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Using molecular tweezers to move and image nanoparticles

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The ability to manipulate nanoparticles is significant in nanoscale science and technology. As sizes of the objects scale down to the sub-10 nm regime, it imposes a great challenge for the conventional optical tweezers. There has been much effort to explore alternative manipulation methods including using nanostructures, electron beams, scanning probes, *etc.* In this paper, an overview of the latest advances in trapping and manipulation of nanoparticles with a focus on the emergent electron tweezers is provided.

1 Introduction

Trapping and manipulation of nanoscale objects have been of significant interest across different scientific fields, especially as nanoparticles are playing an increasingly important role in bio-imaging, quantum optics and energy applications. Optical tweezers are excellent tools for immobilizing and transporting particles with sizes ranging from several micrometers to a few hundred nanometers, where a highly focused laser beam is used to provide a force (typically on the order of pN) due to the refractive index mismatch between the particle and its medium. Optical trapping was pioneered by Ashkin in 1970.[1] Ashkin and colleagues demonstrated the first optical tweezers in 1986 using a tightly focused beam of light capable of holding microscopic particles stable in three dimensions.[2] Since then, optical tweezers have been extensively utilized for applications in cellular and molecular biology as well as physical sciences and technologies. For example, in biosciences optical tweezers are used to trap bacteria, tobacco mosaic virus particles,[3] living cells[4] as well as in noninvasive manipulation of organelles and filaments within living cells.[5] The manipulation of smaller biomolecules (*e.g.* DNA, actin) has been achieved by tethering the molecular species to micrometer dielectric beads that can be stably trapped and manipulated.[6–9] In physics, the optical trapping forces have been applied to measure the displacements of particles with nanometer precision, which is crucial for the study of colloidal and condensed matter systems.[10–13] Translation, rotation and assembly of larger nanowires and nanoparticles down to tens of nanometers have also been reported.[14–21] Optical tweezers have further enabled cooling and trapping of neutral atoms by utilizing resonant laser light and a magnetic gradient trap.[22]

Although optical tweezers have advanced profoundly, stable trapping of objects in the sub-10 nm range remains a great challenge. It is mainly attributed to two aspects. First, due to the diffraction limit, prohibitively high laser power is needed to overcome the Brownian motion. Second, there is a lack of real-time techniques for detecting the trapping events of such small particles, especially nonfluorescent nanoparticles. The effects of diffraction limit on optical trapping have been discussed extensively previously.[2,17,23,24] Since an optical beam can only be focused to a much larger spot than the nanoparticles, the trap is loose. In addition, the optical trapping force is proportional to the intensity and gradient. In the Rayleigh regime where the particle size is smaller than the wavelength, the optical trapping force on a spherical nanoparticle scales with the volume of the particle. Therefore, for trapping of small nanoparticles, the trapping force is too small to be effective. In order to increase the trapping force, illumination intensity needs to be

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increased.[25,26] According to Ashkin's prediction, a 1.5 W laser beam is necessary to trap 9 nm or 14 nm nanoparticles depending on the particles refractive index.[2] However, nanoparticles are prone to be destroyed under such a high energy laser.

Recently nano-optical tweezers have attracted a lot of attention since they can overcome the above two difficulties and have the potential to scale optical trapping down to the sub-10 nm regime.[25,28,32–34] In nano-optical tweezing, nanostructures such as thin metal films, sharp metal tips and so on are used to localize and enhance the electric field in their near-field, which is much smaller than the diffraction limit.[35–38] Consequently, these nanostructures generate a much larger gradient force than the conventional far-field optical trapping with a similar light source. A large variety of nanostructures have been demonstrated for trapping of nano-objects in the past few years. For instance, studies have shown that using plasmonic dipole antennas, the local electric field within the gap can be enhanced significantly (*i.e.*, ~2 orders of magnitude).[39,40] Trapping and sensing 10 nm gold nanoparticles using such plasmonic dipole antennas have been achieved.[27,41,42] Trapping of proteins[43] or polystyrene[44] nanospheres using nano-optical tweezers has also been reported. It has also been demonstrated theoretically that a coaxial plasmonic aperture composed of a dielectric ring embedded in a noble metal is capable of stably trapping sub-10 nm dielectric nanoparticles with a trapping power below 20 mW.[28] Using surface plasmons to trap or immobilize nanoscale objects on a substrate is a powerful manipulation strategy. With the fast expanding field of plasmonics, there is no doubt that nano-optical tweezers will continue to grow and flourish. It may not take long for the three dimensional tweezing of nano-objects to become reality. Excellent reviews on the nano-optical trapping have been given (Fig. 1).[45,46]

Another emergent powerful nanoparticle manipulation means is to use an electron beam.[29,30,47] The electron beam with much smaller wavelength naturally eliminates the diffraction limit that optical tweezers have encountered. 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 down to the sub-nanometer range and can scan over a large surface up to the millimeter scale. Nanoparticles can also be visualized while they are trapped or transported. For example, it has been demonstrated that metal nanoparticles of 10 nm or smaller can be trapped or moved over large distances using an electron beam and simultaneous imaging of the nanoparticles has been achieved.[29] The ability to manipulate nanoparticles using an electron beam has opened a new toolbox for nanoscale science and technology.

