

# Femtosecond Trapping Efficiency Enhanced for Nano-sized Silica Spheres

Anwar Usman,\* Wei-Yi Chiang, Hiroshi Masuhara\*

Department of Applied Chemistry and Institute of Molecular Science,  
National Chiao Tung University, Hsinchu 30010, Taiwan

## ABSTRACT

We present a comparison of optical trapping of 50-nm-sized silica nanospheres, suspended in water medium, by femtosecond laser pulses and by continuous wave laser beam. With bright field microscopic imaging, we demonstrated that intensity of scattering light at the focal area under fs-pulse mode is much higher than that under cw mode. This result offers a basic interpretation that trapping efficiency of nanometer-sized particles by the ultrashort laser pulses is higher than that by the cw mode at the same laser power. We interpret this finding by means of impulsive peak power of the femtosecond laser pulses.

**Keywords:** laser trapping, femtosecond laser pulses, continuous wave laser, silica nanospheres, bright field microscopy.

## 1. INTRODUCTION

A highly focused continuous-wave (cw) laser beam, which can induce trapping force typically of the pN scales to trap target materials with sizes from micron- to a few tens nm,<sup>1-3</sup> has been widely applied to confine and manipulate particle aggregates,<sup>4,5</sup> particle depositions,<sup>6</sup> polymerizations,<sup>7</sup> as well as nucleation, growth, and polymorph control of single crystals.<sup>8-11</sup> The cw laser beam can trap as small as 5.4 nm gold nanospheres for only 2-3 seconds,<sup>12</sup> but it is unable to trap quantum dots with the same size.<sup>13</sup> This indicates that the cw laser beam even at laser power up to 400 mW can not suppress the Brownian motion of a few nm-sized particles.<sup>12</sup> Ultrashort laser pulses have also been utilized as an optical trapping beam substituting the traditional cw laser to explore new applications particularly in optical trapping of nanoparticles,<sup>13-16</sup> though trapping efficiency of cw- and pulsed-laser remains the significant issue. For optically trapped 0.78 or 1.28  $\mu\text{m}$ -sized silica nanospheres, particles in the Lorentz-Mie regime with negligible diffusion during the interval time between consecutive pulses, the femtosecond (fs) laser pulses have been demonstrated to have the same trapping efficiencies as compared with cw laser beam.<sup>17,18</sup> This leads the average power rather than peak power to be the key parameter for the laser trapping. For particles in Rayleigh regime, however, replacing linearly polarized conventional cw- to fs or picosecond (ps) pulsed-laser beam with the laser power less than 100 mW in optical trapping experiments leads to stable optical trapping of gold nanospheres and quantum dots.<sup>13,15</sup> Similarly, fs laser pulses enhance the numbers of 50-nm-sized polystyrene bead-particles optically trapped by a factor of more than forty times as compared with the cw laser beam.<sup>16</sup> Those findings are clearly evident that pulse-mode is advantageous over cw-mode laser beam in trapping ability and control of the Rayleigh particles.

---

Emails: usman@faculty.nctu.edu.tw (AU); masuhara@masuhara.jp (HM);  
Phone +886-3-571-2121 ext. 56595; Fax +886-3-571-2121 ext. 56593

