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Detection of optical trapping of CdTe quantum dots by two-photon-induced luminescence

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Nanometer-sized CdTe quantum dots (QDs) in D_2O can be optically trapped by a high repetition-rate picosecond Nd:YLF laser with an input power as low as 100 mW. A large two-photon absorption (TPA) cross section of 10^4-10^5 GM for CdTe QDs makes it possible to detect the trapping process with TPA induced luminescence. In D_2O, the luminescence intensity of CdTe QDs was found to increase with time, whereas an intensity decrease was clearly detected in H_2O. In addition, the optically trapped CdTe QDs were fixed on a hydrophilic glass substrate. Laser trapping of QDs may provide a basic technique for quantum information and biological applications.

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Single-beam gradient-force trapping (optical tweezer) allows one to manipulate dielectric particles in three dimensions in aqueous solutions. In 1970, Ashkin showed that one could use the force of radiation pressure from a focused laser beam to significantly affect the dynamics of small transparent micrometer-sized neutral particles.[1] For a particle size $>\lambda/20$, the Lorenz-Mie theory based on plane wave scattering is used to describe the optical trapping of an object placed in an arbitrary field distribution. For particles $\ll\lambda/20$, such a small particle behaves as an induced elementary dipole and the gradient and scattering forces act on it. A scattering force results from the scattering of the incident beam by object, which is in the direction of the incident light beam. A gradient force comes from the electrostatic interaction of a particle (dielectrics) with an inhomogeneous electric field, which is in the direction of the intensity gradient of the beam.[2] Optical trapping of particles $>\lambda/20$, such as submicron to micrometer-sized dielectric particles, have been widely reported recently.[3–11]

However, to our knowledge, the optical trapping of particles $\ll\lambda/20$, such as quantum dots (QDs) in solution, has not, been reported yet, although the manipulation of nanosized material will be an important technique for developing biology and quantum information science. Recently, as reported by the American NSF group, semiconductor QDs and semiconductor microcavities have been the focus of nanodevice technology both as optical and electronic devices.[12] Techniques for the trapping and cooling of atomic particles, including semiconductor QDs, and nanofabrication of tiny electrical circuitry offer a different technique in quantum information science.[13–16] Optical trapping of semiconductor QDs can also improve the combined single-molecule force and fluorescence measurement in biology because of its high photostability, broad absorption and narrow as well as symmetric emission spectra, longer luminescence lifetime, and large one- and two-photon absorption (TPA) cross sections.[17–19]

Very recently, optical trapping of gold nanoparticles as small as 40 nm or carbazolyl-containing copolymers of ~20 nm diameter in aqueous solution with cw laser of 100 ~ 300 mW have been demonstrated by Matsuhara and coworkers.[4–11] The calculation of the trapping laser power, as described later, is consistent with the above results. However, in the case of QDs with a diameter of a few nm, extremely high power (~20 W) of cw laser is needed for optical trapping because of the dramatic decrease of particle size. Such high power is difficult to use in conventional optical trapping with a cw YAG laser beam.

In the present study, the optical trapping of CdTe QDs as small as 3.3 to 4.5 nm diam was demonstrated with a high repetition-rate picosecond YLF laser. The trapping process was examined by TPA luminescence of CdTe QDs. The size-dependent trapping properties were also analyzed by two-photon luminescence. In addition, optically trapped CdTe QDs were fixed on a glass substrate.

