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Solvent-dependent optical limiting behavior of lead nanowires stabilized by [60] fullerene derivative

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ABSTRACT The optical limiting performance of lead nanowires in chloroform, ethanol and dimethylformamide was measured with 532-nm, 8-ns-duration laser pulses. Experiments showed that the optical limiting is strong and solvent dependent. The origins and the solvent effect of the optical limiting were analyzed. It is proposed that the absorption-induced scattering is the main role responsible for the optical limiting behavior and the solvent effect.

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1 Introduction

There has been an increasing interest in the design and fabrication of one-dimensional nanostructures because of their potential application in electronic, magnetic and optical devices [1–8]. As a superconductor, metal nanowires have attracted considerable attention in recent years [4, 5]. Yi and Schwarzacher and Michotte et al. reported the synthesis of Pb nanowires embedded in track-etched polycarbonate membranes by using electrodeposition and investigated the superconductivity of the Pb nanowires [4, 5]. Tian et al. reported the synthesis and characterization of conducting single-crystal Sn nanowires [6]. On the other hand, research of magnetic properties of metal nanowires including Fe, Co and Ni was also conducted by some scientists [7, 8].

To our knowledge, however, up to now no investigation of optical limiting properties has been made in metal nanowires. In this paper, we report the new findings of large optical limiting effects of Pb nanowires stabilized by a fullerene derivative. The origins of the optical limiting and the effect of the solvent on optical limiting are discussed.

2 Sample and experiments

The sample studied in our experiments is a Pb nanowire protected by a fullerene-substituted oligopyridine (C_{60}TPY), denoted as C_{60}TPY-Pb for simplicity. C_{60}TPY synthesized according to [9] has molecular structure as shown in Fig. 1. C_{60}TPY-Pb nanowires were synthesized by reducing a lead complex using sodium borohydride in the presence of C_{60}TPY; details of the chemical synthesis are given elsewhere [10]. The transmission electron microscopy (TEM) image in Fig. 2 shows the actual presence of self-assembled Pb nanowires with length in the range of 0.1–0.7 μm and diameter in the range of 30–50 nm. The UV-VIS absorption spectrum of a Pb nanowire in chloroform is shown in Fig. 3, where a specific surface plasmon resonance (SPR) absorption band can be found around 280 nm, which was ascribed to the collective oscillation of conduction electrons under optical excitation.

The investigations of the optical limiting properties of the C_{60}TPY-Pb nanowires were conducted using 8-ns (FWHM)