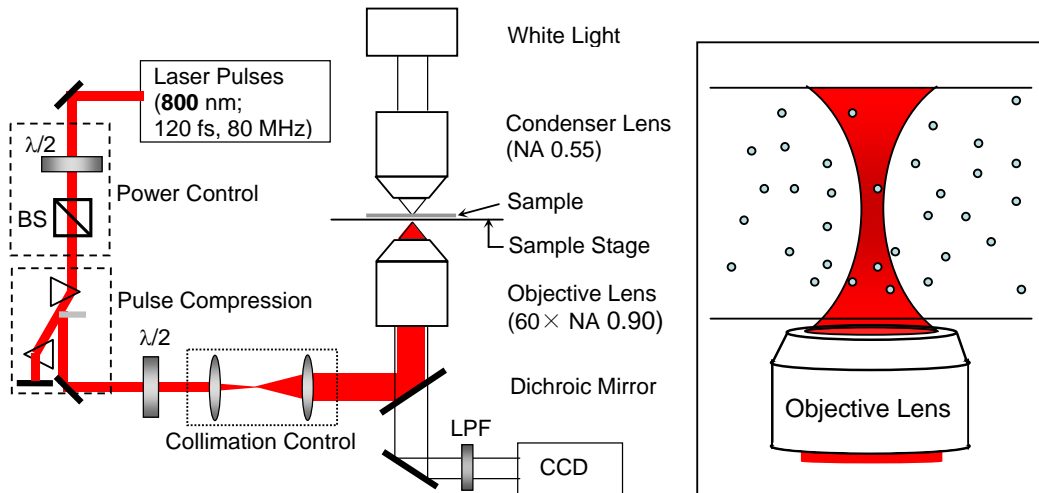
For the polymer nanoparticles, more interestingly, the optical trapping is accompanied by partial ejection of the nanoparticles out of the single trapping site to surrounding area along two directions, in alternating manner, perpendicular to laser polarization. We have proposed that impulsive peak power of laser pulses with its ability to induce the nonlinear optical effects coupled with diffusion of the trapped particles are important aspect to generate high magnitudes of transient restoring force which gathers a large number of the polymer nanoparticles at focal spot.<sup>16</sup> In addition, the axial and lateral fields produced by the high numerical aperture objective lens in the optical trapping experiments induce optical forces that eject the nanoparticles in the directions orthogonal to the laser polarization.<sup>16</sup> Thus, the ejecting forces are responsible to control the off-axis direction of the scattered nanoparticles. This finding therefore highlights the use of fs laser pulses for optical trapping and simultaneously controlling the microscopic flow of NPs out of the trapping site and might lead to the technique for controlling dynamical motion of Rayleigh particles in the evolving area of optical micromanipulation.

In continuation of our recent research endeavors in the development of fs laser trapping of particles in the Rayleigh regime,<sup>16,19</sup> in this study, we investigate the use of fs laser pulses for optical trapping behavior of 50-nm-sized silica nanospheres, the non-metallic nanoparticles with different optical properties than the polystyrene beads. Optical trapping behavior of silica nanospheres using a linearly polarized 800-nm fs-pulse mode was compared with that using the same laser power and spatial profile of cw mode of laser beam. With bright field microscopy imaging, we observed brighter scattering light at focal area than the surroundings. We assume that the scattering light at focal area is proportional to the number of silica nanospheres gathered at the trapping site, and thus we have to discuss the trapping behavior of the silica nanospheres based upon the scattering light intensity at the focal spot. To our knowledge, this is the first optical trapping report of non-coated or coated silica spheres<sup>17,18,20</sup> with a diameter down to 50 nm using 450 mW of laser power. As compared to cw laser trapping, fs-pulsed laser induces higher scattering light intensity. This provides a basic interpretation that trapping efficiency of silica nanospheres by the fs pulses is higher than that by the cw mode. However, there is no observable flow of ejected silica nanospheres as observed in the case of polymer beads,<sup>16</sup> indicating that ejecting forces exerted on the silica nanospheres much lower than those on polystyrene nanoparticles though the average laser power at the sample was at the same level. Their differences in polarizability, interparticle interactions, and particle density in the colloidal solution were considered to be the reasons.

## 2. EXPERIMENTAL

Optical trapping behavior of the nanoparticles by fs laser pulses was obtained using laser trapping system based on an inverted microscope (Olympus IX71), as shown in Fig. 1. A linearly polarized 800-nm beam from Ti:sapphire (Tsunami; Spectra Physics) laser, which can be operated in cw or femtosecond-pulse mode, was used as the trapping beam. When it was operated in the pulse mode, the pulse duration was about 90 fs with the repetition rate being 80 MHz. The polarization direction of the laser beam was controlled by a half-wave plate. The beam was collimated and expanded to ~5 mm in diameter, and then was focused through an objective lens (60 $\times$ , NA 0.90) at normal incidence into a sample cell, mounted on the sample stage of the microscope. The beam waist of the focal spot was estimated to be 460 nm. The light power after the objective lens was controlled at 450 mW.