Picosecond mode-locked Nd:YLF laser (1047 nm, 3.5 ps FWHM, 80 MHz, Microlase Optical Systems) was used as a trapping laser system. A fundamental laser beam was introduced into an inverted microscope (IX-51, Olympus), in which the laser intensity was 80% reduced by the optical setup. The laser intensity was variably controlled by a variable ND filter. An oil immersion objective lens (NA 1.40, X100, Nikon) was used for optical trapping and to collect the two-photon-induced luminescence of CdTe QDs. Beam waist of focusing laser is estimated to be 0.45 μm. Luminescence spectrum was detected with a charge-coupled-device (CCD) camera (PMA U6039-01, Hamamatsu)—polychrometer combination. Morphology images of QDs on a substrate with and without a trapping laser beam were measured by AFM (Solver P47H, NT-MDT). Water-soluble CdTe QDs were synthesized from $Cd(ClO_4)_2$ and H_2Te.[20] UV-visible absorption, luminescence spectra and TEM (JSM-3010, JEOL) images clearly show that 3.3, 3.7, 4.1, and 4.5 nm diameter CdTe QDs were well prepared. CdTe QDs were diluted with D_2O and the sample solution was dropped into a 1-mm-depth well on a glass slide and covered by a cover slip of 0.17 mm thickness.

Optical trapping of CdTe QDs corresponds to a Rayleigh regime ($a\ll\lambda/20$), in which the particle can be treated as a simple dipole, where a is the radius of the particle. Chaumet and Nieto-Vesperinas obtained the expression for the total time average force on a sphere, $\langle F^i\rangle=(\frac{1}{2})\mathrm{Re}[\alpha E_{0j}\partial^i(E_0^j)^*]$, which includes $F_{\mathrm{grad}}\propto a^3\nabla I_0$ and $F_{\mathrm{scatt}}\propto a^6 I_0$, where α is the polarizability of dielectric particles, and E_0 is the incident optical field.[21,22] High incident beam intensity gives the balance between gradient force toward the focusing point and the drag force from medium and scattering force, pushing the particle away from the focusing point.

As described by Ashkin and Chu,[23] a sufficient trapping condition is required: the time to pull particles into the trap potential should be much less than the time for the particles to diffuse out of the trap by Brownian motion. Based on the Stokes law for a small sphere, the viscosity induced drag force is expressed in $\vec{F}_{\text{drag}}=6\pi\eta\nu a$, where η is the viscosity of D_2O, ν is the velocity of the QDs driven by Brownian motion.[24] When $\vec{F}_{\text{grad}}=\vec{F}_{\text{scatt}}+\vec{F}_{\text{drag}}$ is satisfied, QDs can be trapped in the focusing volume with $\pi\omega_0^2/\lambda$ length. Compared with the size of QDs, polarizability plays less effect. With size decreasing, much higher laser intensity to overcome the drag force should be required by the rapid decrease of gradient force from the a^3 term. For example, 3-nm sized CdTe QDs require a power of more than 20 W for cw-mode optical trapping at 1047 nm.

Agate *et al.* have compared cw-mode and pulse mode laser trapping of a 1.28 μm diameter silica sphere using a femtosecond laser in the Lorentz-Mie regime.[25] In this case, the diffusion of trapped particles between successive femtosecond pulses can be negligible. As a result, the average power rather than peak power is the key parameter for laser trapping. This comparison may not be adopted for small particles such as semiconductor QDs with a size of $\ll\lambda/20$, in which the sufficient optical trapping of such Rayleigh particles requires that the Boltzman factor $\exp(-U/t)\ll 1$, where $U=n_b\alpha E^2/2$, the potential of gradient force.[23] When the pulse laser is used to induce the gradient force, the highest dipole interaction between particles and the electromagnetic field of incident light appears on the peak position of the pulse. During the period between successive pulses, particles inside the potential well will be driven by thermal diffusion, which moves toward escaping from the focusing volume. In aqueous solution at room temperature, however, the average diffusion distance is about 1.2 nm for 4-nm-sized QDs within an 80 MHz repetition rate, which is much smaller than the radius of the focusing area and also smaller than the particle size. While, as driven by inertia, particles at the edge of the potential well will experience the motion toward the deep trapping. If the repetition rate is as low as 1 kHz, the particle moves away from the focusing area by thermal Brownian motion. As a result, Rayleigh particles may be optically trapped with a high repetition rate ultrashort pulse laser beam.