Other manipulation methods that are capable of moving sub-10 nm nanoparticles include scanning tunneling microscopy (STM),[48] atomic force microscopy (AFM),[31,49,50] *etc.* Recent

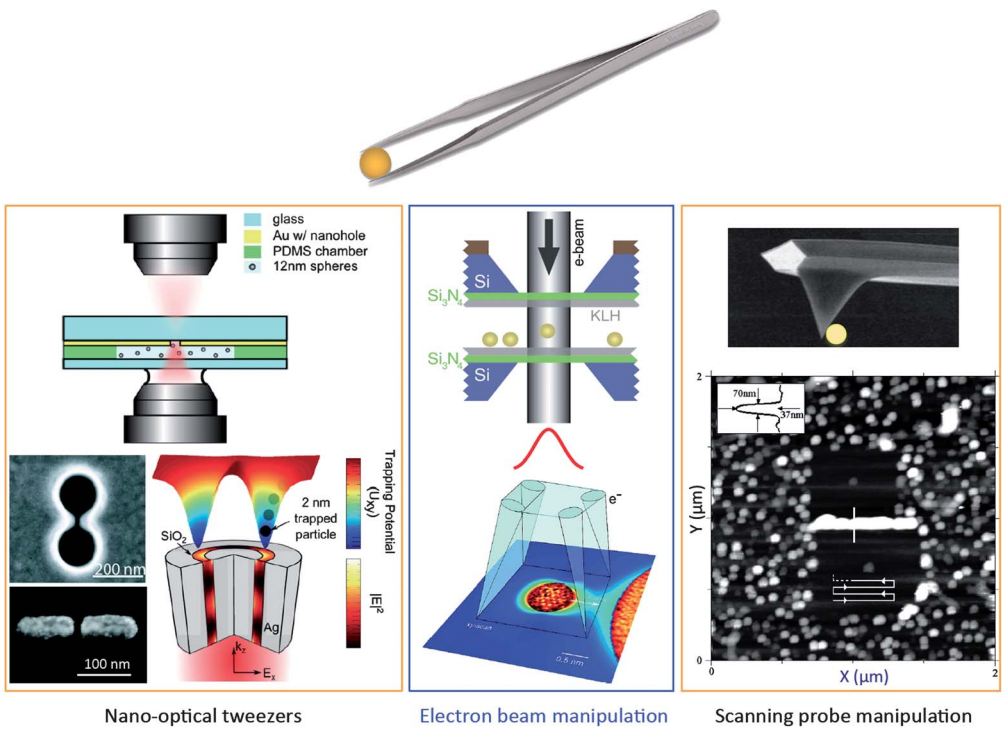

Fig. 1 Recent technical advances in manipulation of nanoparticles. Highlighted are a few examples within the scope of three different approaches. (I) Nano-optical tweezers: schematic of an experimental set-up[25] and some reported nanostructures that were used for trapping of nanoparticles, such as a double-hole on an Au film with 30 nm separation,[25] a nanofabricated antenna with a 10 nm gap,[27] the coaxial plasmonic aperture with a dielectric ring embedded in a noble metal and the trapping potential;[28] (II) electron beam manipulation: electron beam trapping and moving gold nanoparticles in an environmental cell (top)[29] and pushing or pulling gold nanoparticles using swift electrons (bottom);[30] (III) scanning nanoprobe manipulation: using an AFM tip to handle individual Si nanoparticles and create a chain of nanoparticles.[31]

studies have shown that 5 nm silicon nanocrystals can be positioned with 10 nm precision using AFM.[31] The advantage of AFM manipulation over STM manipulation is that nano-objects can be moved on any kind of surface no matter it is conductive or not.

This paper reviews the recent efforts on the manipulation of nanoparticles using an electron beam. Although electron tweezing is a newly discovered technique and there are only a limited number of studies, the achievements have surpassed what optical tweezers have made over the years in trapping on the sub-10 nm scale. The goal of this paper is to introduce readers to the powerful electron tweezing capability and hopefully to inspire more theoretical and experimental studies to advance this technique.

2 Manipulation of nanoparticles with an electron beam

So far, most work on the electron beam trapping and moving of nanoparticles has been conducted with a TEM. The high energy electron beam (100–200 keV) can be focused into a sub-nm spot or a Gaussian beam of tens or hundreds of nanometers. Therefore, the electron beam can be used not only to manipulate single nanoparticles but also to assemble nanoparticles on a surface. Trapping and imaging of nanoparticles with sizes ranging from hundreds of nanometers to sub-10 nm or single molecules have been achieved. Due to the high vacuum environment inside the microscope, dry samples are often required. For nanoparticles sitting on a dry surface, their movements can be limited because of the strong interaction with the substrate. However, this challenge has been overcome by manipulating nanoparticles in fluids using an environment cell.[29] Here, the recent advancements in electron beam manipulation of nanoparticles are reviewed. Various effects that may contribute to the trapping forces are also discussed. At the end, conclusion and further remarks on the electron tweezers are included.

