Tacking Directional Movement of Nanomotors with Liquid Cell Electron Microscopy

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Liquid cell transmission electron microscopy (TEM) has become a powerful tool for the study of nanoparticle movement and self-assembly [1-2]. By tracking the individual nanoparticle motion mechanisms of nanoparticle movement can be achieved. Extensive studies have demonstrated that various interaction forces contribute to the nanoparticle motion, which lead to the self-assembly of nanoparticles into one-dimensional chains [3-4], two-dimensional patterns [4-5], and three-dimensional architectures [6]. For example, the magnetic dipole interaction and Van der Waals force were considered playing a major role in the self-assembly of PtFe nanoparticles [4]. For the self-assembly of CoO nanoparticles around a liquid droplet, the curved surface of a liquid droplet may create a force gradient driving the CoO nanoparticles to the droplet perimeter [6].

Nanoparticle motion can be introduced predominantly by electron beam illumination, in which nanoparticles resemble the light-activated nanomotors. We prepare a solution by dissolving $CdCl_2$ salt in water (0.1 mol L^{-1}). As shown in Figure 1, a droplet of the solution is loaded into a carbon film liquid cell. Under the electron beam irradiation, $CdCl_2 \cdot 4H_2O$ nanocrystals are formed. Interestingly, these $CdCl_2 \cdot 4H_2O$ nanocrystals are asymmetric with a tip formed at one end, and they move directionally under the electron beam illumination. Like a light-powered nanomotor, the $CdCl_2 \cdot 4H_2O$ nanomotor can be manipulated through the "On/Off" switching of the electron beam illumination. They stop moving when the electron beam is shutoff, and when the electron beam is switched on they move in a straight line towards the direction opposite to where the tip is pointing.

Further analysis indicates that the asymmetric shape of $CdCl_2 \cdot 4H_2O$ nanocrystal plays a key role in its directional movement. The radiolysis of water under the electron beam generates hydrated electrons, protons and hydrogen peroxides. Under the electron beam irradiation, $CdCl_2 \cdot 4H_2O$ in water may decompose into Cd and HCl. Cd can also be oxidized into $CdCl_2$ by consuming H^+. The redox reactions of $CdCl_2$ under electron beam irradiation can be written as the following [8]:

$$CdCl_2 \cdot 4H_2O + 2H_2O \leftrightarrow Cd + 6H^+ + 2Cl^- + 3H_2O_2$$
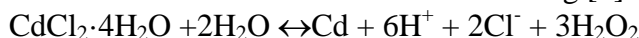
It is expected that there is a higher reactivity of the higher energy facets at the tip, and the faster diffusion of H^+ than Cl^- creating an ion gradient. The ion concentration gradient corresponding to the shape of the nanocrystal is shown in Figure 2a. Thus, an electric field can be generated around the nanoparticle, which has been simulated using finite element method (Figure 2b). It is well-known that Cl^- has a higher affinity to the first Helmboltz layer of Cd^{2+} on the $CdCl_2 \cdot 4H_2O$ nanocrystal. Thus, the electric field around the nanocrystal can drive the nanocrystal to move in the direction as being observed in the experiment [9].
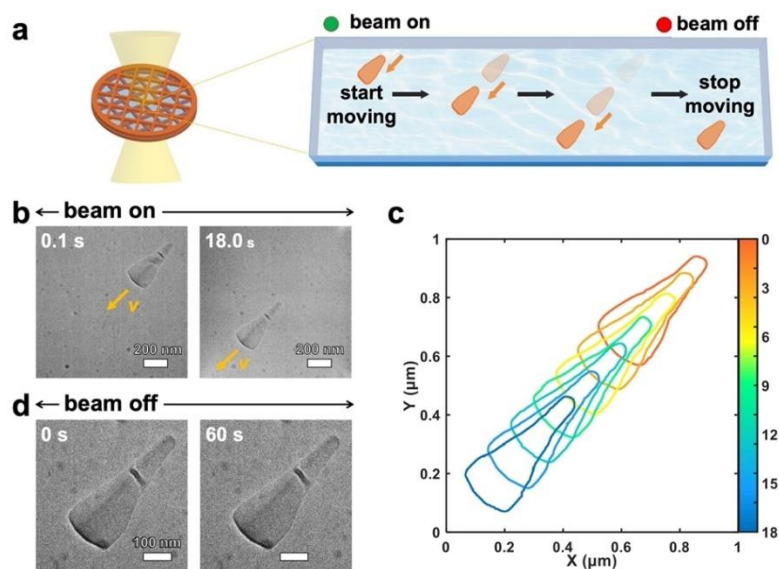
Figure 1. Directional motion of $CdCl_2 \cdot 4H_2O$ nanocrystals under electron beam illumination. (a) A schematic representation of a liquid cell and the motion of a $CdCl_2 \cdot 4H_2O$ nanocrystal. (b) Sequential TEM images from a movie showing the directional motion of a $CdCl_2 \cdot 4H_2O$ nanocrystal under electron beam illumination. (c) The trajectory of $CdCl_2 \cdot 4H_2O$ nanocrystal movement during 18.0 s. (d) No obvious movement of the $CdCl_2 \cdot 4H_2O$ nanocrystal without electron beam illumination.
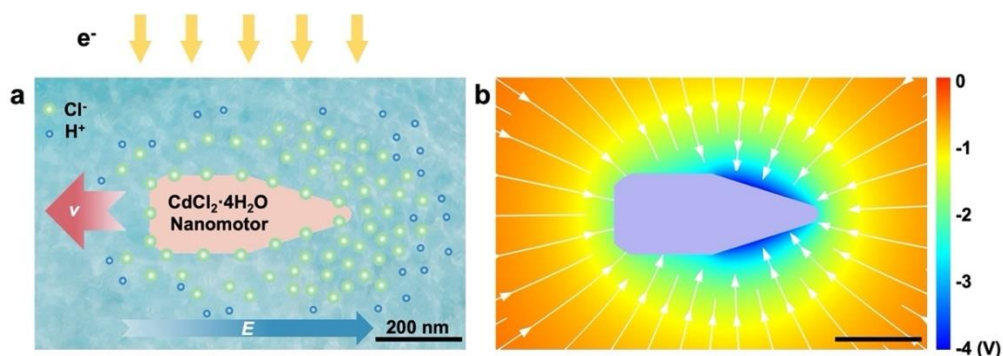

Figure 2. Schematic illustration of the $CdCl_2 \cdot 4H_2O$ nanomotor self-propulsion mechanisms. (a) A schematic showing the ion gradient around the nanomotor. (b) Finite element simulation illustrating the electric field distribution around the nanomotor.

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