Figure 1 illustrates the potential of gradient force against the radius of CdTe QDs based on the calculation of peak power transient trapping by picosecond YLF laser. Since the average distance, r, between QDs is ~260 nm ($r/a>100$), the van der Waals attractive potential and electrostatic Coulomb repulsive potential between particles can be ignored. If F_{grad} overcomes F_{drag}, the particles can be optically trapped. The bulk dielectric constant of CdTe was temporally used for the calculation of trapping force. As clearly shown, CdTe QDs of 3 nm diameter can be trapped with an incident average power larger than 10 mW by the picosecond YLF laser, although an input power as high as 20 W should be used for trapping the same CdTe QDs by cw-mode YLF laser. Thus, ultrafast pulse laser beam with high repetition rate can trap nanosized particles much easier than a cw-mode laser beam under the same average power.

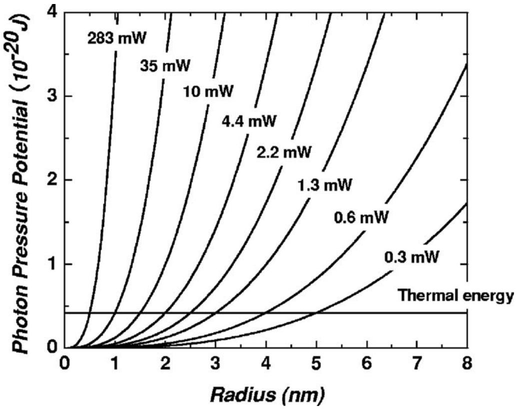

FIG. 1. Calculation of the photon pressure potential against the radius of CdTe QDs. The calculation is based on the peak power $\int_{-\tau}^{\tau}\varepsilon^2(z,t)dt$ of the YLF laser with 3.5 ps FWHM and an 80 MHz repetition rate. The corresponding average power is given in the figure.

With a tightly focused laser beam for optical trapping, the luminescence of CdTe QDs can easily be observed. Figure 2 shows the luminescence spectra of CdTe QDs (4.5 nm diameter) as a function of incident laser intensity. The spectral feature with a peak at 620 nm is very similar to that of one-photon excitation. Since the solution has been diluted to below 10^{-7} M, the effect of re-absorption from two-photon induced luminescence can be negligible. The slope of luminescence intensity against the power is 1.92±0.04, suggesting that the TPA of CdTe QDs is effectively induced. Our *Z*-scan experiments on CdTe QDs revealed that the TPA cross section is in the order of 10^4-10^5 GM (1 GM$=10^{-50}$ cm^4 s (photon)$^{-1}$),[26] which is much larger than a typical organic nonlinear material, such as MPPBT (Ref. 27), and comparable with water soluble CdSe/ZnS QDs reported recently.[28] The other CdTe QDs with 3.3, 3.7, and 4.1 nm show a similar tendency and luminescence slopes close to 2.0 against the incident laser power.

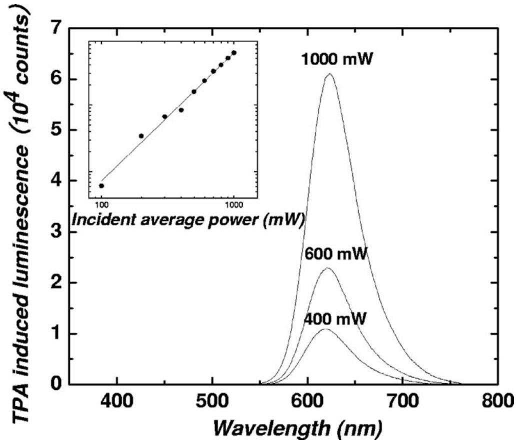

FIG. 2. TPA induced luminescence of CdTe QDs with 4.5 nm diameter in D_2O excited at 1047 nm YLF laser as a function of incident average power. Inset shows power-dependent luminescence peak intensity of CdTe QDs. The slope is 1.92±0.04. The power after the objective lens is 20% of the incident power.