Trapping and tracking of Al nanoparticles in molten alloy

Oleshko and Howe reported the early work on electron tweezers.[47] They showed that 20–300 nm solid aluminum particles inside a molten Al–Si eutectic alloy can be trapped and steered using a focused electron beam inside a TEM. The samples were prepared by placing 20–400 nm Al–11.6 at% Si alloy particles on a TEM grid. At 577–581 °C, the alloy particles are partially molten and form a solid–liquid two-phase mixture. Al-rich solid nanospheres of 20–300 nm in diameter can be generated, trapped and steered inside the submicron-sized molten binary alloy particle using a focused electron beam. Nanospheres show irregular motion within the trap. Typically the nanospheres could be transferred using beam shift, tilting and/or shifting of the microscope stage across a distance of 40–100 nm, which is limited by the available internal volume within the molten particle in chosen directions (Fig. 2). However, particles below 20 nm in diameter become unstable and they melt and then disappear in the molten alloy.

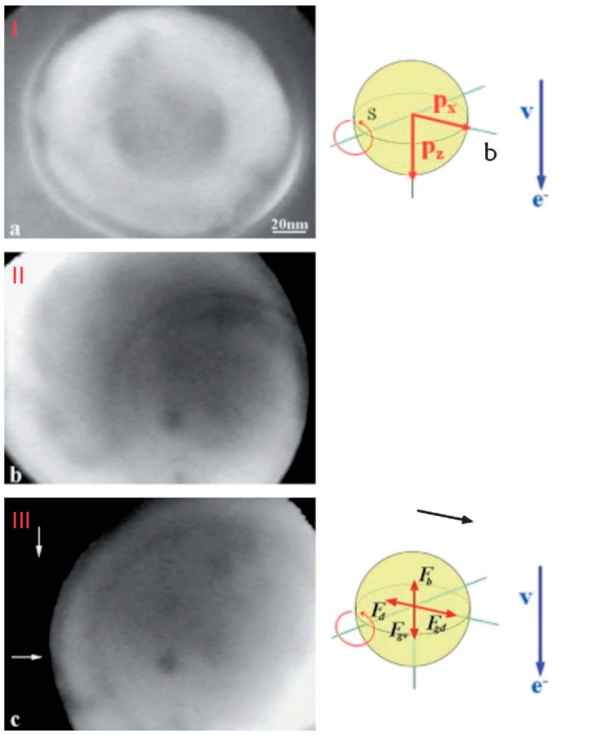

Fig. 2 *In situ* EFTEM, 15 eV energy loss, a 6 eV window. (I) Electron beam-assisted generation of a 70 nm-diameter solid particle inside a partially molten Al–11.6 at % Si sphere surrounded by a 10 nm thick oxide shell. (b and c) Steering of a solid particle by translating the beam and/or moving the microscope stage in directions shown by arrows. The video frame (II) is separated from the frame (III) by 17 s. The upper inset in (a) describes transfer of a momentum $p = (p_x, p_z)$ of a fast electron with impact parameter b and velocity v to a polarizable particle *via* electromagnetic interaction.[16] Here S is a surface embedding the particle. The bottom inset in (c) schematically describes forces exerted on the trapped particle. F_{gv}, F_d, F_b and F_{gd} denote gravitational, drag, buoyant and gradient forces, respectively. The black arrow indicates the direction of the translation of the beam.

This work has demonstrated that it is possible to develop electron tweezers for manipulation of nanoparticles in three-dimensional space, although trapping of smaller nanoparticles is desired. The origin of the trapping force was considered to be similar to optical trapping of dielectric spheres in liquids. The authors proposed that the complex refractive index and density of the solid crystalline nanosphere are slightly higher than the refractive index of the liquid alloy, the aluminum spheres can act as weak positive lens. Forces generated from the elastic collisions by the incident electrons were estimated based on the maximum momentum transferred to the particle[29,47,51] as discussed below.

During an elastic collision between an electron and a particle, the maximum energy transferable from the electron to the particle can be estimated by the following:

$$E_{max} = 4m_eME/(m_e + M)^2 \quad (1)$$

where m_e and M are the mass of the electron and the nanoparticle, respectively, and E is the electron energy. The maximum momentum (P) transferred to the particle from an electron can be calculated by:

$$P = \sqrt{2ME_{\max}} = 2p_e M/m_e + M \approx 2p_e \quad (2)$$

here, $p_e = \sqrt{2m_e E}$ is the electron momentum. The number of incident electrons on the particle can be estimated by $n_e = J_e \cdot \pi r^2$ (in number of electrons per second), where J_e is the current density, r is the radius of the particle. Therefore, the maximum momentum transferred to the particle is estimated by

$$\Delta P_e = P \cdot n_e \quad (3)$$

Although the momentum transferred by a single electron (200 keV) is small ($P \sim 10^{-22}$ N s), the number of incident electrons on the nanosphere per unit time is enormous ($n_e \sim 10^{10}$ e·s^{-1} the projected area of the nanosphere). Forces (F) due to the momentum transfer from the electron beam can be estimated by $F = \Delta P_e/t$ and $F \sim 2$–3 pN was achieved for trapping of 150 nm particles. This force is the same order of magnitude as those in optical trapping.

