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Optical trapping of carbon nanotubes

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Abstract

Optical trapping is a new tool for the manipulation and deposition of single wall carbon nanotube (SWNT) bundles. We present a study on optical trapping and manipulation of SWNT bundles in different environments, aimed at understanding the trapping mechanism. SWNTs are dispersed in water or organic solvents, and a wide range of both ionic and non-ionic surfactants, with different chain lengths, is used. We demonstrate that the surfactant plays a key role in optical trapping, strongly affecting the trapping force. Finally we discuss the calculation of radiation force for quasi-one-dimensional (1D) nanoparticles by means of field expansion in the framework of the T-matrix approach.

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1. Introduction

In the early 1970s Ashkin and coworkers [1,2] demonstrated the possibility of exploiting light to optically manipulate and trap microscopic objects. Refs. [1,2] showed that optical forces can displace and hold micron-sized dielectric particles both in aqueous suspension and in air. The investigation of the trapping capabilities of a single focussed laser beam brought the realization of the so-called *optical tweezers* [3].

Nowadays optical traps find application in many fields of biology and physics [4]. Optical tweezers are important tools to sort and organize cells, control bacterial motion, measure linear and torsional forces, alter biological structures via modification of cellular membranes, cellular fusion, or the interaction between red blood cells and viruses [5]. In physics, the possibility to apply pico-Newton forces to micro- and nanometre-sized particles and, at the same time, to measure their displacements with nanometric precision is crucial. It allows investigation of colloids and polymers properties, of the visco-elastic properties of complex fluids and in general can be applied to a wide variety of soft-matter systems [6].

Single wall carbon nanotubes (SWNTs) are currently the focus of a wide range of research areas, due to their unique properties that arise from their quasi-one-dimensional (1D) character. They easily form ropes or bundles [7–9] due to strong Van der Waals interactions [10], thus much effort has been made to stably disperse SWNTs in a variety of solvents [11–17]. Stable dispersions of individual SWNTs were achieved in water with the aid of surfactants [11], polymers [12] and DNA [13]. Surfactants form micelles that create a hydrophobic environment in which SWNTs are encapsulated [11], whilst polymers and DNA are reported to wrap SWNTs on the sidewalls [12,13], thus facilitating dispersion and individualization. SWNT dispersion and individualization without surfactant have also been reported in amide solvents, especially *N*-methylpyrrolidone (NMP) [14–17].

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Very recently optical trapping of SWNT bundles in aqueous solution was demonstrated [18–20], opening the way to a novel approach for their manipulation and top–down organization. Here, we present an investigation on optical trapping and manipulation of SWNTs dispersed in different liquid environments, checking for trapping stability and evaluating the minimum trapping power required. We demonstrate that the combination of surfactant and solvent plays a crucial role in determining the stability of the optical trap, and discuss the perspectives for a theoretical understanding of optical trapping of 1D mesostructures by the use of electromagnetic scattering theory [21].

2. Materials and methods

Experimentally, optical trapping is accomplished by tightly focusing a laser beam through a high numerical aperture lens (we use an Olympus, Uplan FLN 100× microscope objective with NA = 1.3). In our apparatus (Fig. 1) we have a 830 nm, 150 mW laser diode (Sanyo DL-8032-01) as a radiation source. The laser beam is circularized by a pair of anamorphic prisms (P). Beam steering is attained through a pair of orthogonally mounted, computer controlled galvomirrors (GM). A 1:4 telescope is used to enlarge the beam so as to overfill the microscope objective back aperture and to image the GM into its back aperture. This guarantees control over laser trap position in the sample chamber without loss of power. Furthermore dynamic multiple traps and time-averaged traps can be created via time sharing of the trapping beam [22]. The optical set-up is built around a commercial (M.A.D. Education) inverted microscope. The inverted configuration gives more stability because it helps to counteract gravity with radiation pressure for weak traps. Samples are placed in a small chamber attached on a piezo-stage (Physik Instrumente, P-517 series) with 1 nm resolution. Finally, a CCD camera is used to image the trapped particles. Image calibration is achieved by optical trapping size-standard latex beads (Polysciences).

Force sensing is achieved through back focal plane interferometry [23]. Scattered and unscattered light by the trapped particle is collected by the condenser lens (L2). The back focal plane of the condenser is then imaged with another lens (L1) onto a four quadrant photodiode (QPD). The QPD is oriented with the polarization axis of the laser beam in order to have sensitivity over polarization effects on the optical trap [24]. The outputs from all quadrants are processed through an analog circuit board that generates electrical signals proportional to the trapped particle displacement in the x, y and z spatial directions. The analysis of these signals gives a wealth of information on trapping potential, spring constants, micro-rheology and fluidity, and more generally on Brownian motion spectroscopy [25,26].

