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Investigation of optical limiting in Cobalt nanoparticles synthesized by laser ablation

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ABSTRACT

We present synthesis of Cobalt nanoparticles dispersed in toluene by laser ablation and their optical limiting properties with nanosecond laser pulses. Absorption spectra and concentration dependent optical limiting studies on nanoparticles indicate it as a versatile optical limiter. Cobalt nanoparticles show better optical limiting compared to the reference optical limiter fullerene C_{60}. Optical limiting threshold of Cobalt nanoparticles is about three times less than that of C_{60}. Z-scan experiments, angle dependent scattering, intensity dependent transmission, and temporal profile measurements indicate that the non-linear absorption, nonlinear scattering and thermal nonlinear refraction are responsible for optical limiting behavior of Cobalt nanoparticles.

1. Introduction

The quest for potential optical limiters in the protection of human eyes and sensitive optical instruments from exposure to intense laser light has motivated many researchers to synthesize and examine new materials for superior optical limiting (OL) characteristics [1,2]. The mechanisms that cause OL have different origins. Reverse saturable absorption (RSA), which takes place due to the high absorption from excited states, is responsible for OL in colloidal metal compounds and fullerenes [3,4]. Strong non-linear refraction causes OL in a number of inorganic clusters [5]. Two-photon absorption is responsible for OL in semiconductor structures [6]. Excited state-induced non-linearity is one of the main sources of optical non-linearities which has potential for OL applications [7]. On the material front, synthesis of nano-particles of various materials has received much attention due to possibility of enhancement in their nonlinear optical properties. Optical limiting properties of various nanoparticles including Ag, Au, CdS, Carbon and carbon nanotubes have been widely studied in recent years for their potential use in nonlinear optical devices [8–11].

Recently, laser ablation of solid targets submerged in liquid has attracted increased attention because of its simplicity and potential application in synthesis of nanoparticles directly in liquid. Laser ablation has been widely used for the production of nanoparticles of Au, Ag, Ti, Si, Pt, Ni, Co, and Cu in water and other organic solvents [12–14]. Synthesis of Co nanoparticles has been previously reported with laser ablation using nanosecond pulses at 355 nm and 532 nm wavelengths [15,16]. Tsuji et al. [15] have reported nano and micro size particles in the synthesis at 355 nm using metal powder, while Zhang and Lan [16] have reported much smaller size nanoparticles of size ~25 nm with stabilizing agent PVP and metal target at 532 nm. We have synthesized Co nanoparticles (20–200 nm) with laser ablation at 1064 nm in the solvent itself without any stabilizing agent. There are very few reports on optical limiting properties of Co based systems [17–19]. Ganeev et al. have shown optical limiting in Co doped polymers with picoseconds laser pulses [18]. Reverse saturable absorption and self-defocusing are reported as responsible phenomena for optical limiting at 532 nm wavelength. With nanosecond laser pulses optical limiting properties have been reported in Co nanowires [17] and; pristine Co nanotubes and Co in carbon nanotubes [19]. Optical limiting performance is shown to be comparable or better than carbon nanotubes. Nonlinear scattering is believed to make dominant contribution in Co nanowires [17]. Recently, we have studied optical limiting performance of Co derivative of meso-tetraferrocenyl porphyrin which is comparable to that of fullerene C_{60} [20]. To the best of our knowledge optical limiting in Co nanoparticles has not been explored. Hence, it becomes interesting to investigate optical limiting properties of Co nanoparticles and explore in detail the mechanisms contributing to the optical limiting behavior.

In this Letter, we present synthesis, characterization and optical limiting studies of Cobalt nanoparticles (Co NPs). Toluene is used as a base fluid because the reference medium fullerene C_{60} is most widely reported in this solvent and also it has good temperature dependent refractive index variation capacity, desirable for optical limiting behavior. Optical limiting in Co NPs is studied at different

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concentrations. The Co NPs showed better optical limiting performance than the standard optical limiter C_{60} both in the same solvent i.e. toluene. To explore the mechanisms responsible for the optical limiting behavior of Co NPs we performed near field intensity dependent transmission, angle dependent scattering, Z-scan experiments with nanosecond laser pulses, temporal profile of laser pulses through the samples and far field intensity dependent transmission through an aperture. The results indicate that apart from the non-linear scattering, nonlinear absorption and thermal nonlinear refraction also contribute to the optical limiting behavior in Co NPs. The broadband spectral response indicates that Co NPs can be used as a tunable optical limiter over a wide visible wavelength region.

2. Experimental

The Co NPs were synthesized by pulsed laser ablation in toluene using a Q-switched, Nd:YAG laser at the wavelength of 1064 nm. Nanosecond laser pulses at a repetition rate of 1 Hz were focused with a 10 cm focal length lens on a polished Co target immersed in toluene for 2 h. The Co NPs are produced by pulsed laser ablation at the position of interaction of laser pulse with the target. After sometime, produced NPs start scattering the incident laser beam hence curtailing the further generation of NPs. The petty dish containing liquid and target was rotated with the help of a stepper motor to overcome this problem and for homogenizing the solution. The NPs were characterized by absorption spectroscopy and Atomic force microscopy (AFM).