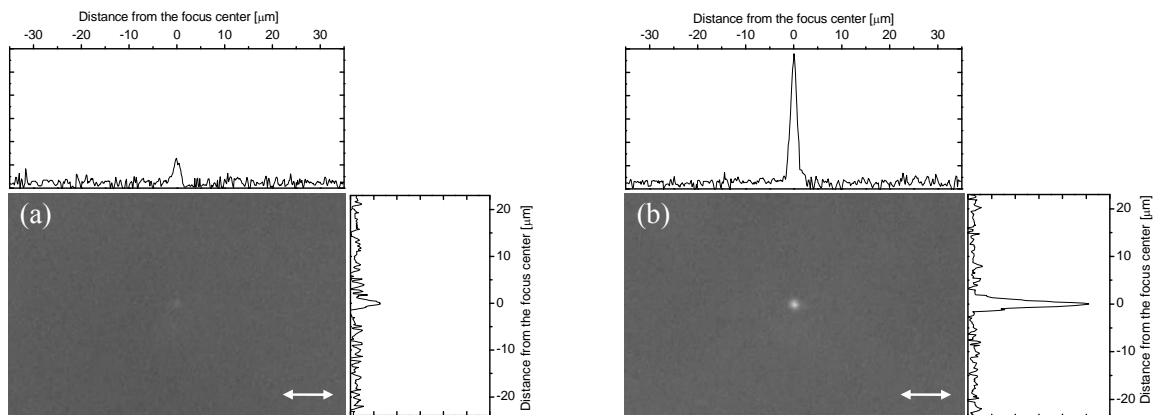
The sample cell consisted of a silicon chamber (1 mm thickness) sandwiched between two cover-glass plates (Matsunami). The inner well of the chamber (10 mm in diameter) was filled with colloidal solution containing nonporous silica nanospheres (PolyScience; radius = 25 nm, refractive index = ~1.43-1.46) suspended in distilled water (refractive index = 1.33 at room temperature). Particle density of the nanospheres in the colloidal solution was  $3.64 \times 10^{11}$  particles/ $\mu\text{L}$ . The sample cell containing the silica nanospheres was illuminated by white light ( $\lambda=400\text{--}750$  nm) from a halogen lamp passing through a condenser lens (Olympus; NA 0.55). The elastic light scattering originated from the laser trapping beam was completely cut by a shortwave-pass filter with transmission at 380–720 nm (Semrock; Brightline 750/SP) before the CCD camera. With such a setup only the scattering light from halogen lamp by the nanospheres was collected by the objective lens, and was detected by using a charge-coupled device (CCD) camera (JAI; CV-A55IR E) running at 30 interlaced frames per second. The positions of the nanospheres were associated with the image of the scattering light detected by the CCD camera. For data analysis, the sample was replaced by a neat solvent, which was used as baseline corrections.



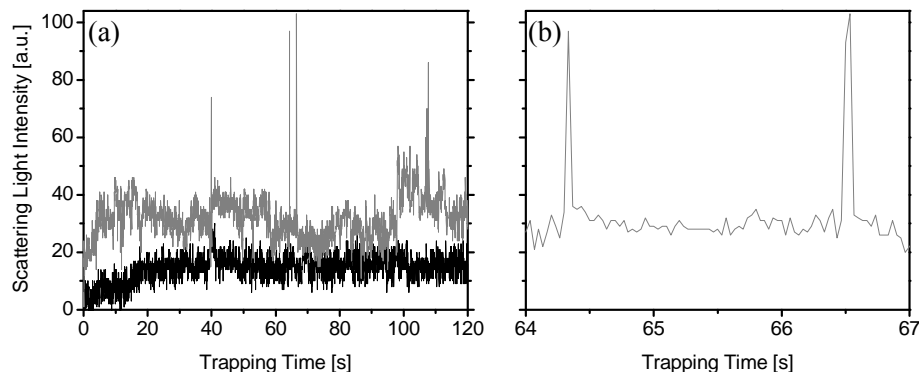
**Figure 1.** A schematic diagram of the experimental setup; BS = beam splitter,  $\lambda/2$ =half-wave plate, LPF = low pass filter with transmission edge at 750 nm. Inset: the cell containing silica nanospheres by highly focused laser beam.

