Photodegradation of Optically Trapped Polystyrene Beads at 442 nm

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Abstract—Polystyrene particles of different sizes are optically trapped with a gaussian beam from a He-Cd laser operating at 442 nm. The particles are observed to exhibit luminescence after a certain trapping time followed by an escape from the optical trap. The observed luminescence is explained in terms of the photodegradation of the polystyrene backbone. It is speculated that these chemical modifications also play a role for the escape of the particles from the trap. Variations of the particle size and the laser power show that these parameters have a great influence on the observed phenomena.

Keywords—Photodegradation, Polystyrene particles, Optical trapping

I. INTRODUCTION

OPTICAL traps use a tightly focused laser beam to immobilize and manipulate microparticles or biological cells. A dielectric particle with a refractive index greater than that of the surrounding medium along the focused laser beam path experiences two kinds of forces. The first one is the gradient force directed towards the region of highest intensity and the second one, the scattering force that pushes the particle along the direction of light propagation. In terms of the radius of the specimen with respect to the electromagnetic wavelength, there are two limiting cases: The Rayleigh regime $(r \ll \lambda)$ and the geometric regime $(r \gg \lambda)$, where r is the particle radius[1]. In the geometric regime, the force acting upon the particle can be explained in terms of ray optics model and it depends upon the particle shape. According to the ray optics model, the change in momentum of the individual ray being refracted at the particle´s surface is the opposite of the momentum change of the particle. When the particle is located symmetrical with respect to the incoming beam, the net momentum transfer is zero, identified with the position of zero trapping force [2]-[3]. In the case of the Rayleigh regime, a particle is considered as a dipole and the electromagnetic field of the laser radiation pulls it towards the high intensity region, where the induced dipole has minimum energy. However, the scattering force acting in the direction of propagation of light pushes the dipole away.

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When the gradient force towards maximum intensity exceeds the scattering force, the particle is stably trapped [2]. The gradient force depends on the laser power and numerical aperture of the focusing lens used for trapping. If the particle size is comparable with the wavelength of the trapping beam, neither the ray optics model nor the dipole approximation model is valid. In this case, more complicated theoretical approaches are needed to explain the behavior of the particle [4]. A detailed review about the theory, applications and recent developments in this field can be found elsewhere [5]-[6]. The potential applications of this technique range from colloidal physics to biochemistry. Depending upon the excitation technique as well as on the experimental setup, different types of optical trapping and optical tweezers are proposed [7]-[8]. Amongst these, the single beam optical trapping technique is still the most popular due to its simplicity, robustness and compatibility with modern microscopy techniques.

In this work, we report the trapping of polystyrene beads and the subsequent behavior of the particle in the optical trap at 442 nm from a He-Cd laser. To the best of our knowledge, this is the first attempt of trapping a particle at 442 nm. The use of shorter wavelengths offers advantages such as a smaller trapping volume, an increased trapping strength and trapping of smaller particles. Being a widely used material in industry as well as in basic research, understanding the response of this polymer under intense laser radiation is extremely important.

II. EXPERIMENTAL SETUP

The experimental setup used for the present studies is shown schematically in Figure 1.
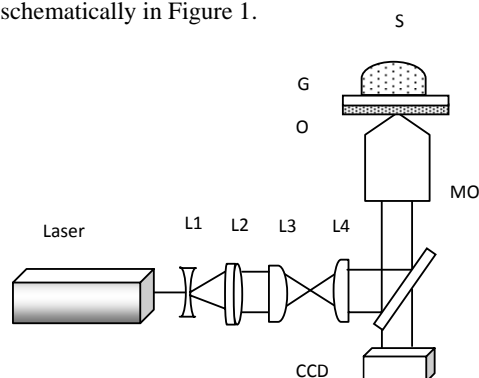

Fig. 1 Schematic view of the experimental setup

The 442 nm from the He-Cd laser (Kimmon Koha Co.Ltd.) is used as the optical tweezer. The linearly polarized gaussian beam with a spot size of 1mm at 442 nm is expanded using an UV beam expander system (L1 and L2 in the setup from Bernhard Halle Nachfolger GmbH, Germany). The laser beam is expanded to a spot size of 9 mm so that it will overfill the back aperture (7.6 mm) of the microscope objective, MO (Nikon Apo TIRF, 100X, NA 1.49), incorporated in a Nikon Microscope (Nikon Eclispse, Ti-U). The input laser radiation is collimated using two plano-convex lenses, L3 and L4 (Edmund Optics, Germany) with a focal length of 25 cm in a 1:1 telescopic arrangement. Such expanded plane waves being focused through the microscope objective result in a diffraction limited spot size at the focal point with large intensity gradient. The particles used in this study are dispersed polystyrene beads with diameters of 2 µm (Micromer 01-00-203) and 5 µm (Micromer 01-00-503) from Micromod, Germany. The dispersed particles are surfactant free and charge stabilized. The focal region is monitored and the images were collected using an Andor UV-VIS CCD camera (ANDOR iXon, Model DU-897D-CSO-UVB) under bright light illumination from the Nikon Microscope. The input laser beam at the back aperture of the microscope objective is measured using a Newport laser power meter (Model1918-C). An oil immersion objective (Nikon 50, Type A oil, MXA 20234 having a refractive index of 1.515) with a transmittance around 62% at 442 nm is used. The aqueous particle dispersion is placed on the surface of a microscope cover slip.