According to the above trapping mechanisms, the critical issue arises as sizes of the nanoparticles shrink to the sub-10 nm range. Since the total number of incident electrons on the small nanoparticles drops significantly with size ($F \propto r^2$), forces from the electron beam momentum transfer become too small to be effective (*e.g.* $F \sim 10^{-3}$ pN for 10 nm nanoparticles).

Moving nanoparticles with swift electrons

Batson *et al.* reported using swift electrons to move 1–2 nm gold nanoparticles on an amorphous carbon film.[30,52,53] The electron beam with a 120 keV acceleration voltage is tightly focused into a diameter of 0.8 Å and scans over an area larger than the nanoparticle itself (Fig. 3A). At the beginning of each line scan, the electron beam is stopped for a short period of time (positioned close to the nanoparticle) polarizing the nanoparticle. Within the scanned area, small nanoparticles (1–2 nm) are moved by the electron beam while larger particles (>4 nm) are stationary.

Movements of the nanoparticles induced by forces from the swift electron beam are complex. They are highly dependent on the transversal distance between the nanoparticle and the beam, which is defined as the impact factor. When the electron beam is positioned close to the nanoparticle (with a small impact factor, *e.g.* ~1 nm), the particle is pushed away from the beam. When the beam is parked far from the particle (with a large impact factor, *e.g.* 4.5 nm), the particle is pulled towards the beam (Fig. 3B). In addition, the position of the beam also affects the interaction between nanoparticles. For example, when the electron beam is positioned close to a nanoparticle pair, the two particles coalesce with the smaller nanoparticle moving towards the larger nanoparticle. However, the electron beam can also drive the two nanoparticles apart if the beam passes through between them.

Forces generated by the fast passing swift electron beam were attributed to the plasmonic effects.[52] Charged particles travelling in the proximity of metallic particles produce longitudinal and transverse forces as the result of the interaction between the oscillating surface charges (surface plasmons) and the incident charges. Nature of the localized surface plasmons depends strongly on the impact factor. A rich variety of forces can be generated depending on the different localized modes excited by the electron beam. Co-workers of Batson calculated the forces by evaluating the total fields on the surface of small nanoparticles (1 nm) imposed by the electron beam. Movements of a small particle in the presence of the passing electrons were attributed to the change in electron momentum $\vec{P}$ after their interaction with the nanoparticles. The mechanical force from the momentum impulse transferred to the nanoparticle was estimated using Maxwell Stress Tensor.[30]

The charge density patterns of the nanoparticles and the corresponding calculated forces produced by the passing swift electrons are shown in Fig. 4. When the electron beam passes near an isolated nanoparticle, the excited modes rely on the ratio between the impact factor and the particle radius. For relatively large impact factors, the small nanoparticle (1 nm) producing a dipolar localized surface plasmon excitation induces an attractive force towards the beam. When the impact factor is smaller, multipolar plasmons are excited at the particle due to the strongly localized excitation close to the surface. A repulsive force pushing the nanoparticle away from beam is achieved at the close distance and the repulsive force gets much stronger as the beam approaches.

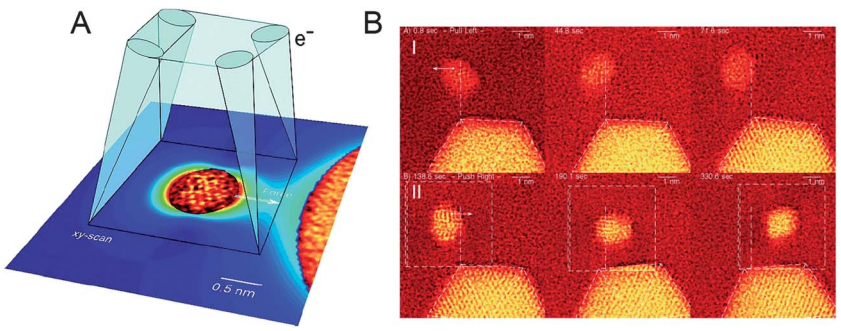

Fig. 3 Directed motion of a 1.5 nm Au particle on amorphous carbon using swift electron.[30] (A) A schematic of experimental set-up. (B) Sequential scanning transmission electron microscopy images of nanoparticles being displaced. (I) Pulling using a dipolar polarization of a single sphere induced by a moderate, 4.5 nm, impact parameter. (II) Pushing the same sphere using multipolar polarization induced by a 1 nm impact parameter. The scanning probe-pair geometry was chosen to minimize forces between the 1.5 nm particle and the larger 4.5 nm particle. Motion was measured relative to the center of the 4.5 nm particle. Time stamps identify image frames.