### 3. RESULTS AND DISCUSSION

Images compiled in Fig. 2 highlight bright scattering light with the line profiles showing a sharp intensity at the focal spot. When the laser trapping beam operated in cw mode at the average power of 450 mW, we observed a very tiny scattering light at the focal spot compared with the surrounding area (see Fig. 2(a)). Most remarkably, with essentially the same laser power and optical condition, fs-pulsed laser trapping exhibited higher light scattering intensity as compared with cw laser trapping (Fig. 2(b)). The peak intensity of the line profile clearly shows a 2.0- $\mu\text{m}$ -fwhm at the focal spot. Such the size is attributable to the cross section of trapping site, equivalent to  $\sim 4$ -5 times of the beam waist.



**Figure 2.** Video image frames and their line profiles showing optical trapping behavior of silica nanospheres by (a) cw-mode and (b) fs pulse-mode Ti:sapphire laser beam ( $\lambda = 800 \text{ nm}$ ). A sharp scattering light at the focal spot indicates the optical trapping of the nanospheres at the focal spot. The laser power for each case is 450 mW after the objective lens. The arrow in each panel indicates polarization direction of the laser beam. The cross sectional line profiles in each panel were taken from the lines passing through the focal center, parallel and perpendicular to the polarization direction.



**Figure 3.** (a) Time-dependent peak intensity of line profile under femtosecond-pulse (gray line) and cw mode (black line). (b) The time-dependent peak intensity zoomed in a few seconds, showing the rise and fall of a bright scattering light with high intensity on short duration within 100 ms.

In Fig. 3, panel (a) shows time dependence of the intensity of line profile at the focal spot. For cw laser trapping beam, in particular, we observe a slow increase in the early 20 s irradiation time before the intensity turns into a steady value. In contrast, the fs-pulsed laser induces unstable and fluctuated intensity throughout the observation window as compared with that of cw beam. The average intensity with fs-pulsed laser, however, is always higher by factor of 2.2 than that with cw laser beam. As we assume that the scattering light intensity correlates linearly with the number of nanospheres trapped in the focal spot, this finding offers a basic interpretation that the fs pulse mode is more efficient to confine the nanospheres than cw mode at the same laser power. To clarify this issue, we evaluate the trapping efficiency of the nanospheres, which is usually expressed by a dimensionless value as,<sup>21,22</sup>

$$Q = Fc / n_m P \quad (1)$$

where  $F$  is trapping force,  $P$  is incident power,  $n_m$  is refractive index of a medium, and  $c$  denotes the speed of light in vacuum. Based on Eqn. (1), if the gradient force is solely governed by the average laser power, one can simply interpret that the fs pulse- and cw-mode will have the same trapping efficiency for the same level of laser power. Thus, the higher efficiency of fs laser pulses as compared to cw mode indicates that the pulse mode laser beam induces higher trapping force. In other words, the trapping efficiency for ultrashort pulsed-laser trapping is determined by the interaction between the nanospheres and the repetitive pulses.

When we consider that the trapping force is linearly correlated to the light intensity or the number of photons per second of the laser; the 90-fs laser pulse has photons per second being about five orders higher during the pulse envelope than the constant photons per second of cw laser beam. The electric field at the same laser power of 450 mW is calculated to be  $E_0 = 3.80 \times 10^3$  V/ $\mu\text{m}$  per pulse and  $= 2.77 \times 10$  V/ $\mu\text{m}$  for cw laser beam. The gradient force and potential trapping well can be estimated based upon the polarizability ( $\alpha$ ) of individual nanospheres by Clausius-Mossotti relation,<sup>23</sup>  $\alpha = 4\pi a^3 (m^2 - 1/m^2 + 2)$  to be  $1.07 \times 10^{-23}$  m<sup>3</sup>, where  $a$  and  $m$  are the radius of the nanosphere and dielectric constants of the particle relative to the surrounding medium. With the electric fields given above, we estimated the maximum transient gradient force and potential well to 2.62 nN and  $2.90 \times 10^5$  k<sub>B</sub>T for the fs pulse, and the constant gradient force and potential well of 0.14 pN and  $1.55 \times 10$  k<sub>B</sub>T throughout the irradiation for cw mode. This clearly indicates that fs pulses induce extremely strong transient restoring force and deep trapping potential that can easily trap the nanospheres at the focal center temporarily within the pulse envelope.