III. RESULTS AND DISCUSSION

A specific particle is immobilized in three dimensions using the gradient force from the He-Cd laser. Such an image of the optically trapped particle with a size of 5µm is shown in Figure 2 (a). However, after a certain residence time in the optical trap, the polystyrene particle exhibits luminescence as shown in Figure 2 (b).
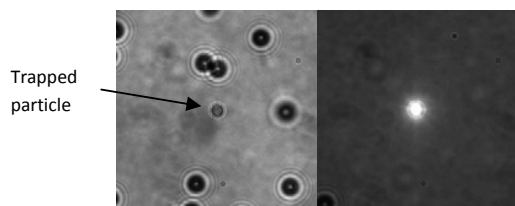

Fig. 2. Optically trapped polystyrene particle (a) Immediately after trapping (b) Exhibiting luminescence

Although there has been a report on trapping of polystyrene particles at lower wavelengths of the visible spectrum (410 nm and 413 nm), the authors have not been able to observe any luminescence from the particle [9]. It is important to mention here that in their work, no attempts have been made to investigate the temporal stability of the optical trap and the influence of laser beam power. Moreover, the laser beam used in the present study has Gaussian profile in comparison to the beam with circular profile employed previously [9]. The observed luminescence can be attributed to the photodegradation of the polystyrene molecules [10] under intense radiation at 442 nm. A polymer molecule is said to be degraded when its molecular weight changes, resulting in changes of its physical properties. The common mechanisms that can result in photodegradation of a polymer molecule are: cross-linking, double-bond formation in the backbone of the polymer and chain scission (with or without oxygen incorporation). Polystyrene is reported to exhibit photodegradation under illumination with diffuse light having a wavelength smaller than 360 nm. There is no report about radical formation and subsequent photodegradation of polystyrene under diffuse illumination with a wavelength greater than 440 nm. However, it is well known that polystyrene exposed to sunlight for a long duration develops a yellow color due to the formation of polyene type structures in the polymer. It is also reported that the degradation of the polymer is sensitive to temperature and environment [11].

In the case of an optically trapped polystyrene particle, one can expect photodegradation due to the spatial localization of photon flux and the increase in temperature of the particle. Being a polymer with very low thermal conductivity 0.08W/mK [12], the observed luminescence in the present study may be a combined effect of localized temperature rise and photon induced damage in the polymer chain. The threshold energy required to break the C-H bond without considering the radical stabilization is 71 kcal/mol [13]. But the stabilization of the C-H radical species by a nearby double bond in the polystyrene backbone can significantly lower the activation energy for the production of the radical. The energy of the radiation employed in the present study corresponds to 65 kcal/mol (counting one photon per molecule), which is close to the isolated C-H bond-breaking energy. Hence there is a high possibility that a C-H bond near a double-bond on the back bone chain of polystyrene can be broken under irradiation at 442 nm. The high photon flux could provide the possibility that this event can occur with the phenyl group directly with impurities such as peroxides (oxygen incorporated into the polymer chain during the polymerization process), or regions of conjugation in the polymer. Thus bond stabilization in combination with high photon fluxes provides a means of generating polystyrene radicals as shown in Figure 3.

The hydrogen radical formed in this way is free to move down in the polymer backbone to abstract a hydrogen atom from a second carbon atom. A lower energy state for hydrogen abstraction can be found in the vicinity of the double bond or conjugated region of the backbone since radicals are stabilized by resonance. The radical recombination results in the formation of a double bond in the backbone. This series of double bonds in the polymer chain is responsible for the observed luminescence. It has already been reported that a polymer backbone with more than six double bonds can

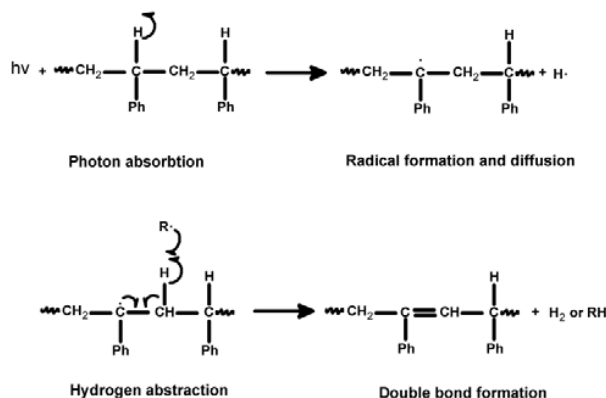produce a polyene chromophore with an emission wavelength greater than 500 nm [14].