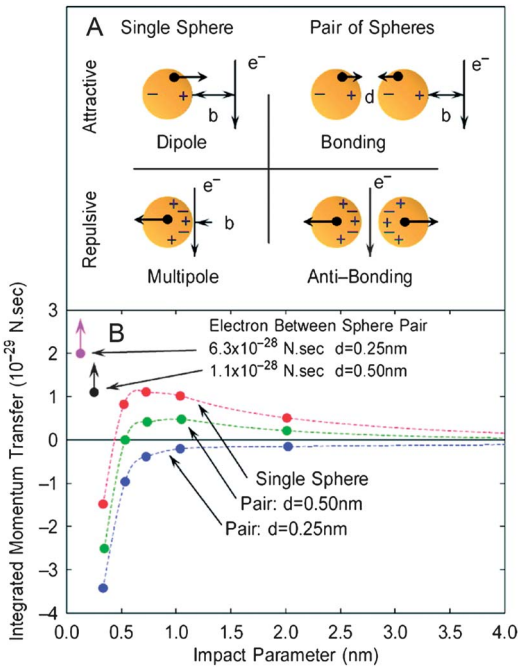

Fig. 4 (A) Summary of the four physical geometries tested in this work. These include repulsive and attractive forces, distinguishing between dipole and multipole modes in single spheres, and bonding and antibonding modes in pairs of spheres. (B) Transferred momentum for various nanoparticle situations, including an isolated 1 nm radius Au sphere (red), pairs of 1 nm radius spheres separated by $d = 0.25$ nm (blue) and 0.5 nm (green), for the electron impact parameter, b. For the isolated sphere the momentum transfer is positive (toward the electron) for moderate impact parameter and negative (away from the electron) for small impact parameter. For a pair of spheres sufficiently close together, the momentum transfer is always negative, forcing the two spheres together. Positioning the electron beam between a pair (black and pink points) forces them apart.

According to the estimation, an instantaneous force $F \sim \vec{P}_z/\Delta t \approx 1 \times 10^{-29}$ N s/0.01×10^{-15} s = 1 pN has been achieved, where the force is from the momentum transfer during a short time interval (*e.g.*, 0.01 fs) when the electron beam passes the nanoparticle. And, a repulsive instantaneous force between two nanoparticles in the pair can be as large as 60 pN. However, movements of a nanoparticle span much longer than the time used in estimating the instantaneous forces. Therefore, an instantaneous force may not be comparable to the continuous force in optical tweezers. And, since the separation between the nanoparticle and electron beam can reversibly affect the sign of the forces (attractive or repulsive), more controllable tweezing of nanoparticles using electron beams needs to be explored.

Manipulation of nanoparticles in an environmental cell

It has been demonstrated recently that 10 nm gold nanoparticles can be trapped and moved over large distances inside an environmental cell.[29] Zheng *et al.* reported the environmental cell developments previously that two ultra thin silicon chips form an compartment with a silicon nitride membrane window allowing nanoparticles in a fluidic environment to be examined using TEM.[54,55]

Samples were prepared by first loading an aqueous solution of 10 nm gold nanoparticles inside the cell, where the membrane surfaces were coated with a layer of proteins (keyhole limpet hemocyanin, KLH) to prevent nanoparticles from adhering to the surfaces. Under the electron beam, the liquid film retracts thus leaving nanoparticles loosely sitting on a wet surface. When the electron beam (120 keV) is converged into a small spot (*e.g.* 50–100 nm), nanoparticles are trapped within the beam and move with the displacements of the beam. It appears that nanoparticles move within the trap in a random fashion while their global movements follow the beam displacements. It was shown that a gold nanoparticle trapped inside the beam can be dragged along with the beam while the particle moves chaotically inside the beam trap. Movements of the nanoparticles are within the space between the bottom and top membranes filled with water vapor. Nanoparticle motion is mostly close to one side of the membrane. However, it can bounce over to the other side of the membrane suggesting a two dimensional trap.

Multiple gold nanoparticles can also be trapped and manipulated with the beam. Two or three nanoparticles frequently change the relative position inside the beam while their global movements follow the beam. By tracking the trajectories of each nanoparticle, the distance between two nanoparticles as a function of time can be plotted. Statistical analysis of the probability distribution of the inter-particle distance gives the forces between nanoparticles. An attractive force in the sub-pN range has been achieved when nanoparticles are within a close distance. Interestingly, such an attractive force is long ranged (up to ~10 nm). The interaction[54] between nanoparticles can be complex and may include van der Waals' interaction, electrostatic interaction, dipolar interaction and so on. This work opens the opportunities of using electrons to probe nanoparticle interactions or direct the assembly of nanoparticles (Fig. 5).

Electron beam can also used to collect nanoparticles on the surface and assemble them into a cluster. Gold nanoparticles on the membrane surface are motionless under the electron beam when the beam current density is low. As the electron beam flux increases by shrinking the beam size, nanoparticles move toward the beam center. Movements of the nanoparticles follow the electron beam density gradient towards the high-density spot. Nanoparticles move smoothly on the surface without significant scattering motion. Trajectories of the each nanoparticle movement can be tracked. As the beam is converged into a ~50 nm spot, nanoparticles within the trap coalesce into a cluster. The cluster of the aggregated nanoparticles can be subsequently directed on the surface by the electron beam. This experiment suggests future fascinating applications of the electron beam, such as removing toxic nanoparticles on a surface which is hard to achieve by other approaches (Fig. 6).