However, we should consider that, firstly, a single pulse may not be able to induce such efficient optical trapping due to ultrashort time of interaction between the nanospheres and the pulse, secondly, the particle density plays a role to

fill up the trapping site and to form nanoparticle flow out of the trapping site,<sup>16</sup> and thirdly, there is no force exerted on the nanospheres during the interval time between two consecutive pulses. The dynamic of nanospheres at around the focal spot is therefore governed by a large number of repetitive pulses, though it may not be fairly determined by the average laser power per second. As a result, the trapping efficiency of silica nanospheres by fs laser pulses is enhanced, similarly to the case of polystyrene nanoparticles. One of the physical reasons for such enhancement is the diffusion of trapped nanospheres between successive fs pulses is much larger and not negligible, as compared to micron-sized silica spheres.<sup>17</sup> Thus, the dynamic motions of the nanoparticles with diffusional coefficient being inversely proportional to the radius affect the process of filling up the trapping site by high repetition of fs laser pulses.

We have demonstrated that fs pulses also generate scattering and temporal pulse radiation forces that eject the nanoparticles out of the focal spot orthogonal to the incident laser polarization,<sup>16</sup> and such ejecting forces are negligible or omitted for small particles optically trapped by cw mode.<sup>23</sup> With this consideration, dynamics of optically trapped nanospheres by laser pulses should involve their gathering in and ejection out of the focal spot. Moreover, optical trapping and ejection are related to the dynamic and statistic of a large number of nanospheres, which may optically form transient assembly and be ejected out as individual or clusters of nanospheres. This is supported by fluctuation of the scattering light intensity in the order of a few seconds to a few tens of seconds (Fig. 3(a)), which is on the same order to the alternation of ejection directions of polystyrene nanoparticles.<sup>16,19</sup> The fluctuation can also be qualitatively related to the transient restoring and ejecting forces of the laser pulses, the diffusion of the nanospheres during the interval times between consecutive pulses, and the dynamic and statistic of a large number of nanospheres by a large number of repetitive pulses. Those are absent in cw laser trapping.

Since the fs trapping efficiency of the nanospheres is based on the CCD detection with the integrating time of 33 ms, we can estimate that the fs trapping efficiency of the nanospheres is likely related to an average of interaction between large numbers of repetitive pulses and nanospheres. It should be mentioned that, in particular, optical trapping with the fs laser pulses induces bright scattering light with a threefold higher than the average intensity, on short duration within 100 ms, as shown in Fig. 3(b). The blinking scattering light appears throughout the observation window. The blinking feature, which can be considered as unstably gathering of large number of nanospheres in short time, indicates (i) the existence of clusters of nanospheres in the colloidal solution, where high dynamic motions of particles due to fs pulse trapping may induce accompanying flow around the focal spot, leading to the gathering and ejection of the clusters, and (ii) a large number of nanospheres packed in the micron-sized focal spot by fs pulses may optically form a transient assembly, which is then ejected out of trapping site as clusters of nanospheres and re-trapped. Therefore, such blinking feature was not observed under cw laser trapping.