All our samples are prepared using purified HiPCO SWNTs purchased from Carbon Nanotechnologies Inc. 1.5 mg SWNT powder is dispersed in 15 ml of pure solvent such as ethanol, chloroform, NMP or in water solutions with 15 mg surfactant of different length and polarity, such as sodium dodecyl sulphate (SDS), sodium dodecyl benzene sulphonate (SDBS), Triton X-100. All solutions are ultrasonicated (Diagenode Bioruptor ultrasonicator) for 1 h (H_2O) or 2 h (NMP) and filtrated through 0.5 μm retention filter [16,27]. This ensures breaking and removal of residual large bundles and ropes. When surfactants are employed, micelle formation gives long-term stability to the solution.

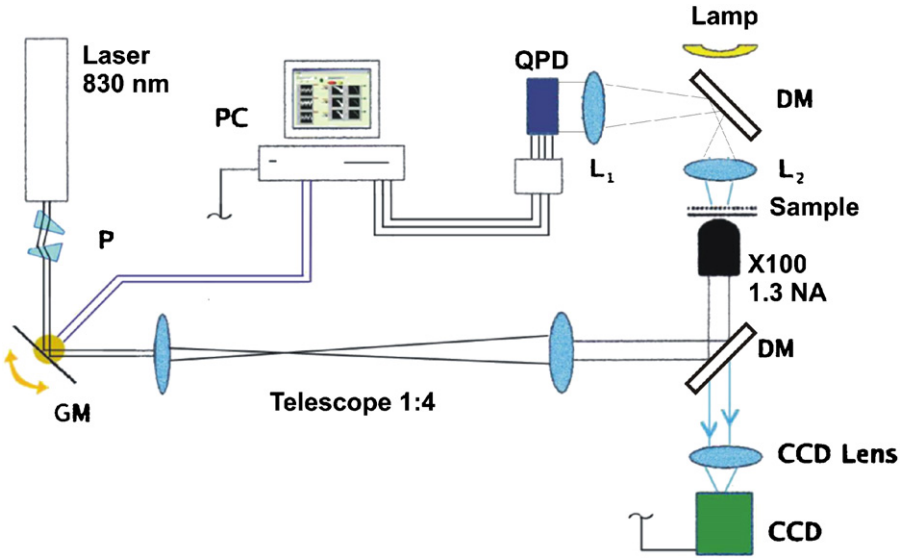

Fig. 1. Optical tweezers experimental set-up. (P) Anamorphic prisms, (GM) galvomirrors, (DM) dichroic mirror, (L2) condenser lens, (L1) detection lens, (QPD) quadrant photodiode.

3. Results and discussion

Different sample solutions are used to check for optical IR trapping stability. A summary of the experiments carried out with different solvents and surfactants combinations is listed in Table 1.

SWNTs bundles are not trappable when dispersed in pure solvents such as chloroform, ethanol or NMP. Conversely, when a surfactant is used for SWNTs dispersion, stable optical trapping can be achieved. When using SDS solutions, CNTs are trapped and can be manipulated with a minimum trapping power of 4 mW. The use of SDBS, a longer chain surfactant, reduces the trapping power threshold to 1 mW (Table 1). On the other hand when Triton X-100 is used, nanotubes are repelled from the trap centre and pushed away from the focal region. This evidences that surfactants play a crucial role in stabilizing optical trapping of nanotube solutions. On the other hand not all surfactants lead to stable trapping, indicating that the physical–chemical properties of the surfactants affect the trapping mechanism.

Table 1
Comparison of optical trapping of carbon nanotubes in different fluidic environments

Sample	IR trapping	Min. power (mW)
Chloroform	No trapping	–
NMP	No trapping	–
Ethanol	No trapping	–
H_2O + SDS	Stable	4
H_2O + SDBS	Stable	1
H_2O + Triton X-100	No trapping	–

Different behaviours in different aqueous solutions clearly shows a role of the surfactant used for dispersing carbon nanotubes in water.

It is reported that surfactants form core–shell micelle structures, with a nanotube core (1–2 nm) and a surfactant shell of similar transverse size [11]. Thus the optical properties of the core–shell have to be taken into account if a correct analysis of optical trapping has to be attempted. In particular the different dynamic dielectric constants of the surfactant-nanotube micelles could be the key parameter for optical trapping stability, and will be the focus of further investigations.