The trapping force

Direct measurement of the electron trapping force has also been achieved.[29] The electron beam is parked on the surface

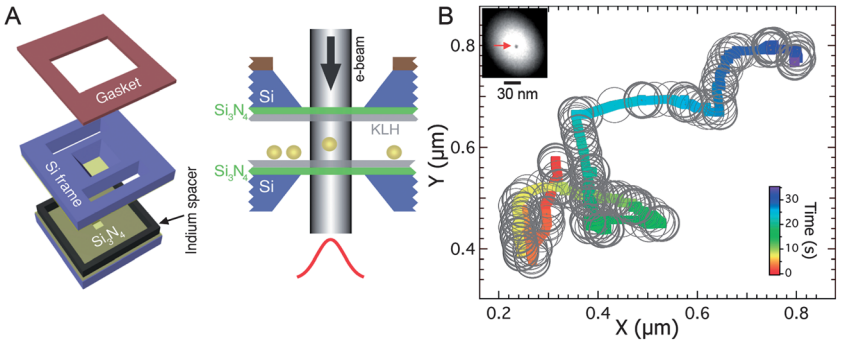

Fig. 5 Manipulation and imaging of a gold nanoparticle movements in a liquid cell using an electron beam. (A) A schematic of experimental set up, where an electron beam passes through the silicon nitride window and traps gold nanoparticles inside the beam. (B) Trajectories of the electron beam movement and the global movement of the gold nanoparticle.

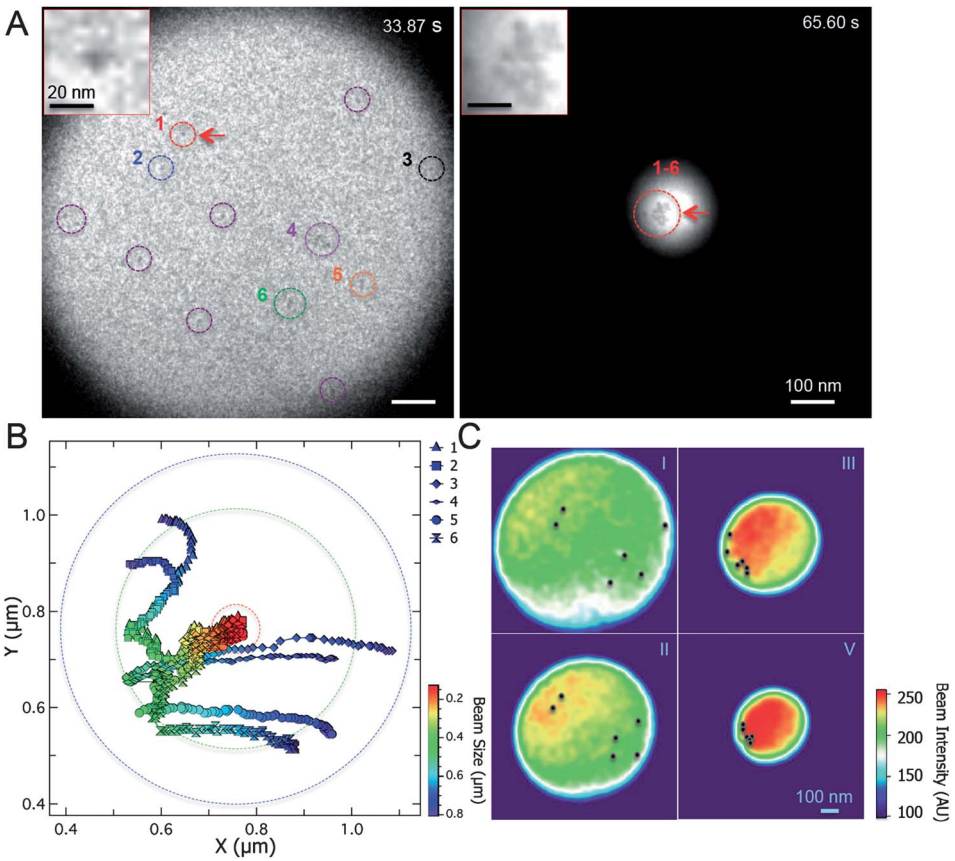

Fig. 6 Assembly of gold nanoparticles on the membrane surface by rapid changing of the electron beam size. (A) Sequential images showing assembly of the nanoparticles resulting from beam convergence. (B) Trajectories of the selected gold nanoparticle movements. Color corresponds to the sizes of the beam. (C) Color maps of the electron beam show the electron beam density variations inside the beam. Those selected nanoparticles are highlighted in black dots.