Atomic force microscopy (AFM) was done to measure sizes of Co NPs after drying the samples on GaAs substrates under ambient conditions. Surface topographies of Co NPs samples were imaged using a multimode scanning probe microscope (NT-MDT, SOLVER-PRO, Russia). AFM measurements were carried out in a non-contact mode using silicon cantilever tips having radius of curvature ~20 nm and a spring constant 5.5 N/m with a resonant frequency of 190 kHz under ambient conditions. Top surface was electrically grounded during measurements. Phase image is also recorded because phase information obtained during non-contact mode using oscillating silicon cantilever tips is considered to be much more sensitive than topographic information. Mean length and width of individual nano clusters were estimated using the imaging software (SOLVER-PRO). Analysis was carried out at various places on the surface of samples.

Optical limiting experiments were carried out with linearly polarized frequency doubled Q-switched Nd-YAG laser pulses with pulse duration of 28 nsec (FWHM). Optical limiting characteristics were recorded in Co NPs samples having 50%, 70% and 80% linear transmission at excitation wavelength of 532 nm. For comparison of optical limiting performance between the Co NPs and fullerene C_{60}, the transmission of both the samples in toluene was kept 70% at 532 nm. Input laser beam was focused using a 20 cm focal length lens on a 5 mm path length cell containing the sample. The incident energy on the sample was varied with the help of neutral density filters. Angle dependent scattering was measured by keeping the photodiode 30 cm away from the sample at different angles. Open and closed aperture Z-scan experiments were also carried out with nanosecond laser pulses. 10% transmission aperture was used for closed aperture Z-scan measurements. Proper care was taken to avoid the background optical noise while recording the scattered signal. Toluene was used as reference in all the experiments to exclude solvent dependent effects.

3. Results and discussion

Linear optical absorption spectra of the samples containing Co NPs are shown in Figure 1. Pure toluene shows negligible absorption in the visible region. The presence of a hump in the transmission spectra near 420 nm is an indication of formation of Co NPs [18]. The direct evidence of formation of the nanoparticles is observed in the AFM figure. The large size variation observed in Figure 2 may also result in a very broad surface plasmon resonance (SPR) peak. Based on Mie theory, Creighton and Eadon [21] have reported the calculated optical spectra for Co NPs showing a very weak and broad SPR peak in the range of 250–400 nm. There have been reports on synthesis of Co NPs by laser ablation at 355 and 532 nm [15,16]. Since, Co NPs exhibit absorption feature in visible wavelength region, hence to avoid re-absorption of laser beam by the produced nanoparticles, we have used 1064 nm wavelength for ablation. Moreover, it has also been reported earlier that in a focusing geometry nanoparticles production yield is more with 1064 nm than its second and third harmonic [22].

The representative topographic and corresponding phase images of Co NPs on GaAs are shown in Figure 2. Simple topographic image shows presence of large number of small particles and also few large particles. However, the phase image clearly shows that actually large size particles consist of several small Co-NPs. Moreover isolated small size particles of sizes 20–200 nm are clearly seen in the phase image.

The transmission through the sample with variation in input energy was measured in two geometries. In geometry (i), the transmitted beam was collected in the far field through an aperture with 90% transmission placed in front of the photodiode. In this geometry, decrease in the transmission would account for nonlinear absorption, defocusing and scattering originating from absorption induced thermal effects. Figure 3 shows the experimentally observed variation of transmitted energy with input energy for Co NPs samples with different linear transmissions namely 80%, 70% and 50% at 532 nm wavelength in geometry (i) i.e. optical limiting geometry. At low energy, all the samples exhibit linear transmission. With increase in input energy, output starts deviating from linear transmission and shows saturation trend at high input energy leading to strong optical limiting action.

To compare the performance of Co NPs, the same experiment was performed with fullerene C_{60} solution in toluene with 70% linear transmission at 532 nm and the experimental data is shown in Figure 3. Output energy is high in C_{60} compared to Co NPs. In other words decrease in the transmission with increase in input energy is more for Co NPs compared to C_{60}, indicating superior limiting behavior in the case of former. It may be further noted that even

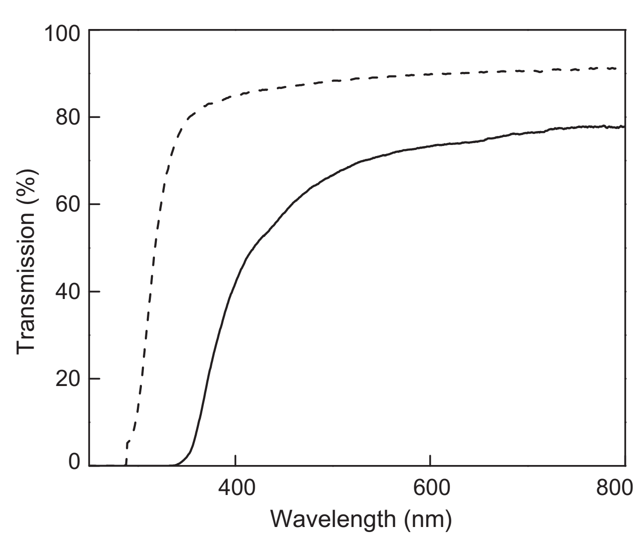

Figure 1. Transmission spectra of Co NPs in toluene (solid line) and toluene (dashed line).