We now consider the potential of our optical tweezers to create dynamic patterns. We first use latex beads as model for our experiments to ensure correct calibration of the dynamic patterns. Figs. 2(a) and (b) show two applications of dynamic optical traps using both spherical and non-spherical latex beads. In (a) the GM are computer controlled to fast jump (400 Hz) between two positions so to create two stable optical traps. At the same time a slow modulation (below 100 Hz) is superposed to the GM driving voltages so as to ensure a controlled rotation of the two trap positions. In (b) a non-spherical double latex bead (Polysciences) is horizontally trapped by a fast linear scan (400 Hz) and rotated by a controlled slow modulation of the linear trap axis.

Figs. 2(c)–(f) show dynamic manipulation of SWNTs dispersed in water with SDS surfactant. In (c) the SWNTs are trapped in a circular dynamic trap obtained by sinusoidal out-of-phase fast scanning (400 Hz) of the GM. The SWNTs follow the laser beam pattern and lay strongly trapped in the high-intensity part of the beam profile.

In Figs. 2(d)–(f) we trap and stretch SWNTs using a linear scan and creating a dynamic linear tweezer (the red dashed line in Fig. 2 identifies the trapped SWNT bundles). In principle any pattern can be created by computer control of the GM. Such patterns could then be transferred

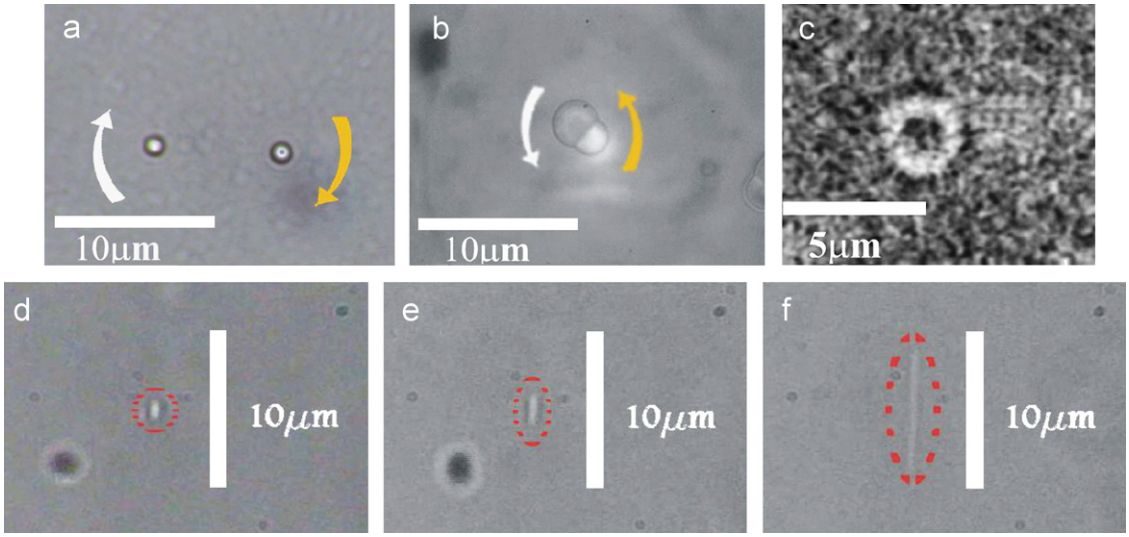

Fig. 2. Pictures of optically trapped latex beads and carbon nanotube bundles in dynamic traps. (a) Two beads in a dynamic double trap obtained by fast scanning the laser beam with the galvomirrors. (b) Axisymmetric double-shaped bead in a rotating linear trap obtained by composing a fast and slow modulation to the galvomirrors. (c) Carbon nanotube bundles collectively trapped in a dynamic circular trap. (d)–(f) Image sequence of SWCNT bundles collectively trapped and stretched in a dynamic linear optical trap. Red dashed line identifies the trapped bundles.

on a substrate by moving the trap vertical center onto the microscope slide.

We now discuss a theoretical approach for optical trapping of non-spherical particles [28], which could be useful to understand the trapping of nanotubes, because it enables to treat a core–shell case (analogous to surfactant coated nanotubes) by using tabulated dynamic optical constants. This helps understanding the different trapping behaviours in Table 1. We use the Maxwell stress tensor, in the framework of the transition matrix approach [29] that, in principle, does not require trapped particles to be spherical or small with respect to the wavelength.