for an extended period of time allowing motion of the nanoparticle inside the trap to reach a quasi equilibrium condition. Then, two-dimensional nanoparticle movements can be tracked and the probability distribution of the nanoparticle within the trap was achieved. The trapping force responsible for the nanoparticle movements toward the beam center can be estimated using Boltzmann's distribution function. Under the quasi equilibrium condition, the probability distribution $P(x,y)$ of the nanoparticle movements can be expressed as

$$P(x,y) = A_0 e^{-\phi(x,y)/k_B T} \quad (4)$$

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

$$\phi(x,y) = -k_B T \ln[P(x,y)/A_0] = -k_B T[\ln P(x,y) - \ln A_0] \quad (5)$$

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

$$\vec{F} = -\frac{\mathrm{d}\phi}{\mathrm{d}r}\cdot\hat{r} = k_{\mathrm{B}}T\frac{1}{P(r)}\frac{\mathrm{d}P(r)}{\mathrm{d}r}\cdot\hat{r} \quad (6)$$

where $\mathrm{d}\hat{r} = \mathrm{d}\hat{x} + \mathrm{d}\hat{y}$. Using eqn (6), the trapping force as a function of the displacement can be estimated. 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. A trapping force in the piconewton range has been achieved at the location close to the beam center. Although the mechanisms of electron trapping remain elusive, forces from such experimental measurements provide a significant reference point for future development of electron beam tweezers (Fig. 7).

Origin of the trapping force

Both Oleshko[47] and Batson[30] estimated forces from electron beam momentum transfer. According to Oleshko *et al.*, forces in the piconewton range can be achieved for trapping of large nanoparticles over 100 nm by assuming the complete momentum transfer from the electron beam. However, such forces become so small when the size of the nanoparticle reduces to the sub-10 nm range. Batson *et al.* estimated forces as a function of interparticle distance using the Maxwell Stress Tensor. An instantaneous force of piconewton was achieved, which is due to the momentum transfer when the electron beam passes the nanoparticle within a short time interval of 0.01 fs. However, such an instantaneous force is not comparable to the continuous force in optical tweezers. Zheng *et al.* for the first time directly measured the trapping force and a trapping force of piconewton was achieved.[29] The origin of the forces was attributed to a negative pressure within the illuminated area, which may keep the nanoparticle within the trap and drag the nanoparticle towards the beam center. The negative pressure can be generated by more rapid water vaporization under the beam compared to the surrounding area. However, more generic trapping mechanisms need to be further explored. For trapping in vacuum, it is possible that only a smaller force is needed. In any case, factors such as electron beam scattering,[56] static charge–electron beam interaction, thermophoresis,[57,58] *etc.* need to be considered. It is noted that charging on the nanoparticle due to knock-on damage, sample heating and ionization from electron beam interaction impose challenges in practical applications of electron beam trapping. We estimate forces from different mechanisms, such as electron beam scattering, electrostatic interaction and thermal gradient (thermophoresis) in the following section.

Electron beam scattering effects

Electron beam scattering has been considered to be responsible for trapping and moving of nanoparticles, although its role in the manipulation of small particles in the sub-10 nm range needs to be re-evaluated. In conventional optical trapping, frequency-dependent refraction contributes to a backward gradient force in a single-beam gradient force trap, which overcomes the scattering and gravitational forces. Oleshko and Howe proposed that trapping forces originate from the different reflection indices of the nanoparticle being trapped and its surrounding medium, which is similar to the optical trapping.[47] It is also possible that when the incident electron beam interacts with a metallic nanoparticle, the particle can be pulled towards the beam center due to a negative potential well of the particle.[29] A simple estimation independent of the details of the electron–particle interaction is to assume that the momentum of the electron beam is completely transferred to the nanoparticle. The maximum force exerted on the nanoparticle can be calculated.

Forces from the electron beam momentum transfer are dependent on the particle size. As discussed in the earlier section, according to eqn (3) the total momentum transfer is proportional to the number of incident electrons or the projected area of the nanosphere. Typically, for nanoparticles of sub-10 nm, forces from maximum electron momentum transfer are calculated to be in the range of 10^{-3} pN, which is 3 orders of magnitude smaller than the experimental value.

Electrostatic interaction effects

Due to a negative potential of gold nanoparticles, the electron beam interaction with the particle may lead to the particles being pulled towards the beam center. The energy (E) resulting from the electrostatic interaction between a nanoparticle and the electron beam can be estimated by:

$$E = Q\cdot\varepsilon_{\mathrm{ave}} \quad (7)$$

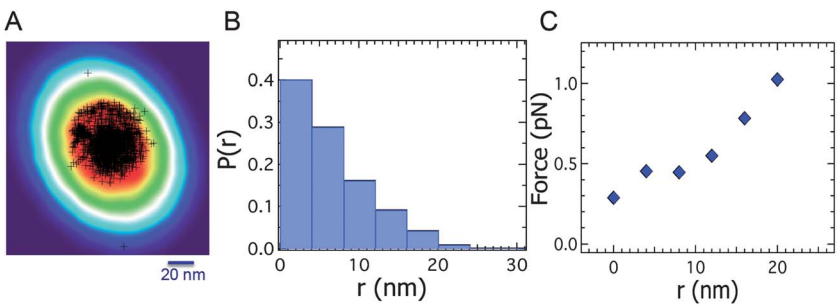

Fig. 7 Estimation of the trapping force. (A) Two-dimensional projection of the gold nanoparticles inside the beam over an extended period of time. Positions of the gold nanoparticles are highlighted in black cross. Color gradient map shows the intensity of the beam. (B) Probability distribution of the gold nanoparticles as a function of displacement from the center. (C) Trapping force as a function of the displacement from the beam center.