Fig. 3 Photodegradation path of the polystyrene molecule

The important feature to be noticed here is that this luminescence from the particle can be observed only after a finite residence time in the optical trap. Although the radical formation following photon absorption can be instantaneous, the diffusion of hydrogen radicals, the subsequent hydrogen extraction and double-bond formation require a certain amount of time. In order to understand the influence of the laser power on the initiation of luminescence, the particle is trapped with different power levels. The initiation time required to exhibit a visible luminescence in the CCD sensor is plotted as a function of input power at the back aperture of the microscope objective is shown in Figure 4.
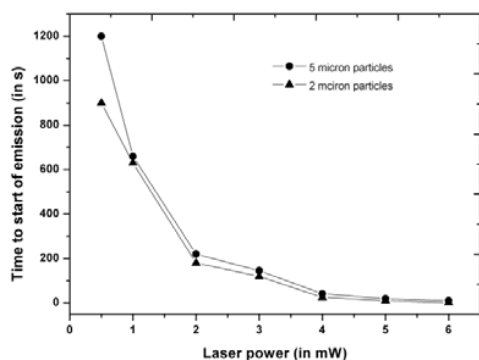

Fig. 4 Effect of particle size and laser power on luminescence initiation time from optically trapped (at 442 nm) polystyrene particles

It is clear from the Figure 4 that for both types of particles, the initiation time decreases drastically (almost exponentially) with increasing laser power. At lower power levels, the particle size also plays an important role. In the case of optically trapped micron size particles, the particles are normally trapped away from the focal point at distance corresponding to the particle size. As a result, the 2 micron particles experiences large radiant flux density in comparison

to the 5 micron particle. It has already been reported that the rate of production of hydrogen free radicals in the polystyrene molecule is proportional to the light intensity [14]-[15]. The higher rate of production of free hydrogen radicals results in shorter initiation time for the luminescence. The conventional reciprocity law ($I.t$ = constant), which states that the progress of a photochemical reaction mechanism depends only on the absorbed energy. i.e. the product of light intensity I and exposure time t, fails to apply to most reactions [16]. A more general relationship applying to the photodegradation of polymers is Schwarzchild´s law, reading $I^p t$ = constant, where p is the Schwarzchild coefficient [17]. The reported values of this coefficient for polystyrene under polychromatic illumination range from 0.6 to 0.75 [16]. Accordingly, in the case of an optically trapped polystyrene particle, the initiation time for the luminescence is given by $t = kI^{-p}$, where k is a constant. This dependence explains the observed decrease of luminescence initiation time with increasing laser power. The difference in luminescence initiation time for particles with different sizes at low laser power levels can be explained in terms of the differential form of Schwarzchild´s law $\Delta t = k(-p)I^{-p-1}\Delta I$. As explained earlier, an optically trapped smaller particle experiences a high intensity. However, since $\Delta t \propto \frac{1}{I^{p+1}}$ this difference decreases quiet rapidly with increasing laser power. This explains why both particles exhibit almost the same initiation time for the luminescence at 6 mW.

In contrast to the optical trapping of polystyrene beads at 488 nm reported earlier, in the present study the particle escapes from the optical trap after exhibiting luminescence over a certain time. Figure 5 shows the trapping time as a function of the input laser power at the back aperture of the microscope objective.
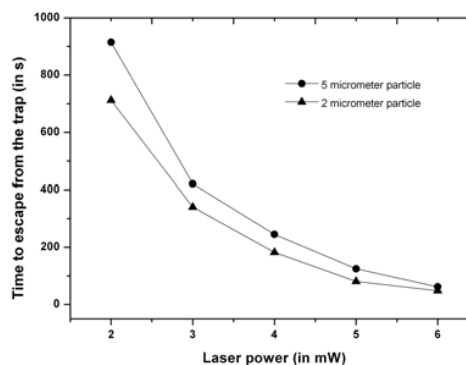

Fig. 5 Effect of particle size on trapping time (at 442 nm)

In the case of a conventional optical trap, the trapping stability increases with increasing power of the trapping beam. However, in the present case the reverse is found. A number of different effects could explain this observation. Apparently,

the irradiation with light changes the chemical structure of the polymer beads. Chemical modifications could bring along an increase in light absorption, leading to radiation pressure forces driving a particle away from the laser focus. On the other hand, since the refractive index depends on chemical composition, the refractive index contrast being the origin of the gradient force could get reduced.

IV. CONCLUSIONS

A temporal response study of an optically trapped polystyrene particle at 442 nm indicates that the particle undergoes photodegradation and escapes out of the trap after certain residence time. Photodegradation accompanied by luminescence. The dependence of the initiation time for the luminescence on the laser power and particle size can be explained based on Schwarzschild´s law. By contrast to the usual relationships known from optical trapping, the trapping time decreases as a function of laser power. This observation could be explained via chemical modifications occurring in the particle. In summary, it can be stated that a number of novel and perhaps unexpected phenomena occur when the polystyrene particles are trapped at 442 nm instead of the usual near-infrared wavelengths.

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