In general the radiation force exerted on particles is given by the integral [30]

$$\mathbf{F}_{\mathrm{rad}} = r'^2 \int_{\Omega'} \hat{\mathbf{r}}' \cdot \mathbf{T}_{\mathrm{M}} \mathrm{d}\Omega', \tag{1}$$

where the integration is over the full solid angle, r' is the radius of a large sphere centred at $\mathbf{R}_{O'}$ surrounding the particle centre, and $\mathbf{T}_{\mathrm{M}}$ the time averaged Maxwell stress tensor.

When the incident field is a polarized plane wave, the components of the radiation force along the direction of the unit vector $\mathbf{v}_\zeta$, are given by

$$\mathbf{F}_{\mathrm{rad}\,\zeta} = -\frac{r'^2}{16\pi} \int_{\Omega'} (\hat{\mathbf{r}}' \cdot \hat{\mathbf{v}}_\zeta)[n^2(|\mathbf{E}'_{\mathrm{s}}|^2 + 2\mathbf{E}'^{*}_{\mathrm{I}} \cdot \mathbf{E}'_{\mathrm{s}}) + (|\mathbf{B}'_{\mathrm{s}}|^2 + 2\mathbf{B}'^{*}_{\mathrm{I}} \cdot \mathbf{B}'_{\mathrm{s}})]\mathrm{d}\Omega', \tag{2}$$

where $\mathbf{E}_{\mathrm{S}}$ and $\mathbf{B}_{\mathrm{s}}$ are the fields scattered by the particle.

Expanding the incident field in a series of vector spherical harmonics with (known) amplitudes $\boldsymbol{W}$, the scattered field can be expanded on the same basis with amplitudes $\boldsymbol{A}$. The relation between the amplitudes $\boldsymbol{A}$ and $\boldsymbol{W}$ is given by $\boldsymbol{A} = \mathbf{S}\boldsymbol{W}$, where $\mathbf{S}$ is the transition matrix of the particle [29].

In this framework, any non-spherical particle can be modelled as an aggregate of spheres with size well below the radiation wavelength. We calculate in a given frame of reference the elements of the $\mathbf{S}$-matrix through the inversion of the matrix of the linear system obtained by imposing to the fields the boundary conditions across each of the spherical surfaces [31,32]. A comprehensive treatment of the calculation of the transition matrix can be found in Ref. [21]. Here we stress that these elements turn out to be independent from both the direction of propagation and the polarization of the incident field [21]. Thus they do not change when the incident field is a superposition of plane waves with different directions of propagation, i.e. the description of a focused laser beam in the angular spectrum representation [33]. This establishes a complete formalism based on the transition matrix approach that we can apply to optical tweezer experiments.

First we calculate the optical trapping of individual latex beads like the ones shown in Fig. 2(a). To match the experiment we include in the theory all possible aberration and field corrections. We perform calculations for several beads with different transverse diameters, both below and above our experimental trapping wavelength of 830 nm. We find an excellent agreement between theory and experiments by comparing the trapping efficiencies and polarization effects [28]. We then consider a binary cluster (such as that in Fig. 2(b)). We find a dependence of the trapping position on cluster orientation. For size much smaller than the trapping wavelength, the cluster is stably oriented along the polarization axis. Otherwise the radiation torque changes the cluster orientation along the optical axis (propagation direction), as observed for the cluster in Fig. 2(b).

A complete theory for nanotubes was never developed before. However we can give some estimations based on what we learned from optical trapping of individual bead and binary clusters. Due to the very small nanotube transverse size, polarization effects will also be important when linearly polarized light is used, as observed in Fig. 2(d). This can lead to different stability regimes depending on the length-to-diameter ratio of the nanotube. When this ratio is shorter than a critical value the object will align with the polarization direction. When longer, the radiation flux will align the nanotubes with the propagation direction of the laser beam. Furthermore, we expect a dramatic change in trap anisotropy (radial–azimuthal aspect ratio of the trap) due to the elongated structure of the trapped particle.

4. Conclusions

We have shown how optical trapping and manipulation of SWNTs can be used to create and shape SWNTs structures in aqueous solutions, with a wide range of ionic and non-ionic surfactants. In the case of SWNTs dispersed in water we find that the trapping force depends on the type of surfactant used to dissolve them.

We discussed the calculation of radiation force on non-spherical particles by means of field expansion in the framework of the T-matrix approach. This method paves the way for understanding optical trapping on nanotubes, where one dimension is much larger than the trapping wavelength while the other two are much smaller.

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