where ε_{ave} is the average potential inside the nanoparticle, $\varepsilon_{ave} = -13.4$ eV for a 10 nm Au nanoparticle.[29] Q is the average number of beam electrons inside the nanoparticle at any given moment. It is a function of the current density (J), electron velocity (v) and volume of the nanoparticle (V). $Q = V\cdot(J/v) \sim 10^{-10}$. The calculations show that $E \sim 10^{-9}$ eV which is much smaller than thermal fluctuation (0.025 eV). Therefore, the electrostatic interaction in this case is too small to be the primary source of the trapping force.

From another aspect, if the gold nanoparticle is positively charged (*i.e.*, due to knock-on damage from the high energy electron beam) the interaction with the beam may drag the particle towards the beam center with a higher electron beam density (gradient force). Assuming the electron beam current has a Gaussian distribution $J(r) = J\exp(-\alpha r^2)$, where $\alpha = 1/(2\sigma^2)$ ($\sigma \sim 50$ nm is the typical beam width). Based on Gauss law $\vec{\nabla}\cdot\vec{E} = \frac{\rho_0\cdot e^{-\alpha r^2}}{\varepsilon_0}$, forces ($F = QE$) on the particle with the total charge of Q can be estimated by:

$$F \cong \frac{Q\cdot\rho_0\cdot(1-\exp(-\alpha r^2))}{2\alpha\varepsilon_0 r} \quad (8)$$

where $\varepsilon_0 = 8.85 \times 10^{-12}$ F m^{-1} is the vacuum permittivity and $\rho_0 = J/v$ is the volume charge density of electron beam.

Calculation results show that in order to achieve the force of 1 pN, the accumulated charges on each particle need to be 2.8×10^6 e$^-$, or each atom needs to lose 90 electrons (there are about 30 000 atoms in a 10 nm gold nanoparticle). However, it is unlikely for the nanoparticle to hold such high density of charges. In addition, if two nanoparticles are highly positively charged a repulsive force between nanoparticles is expected, which is inconsistent with the experimental observations. In summary, electrostatic interaction may not be the origin of the electron beam trapping.

Thermal effects

Electron beam interaction with the nanoparticles and the medium can lead to temperature increase. If thermal conductivity of the sample is poor (*i.e.*, less than 0.02 W m$^{-1}\cdot$K^{-1}), a few degrees of temperature increase can be achieved.[55,59] Intuitively, nanoparticles should be pushed towards the location away from the center of the beam. This is opposite to the experimental results.[29] From another aspect, energy change due to surfactant binding on the particle surface may contribute positively. For example, the binding energy of citric acids to water molecules is lower at high temperature than that at lower temperature. The total Gibbs binding energy difference may provide a dragging force to move the nanoparticle towards the beam center (force is the derivative of this energy by the particle position). However, such thermal dynamic arguments based on equilibrium theory may not be applicable since the system is not in equilibrium.

3 Concluding remarks

In conclusion, trapping, moving and assembly of metal nanoparticles using an electron beam have been achieved. Using swift electrons 1–2 nm gold nanoparticles can be pulled or pushed depending on their relative position to the particle. Trapping and steering of 20–300 nm solid aluminum particles inside a molten Al–Si eutectic alloy using an electron beam have been demonstrated. Although there is limited space around the solid particle and the high temperature melting conditions may introduce complex trapping mechanisms, trapping under those conditions seems to resemble conventional single beam optical tweezers. Manipulation of nanoparticles using an electron beam beyond the current capability of optical trapping has been also achieved, where 10 nm gold nanoparticles are moved and assembled over large distances in a controlled manner inside an environment cell. All these studies use the high energy electron beams (*i.e.*, 100–200 keV) inside a TEM. There are many advantages of using electron beams to manipulate nanoparticles. For example, (1) electron beam does not have diffraction limit related issues that conventional optical trapping has encountered in trapping nanoscale objects; (2) imaging of nanoparticles while they are trapped or transported adds significant value in handling nanoparticles for practical applications; (3) an electron beam can be focused into a sub-nm spot or its size can be adjusted rapidly to sweep a surface, thus flexible electron beam tweezers may be achieved; (4) although a high energy electron beam has been used damage to the nanoparticles is not obvious. In the future, it might be possible to use the high energy electron beam for trapping small biological objects without destroying them.

There is no doubt that electron beam manipulation of nanoobjects has the great potential for bringing high impact in nanoscale science and technologies. However, the current electron beam tweezing is only nascent and there is room for future development. For the success of electron tweezing technology, it requires a better understanding of the trapping mechanisms and more stable trapping with three-dimensional control. In addition, manipulation inside a TEM imposes restraints on the applications, such as special sample geometry is required, the high vacuum environment needs to be accommodated, *etc.* Creating a dedicated electron microscope for electron beam manipulation can facilitate the applications and advancement of electron tweezers.

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