prevents nanoparticles from attaching together. In addition, the citric acid ligands may also play a role to passivize the nanoparticle surface.

The movements of the gold nanoparticles respond to the changes of the electron beam flux. When the electron beam flux is low (<10 e·nm^2·s^{-1}), no obvious movement of the gold nanoparticles is observed. As the electron beam flux increases (diameter of the beam decreases), gold nanoparticles move toward the electron beam center with the shrinking electron beam size. Figure 4A shows trajectories of a few selected nanoparticles' movements as the beam size is reduced, where changes in the beam size are presented by the color gradient (nanoparticles are highlighted in Figure S3, Supporting Information). It is interesting that trajectories of the nanoparticle movements show that at an early stage all the nanoparticles move toward to a location away from the beam center (also see Movie S5, Supporting Information for details). This is likely due to the nonuniformity of the electron beam, see the snap shots of the electron beam density maps along the trajectory in Figure 4B. Nanoparticles move following the density gradient of the electron beam toward the location with

dx.doi.org/10.1021/nl302788g | Nano Lett. 2012, 12, 5644−5648

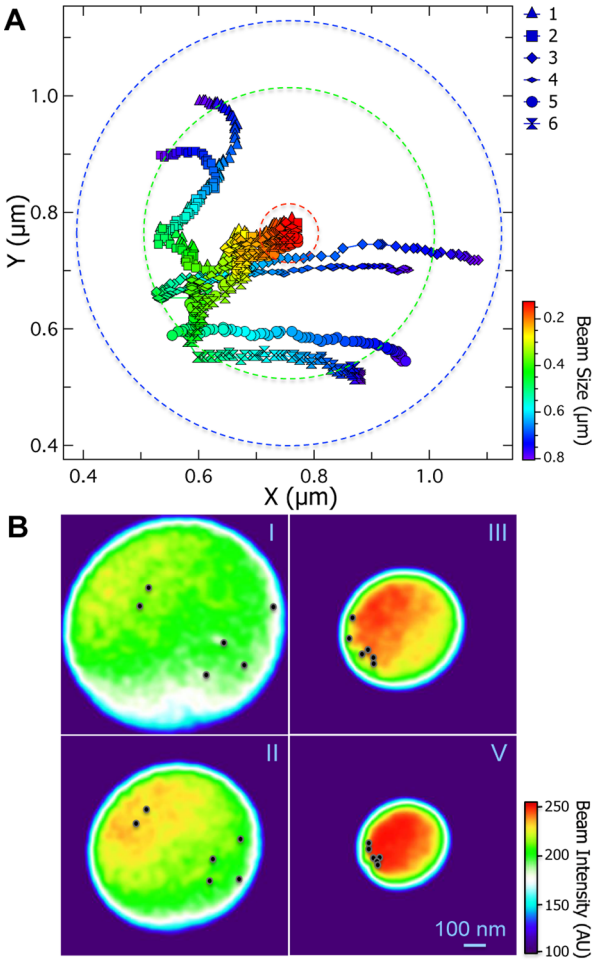


Figure 4. Assembly of gold nanoparticles on the membrane surface by rapid changing of the electron beam size. (A) Trajectories of the selected gold nanoparticles. Color corresponds to the beam size. (B) Color maps of the electron beam show the electron beam density variations inside the beam. Selected nanoparticles in part A are highlighted in black dots.

higher electron density. Movements of nanoparticles along the surface are smooth without significant scattering motion. It might be possible that nanoparticles are rolling on the surface[19] (Figure S4, Supporting Information). When the size of the electron beam changes suddenly, directions of the nanoparticle movements also change rapidly (Movie S5, Supporting Information). These results strongly suggest that electron beam can be used as a highly effective tool to manipulate nanoparticles at will. As the electron beam size is reduced to 50 nm, all the nanoparticles are collected and assembled into a cluster (Figure S3, Supporting Information). The cluster of aggregated nanoparticles can be subsequently directed on the surface by the electron beam. The ability to assemble nanoparticles on the surface opens the opportunity of using electron beam to clean a surface, i.e., to reduce toxic nanoparticles, which is hard to achieve by other approaches.

In summary, we have demonstrated manipulation of gold nanoparticles movements in an environmental cell using an electron beam. Nanoparticles are trapped inside the beam and their global movements follow the movement of the beam. Forces in the piconewton range have been achieved at the electron beam flux gradient of $\sim 10^3-10^4$ $(e\cdot nm^{-2}\cdot s^{-1})\cdot nm^{-1}$. Using the electron beam, we can also trap multiple nanoparticles and assemble nanoparticles on the surface. Manipulation of the nanoparticles using the electron beam can be easily combined with the conventional electron microscopy techniques, so that both manipulation and directly imaging the nanoparticles of interest can be achieved. The integrated platform based on nanofluidic environmental cell inside the electron microscope with the ability to manipulate nanometer size objects using an electron beam tweezing opens the possibilities of developing new force spectroscopy where nanostructures can be assembled one nanoparticle at a time. Since its invention, optical tweezers have transformed our understanding of forces involved in biological processes.[20−22] We believe an electron beam trap that can manipulate nanoparticles and probe the interaction forces between nanoparticles as what we have demonstrated here can bring profound impact in physical and chemical sciences.

■ ASSOCIATED CONTENT

Supporting Information

Materials and methods, supporting text, additional figures (Figure S1−S5), and supporting movies (Movies S1−S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

‡These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

H.Z. thanks Prof. Paul A. Alivisatos and Prof. David Chandler at the University of California, Berkeley for helpful discussions. She also thanks the support of US DOE Office of Science Early Career Research Program.

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