We note that in both laser trapping with fs pulse- and cw-mode, as compared to the polystyrene beads, silica nanospheres do not show any detectable flow of scattering from the trapping site to the surrounding area, though the laser power, numerical aperture of objective lens, the optical detection system, and particle size are the same for the both kinds of nanoparticles. Theoretically, interaction between the polarization and the transient axial and lateral fields produced by high numerical aperture objective lens induces ejecting forces that overcome transient restoring forces perpendicular to the incident laser polarization. Thus, we could expect that the same phenomenon also occurs in fs laser trapping of silica nanospheres. However, the particle density, intrinsic optical properties, and dynamic and statistic of a large number of nanoparticles determine the optical trapping and ejection, as pointed out in our earlier work on the polystyrene beads.<sup>16</sup> Undetectable flow of ejected nanospheres can therefore be attributed to the physical reasons as follows. Firstly, with the refractive index of silica nanospheres and polystyrene beads being  $n=1.44$  and  $1.59$ , respectively, the  $\alpha$  of the nanospheres is actually lower by factor of 2 than that of the polymer beads. Thus, it needs a double laser power of the fs pulses to generate the same level of optical gradient, scattering, and temporal radiation forces on the nanospheres as they are exerted on the polymer beads, but such a condition is difficult to be realized on our optical trapping system. We should also avoid cavitation bubble generation due to high power of laser pulses. Secondly, particle density of the silica nanospheres in the suspension is limited by their aggregation, and the maximum density can be reached is only about the same order to polystyrene beads. With those optical properties, it is difficult to observe the gathering in and ejection of a large number of silica nanospheres out of trapping site. In other words, the flow of the ejected nanoparticles out of the trapping site is material-side phenomenon, rather than pulse-determined phenomenon.

Finally, the results reported in this proceeding, for the first time, quantitatively support the advantages of fs pulse-over cw-mode laser beam in trapping ability on the silica nanospheres, similarly to optical trapping behavior of other Rayleigh particles by laser pulses. This finding also opens some future works, e.g. further evaluation and exploration on the advantage of fs laser trapping, particularly in characteristic peak powers.

## 4. CONCLUSION

We have performed a comparison of optical trapping of 50-nm-sized silica nanospheres using fs pulse- and cw-mode laser beam. We demonstrated that the use of fs laser pulses in optical trapping of the nanoparticles gives higher intensity of bright spot at the focal area, indicating more nanospheres gathered in the trapping site, as compared to cw mode. By considering that the trapping efficiency is related linearly to the number of the nanospheres gathered in the trapping site, we conclude that trapping efficiency of nanometer-sized particles by the ultrashort laser pulses is higher than that by the cw mode at the same laser power. We interpret this finding by means of impulsive peak power of the fs laser pulses, although the CCD detection with integrating time of 33 ms indicates the average efficiency of a large number of repetitive pulses. We conclude by mentioning some potential further evaluation and exploration on the advantage of fs laser trapping by taking into account the transient restoring and ejecting forces, the diffusion, and the dynamic of a large number of nanospheres.

## ACKNOWLEDGEMENT

Funding(s) from the MOE-ATU Project (National Chiao Tung University) from the Ministry of Education of Taiwan, the National Science Council of Taiwan (Grant No. NSC 100-2113-M-009-001), and Foundation of the Advancement for Outstanding Scholarship of Taiwan to H. M. are gratefully acknowledged.