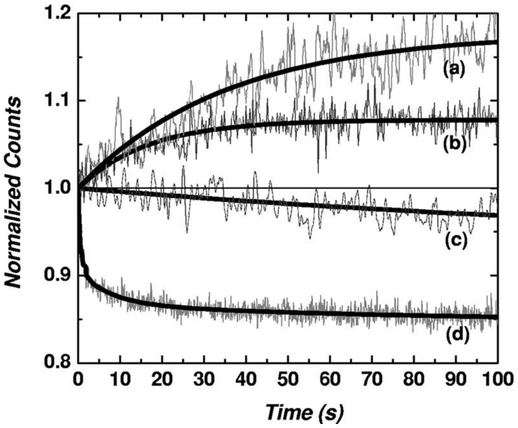

FIG. 3. TPA induced luminescence of CdTe QDs in D_2O and H_2O prepared from the spectrum as a function of time. The diameter and solvent are (a) 4.5 nm diam in D_2O, (b) 3.7 nm diam in D_2O, (c) 4.5 nm diam in H_2O, and (d) 3.7 nm diam in H_2O. Incident average laser power after the objective lens is 140 mW.

We found that the intensity of TPA induced luminescence of CdTe QDs depends on time. Figure 3 illustrates the time-dependent luminescence intensity of CdTe QDs in D_2O and in H_2O. In D_2O, two-photon luminescence of CdTe QDs is increasing with time. The initial slope of large sized CdTe QDs is larger than that of small sized CdTe QDs. No spectral change of QDs was detected in both solvents during the measurement, suggesting photophysical/chemical changes cannot be detected under the illumination of a 1047 nm laser beam. These results suggest that the number of CdTe QDs increases with time within a focusing volume, indicating that CdTe QDs are optically trapped by the picosecond YLF laser. On the other hand, the two-photon luminescence intensity of CdTe QDs in H_2O decreases with time. This is probably due to the local heating of water by the vibrational overtone excitation of H_2O at 1047 nm.[11] The local heating plays a dominant role in increasing the thermal Brownian motion and the number of QDs decreases with time. The gradient force toward the focusing point competes with the drag force away from the focusing point, thus the time-dependent luminescence intensity is strongly dependent on the size of CdTe QDs. As clearly shown in the figure, the intensity decrease of 4.5 nm CdTe QDs in H_2O is almost negligible, although the faster decay is observed for 3.7 nm CdTe QDs, suggesting that the gradient force on 4.5 nm CdTe QDs is comparable to the drag force coming from solvents.

The optically trapped CdTe QDs can be fixed on a substrate. The glass substrate was treated with Extran (MA01, 5%, Merck) before using to make the surface hydrophilic. The D_2O solution of CdTe QDs was dropped on the glass without any cover and the sample was naturally dried with and without trapping the laser beam. The evaporation of the solvent takes as long as 30 min, while the trapping laser beam was continuously illuminated.

After drying, the sample was further kept on the microscope for complete drying without the trapping beam. The volume of trapping particles may be similar to or less than a

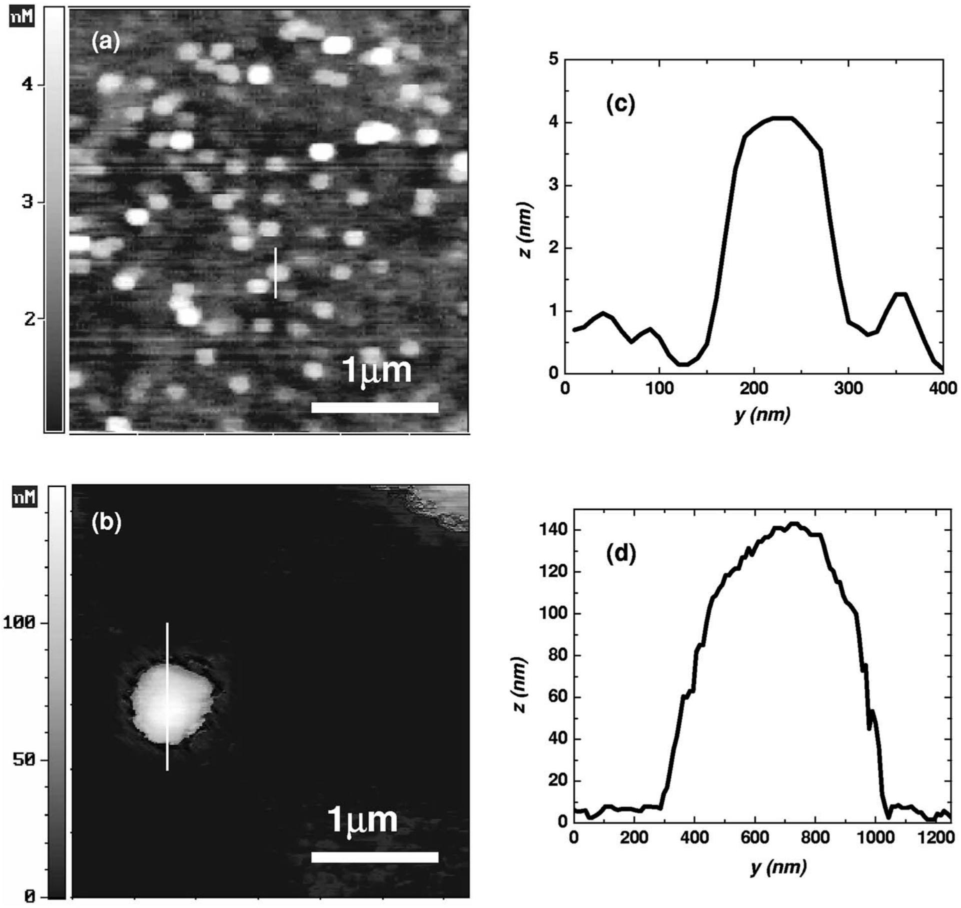

FIG. 4. AFM images of CdTe QDs (3.3 nm) on a hydrophilic glass substrate after the drying of D_2O solution without (a) and with (b) trapping laser beam. Corresponding *z* direction cross sections in (a) and (b) are given in (c) and (d). Incident average laser power after the objective lens is 120 mW.

focusing beam. Surface topography was examined by AFM on the microscope, in which the tip position was geometrically determined to the focusing position with a combination of a CCD and a cross mark of the microscope. Figure 4 illustrates the surface topography of a naturally dried sample with and without the picosecond YLF laser. As clearly shown, an assembled structure of CdTe QDs less than 1 μm in diameter is detected only when the trapping beam is applied. Furthermore, the height of the assembled structure in Fig. 4(b) is much larger than QDs dried without trapping laser in Fig. 4(a). A cover slip is removed during the fixation process, thus the concentration of QDs increases by the solvent evaporation, and the gathering efficiency by optical field will increase with time. So, the number of QDs after the fixation on a glass plate will be much larger than that expected from Fig. 3. D_2O has no overtone absorption at the wavelength (1047 nm) of trapping laser and no sample absorption exists at the wavelength. As indicated previously, no photochemistry is induced during the trapping experiments. The formed structure on a glass substrate is initiated by gathering QDs with the electric field of the trapping laser beam. This is clear evidence that optically trapped nanosized CdTe QDs were fixed on a glass surface.

By using a high repetition-rate picosecond YLF laser with much lower than average power compared to that of the cw laser, water-soluble CdTe QDs with a size less than the Bohr exciton radius were trapped stably and fixed on a hydrophilic substrate. The results shown here may offer a basic technique for quantum information science to control and arrange semiconductor QDs freely. In addition, this may also provide applications for biological tracking and observation. A single semiconductor trapping is also now in progress.

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