## REFERENCES

- [1] Ashkin, A. "Acceleration and Trapping of Particle by Radiation Pressure" *Phys. Rev. Lett.* **24**, 156-159 (1970).
- [2] Ashkin, A. "Optical Trapping and Manipulation of Neutral Particles Using Lasers" *Proc. Natl. Acad. Sci. USA* **94**, 4853-4860 (1997).
- [3] Hansen, P. M., Bhatia, V. K., Harrit, N., and Oddershede, L. "Expanding the Optical Trapping Range of Gold Nanoparticles" *Nano Lett.* **5**, 1937-1942 (2005).
- [4] Neuman, K. C., and Block, S. M. "Optical Trapping" *Rev. Sci. Instrum.* **75**, 2787-2809 (2004).
- [5] Bartlett, P., and Henderson, S. "Three-Dimensional Force Calibration of a Single-Beam Optical Gradient Trap" *J. Phys.: Condens. Matter* **14**, 7757-7768 (2002).
- [6] Urban, A. S., Lutich, A. A., Stefani, F. D., and Feldmann, J. "Laser Printing Single Gold Nanoparticles" *Nano Lett.* **10**, 4794-4798 (2010).
- [7] Hofkens, J., Hotta, J., Sasaki, K., Masuhara, H., Taniguchi, T., and Miyashita, T. "Molecular Association by the Radiation Pressure of a Focused Laser Beam: Fluorescence Characterization of Pyrene-Labelled PNIPAM" *J. Am. Chem. Soc.* **119**, 2741-2742 (1997).
- [8] Masuhara, H., Sugiyama, T., Rungsimanon, T., Miura, A., and Tu, J.-R. "Laser-Trapping Assembling Dynamics of Molecules and Proteins at Surface and Interface" *Pure Appl. Chem.* **83**, 869-883 (2011).
- [9] Rungsimanon, T., Yuyama, K., Sugiyama, T., and Masuhara, H. "Crystallization in Unsaturated Glycine/D<sub>2</sub>O Solution Achieved by Irradiating a Focused Continuous Wave Near Infrared Laser" *Cryst. Growth Des.* **10**, 4686-4688 (2010).
- [10] Rungsimanon, T., Yuyama, K., Sugiyama, T., Masuhara, H., Tohnai, N., and Miyata, M. "Control of Crystal Polymorph of Glycine by Photon Pressure of a Focused Continuous Wave Near-Infrared Laser Beam" *J. Phys. Chem. Lett.* **1**, 599-603 (2010).
- [11] Tsuboi, Y., Shoji, T., and Kitamura, N. "Optical Trapping of Amino Acids in Aqueous Solutions" *J. Phys. Chem. C* **114**, 5589-5593 (2010).
- [12] Hajizadeh, F., and Reihani, S. N. S. "Optimized Optical Trapping of Gold Nanoparticles" *Opt. Express* **18**, 551-559 (2010).
- [13] Pan, L., Ishikawa, A., and Tamai, N. "Detection of Optical Trapping of CdTe Quantum Dots by Two-Photon-Induced Luminescence" *Phys. Rev. B* **75**, 161305 (2007).
- [14] Sanz, M., de Nalda, R., Marco, J. F., Izquierdo, J. G., Bañares, L., and Castillejo, M. "Femtosecond Pulsed Laser Deposition of Nanostructured CdS Films" *J. Phys. Chem. C* **114**, 4864-4868 (2010).

- [15] Jiang, Y., Narushima, T., and Okamoto, H. "Nonlinear Optical Effects in Trapping Nanoparticles with Femtosecond Pulses" *Nature Physics* **6**, 1005-1009 (2010).
- [16] Usman, A., Chiang, W.-Y., and Masuhara, H. "Polarization-Controlled Scattering in Optical Trapping of Dielectric Nanoparticles with Femtosecond Laser Pulses" *Phys. Rev. Lett.* (2012), submitted.
- [17] Agate, B., Brown, C. T. A., Sibbett, W., and Dholakia, K. "Femtosecond Optical Tweezers for In-Situ Control of Two-Photon Fluorescence" *Opt. Express* **12**, 3011-3017 (2004).
- [18] Shane, J. C., Mazilu, M., Lee, W. M., and Dholakia, K. "Effect of Pulse Temporal Shape on Optical Trapping and Impulse Transfer using Ultrashort Pulsed Lasers," *Opt. Express* **18**, 7554-7568 (2010).
- [19] Usman, A., Chiang, W.-Y., and Masuhara, H. "Optical Trapping and Polarization-Controlled Scattering of Dielectric Spherical Nanoparticles by Femtosecond Laser Pulses" *J. Photochem. Photobiol. A: Chemistry* **234**, 83-90 (2012).
- [20] Bormuth, V., Jannasch, A., Ander, M., van Kats, C. M., van Blaaderen, A., Howard, J., and Schäffer, E. "Optical Trapping of Coated Microspheres," *Opt. Express* **16**, 13831-13844 (2008).
- [21] Ashkin, A. "Forces of a Single-Beam Gradient Laser Trap on a Dielectric Sphere in the Ray Optics Regime" *Biophys. J.* **61**, 569-582 (1992).
- [22] Felgner, H., Müller, O., and Schliwa, M. "Calibration of Light Forces in Optical Tweezers," *Appl. Opt.* **34**, 977-982 (1995).
- [23] Svoboda, K., and Block, S. M. "Optical trapping of metallic Rayleigh particles" *Opt. Lett.* **19**, 930-932 (1994).