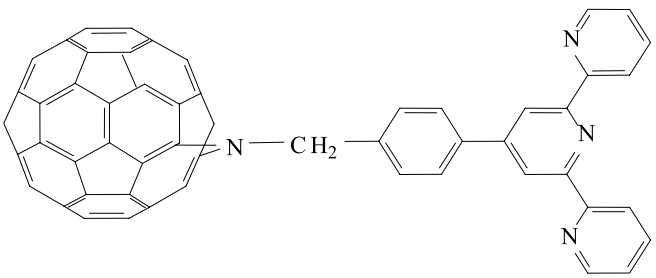

FIGURE 1 Molecular structure of C_{60}TPY

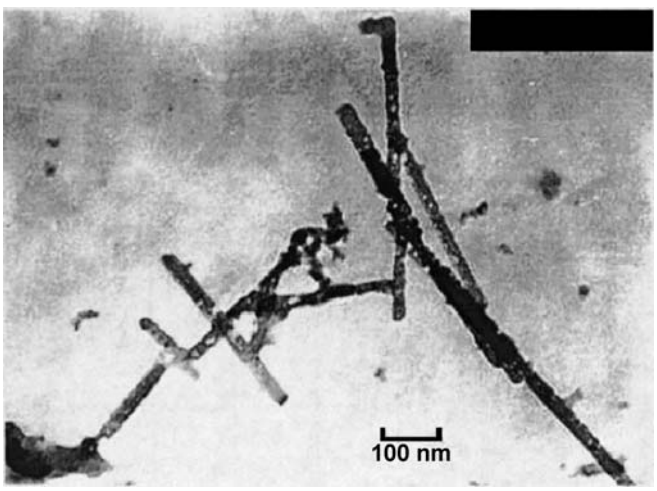

FIGURE 2 TEM image of C_{60}TPY-Pb nanowires

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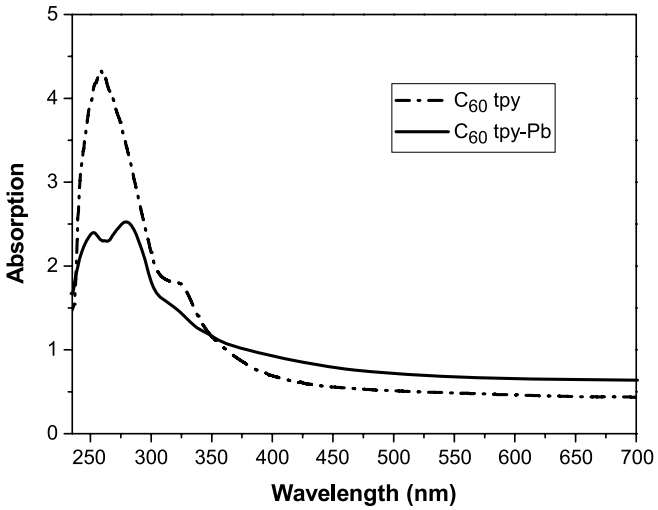

FIGURE 3 Linear absorption spectra of C_{60}TPY-Pb nanowire and C_{60}TPY in chloroform

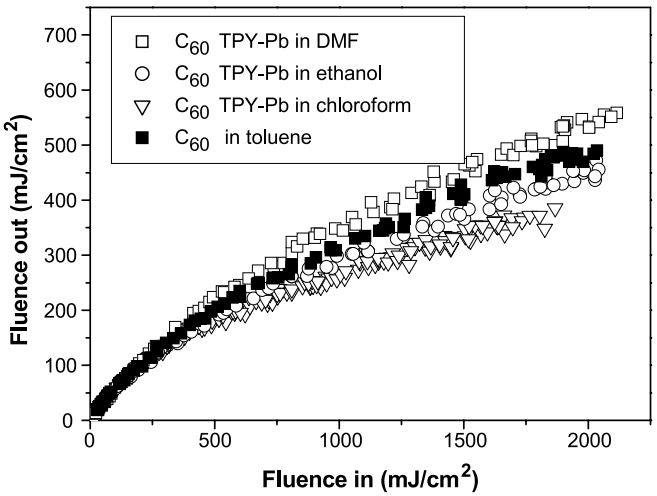

FIGURE 4 Optical limiting response of C_{60}TPY-Pb nanowires in chloroform, ethanol, DMF and C_{60} in toluene

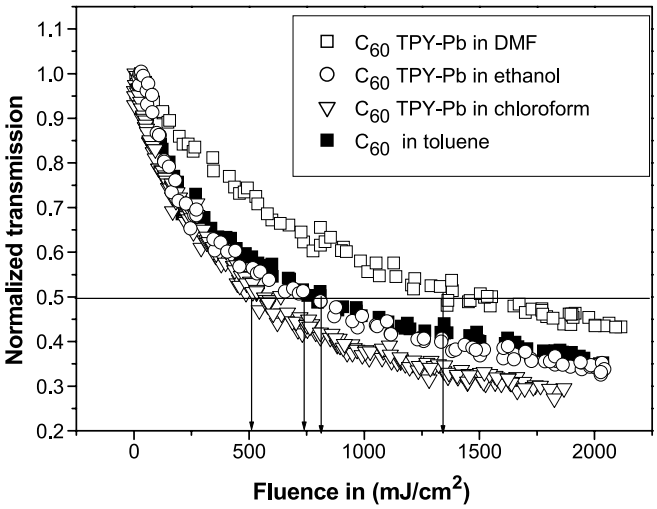

FIGURE 5 Normalized transmission curves versus input fluence for C_{60}TPY-Pb nanowires in chloroform, ethanol, DMF and C_{60} in toluene

laser pulses at 532 nm. The laser pulses were supplied by a frequency-doubled, Q-switched, mode-locked Continuum ns/ps Nd:YAG laser system, providing linearly polarized optical pulses with the repetition rate of 1 Hz. The transverse mode of the laser pulse is nearly Gaussian. The experimental setup is the same as that used in our previous work [11]. The input laser pulses adjusted by an attenuator were split into two beams. One was employed as a reference to monitor the incident laser energy, and the other was focused onto the sample cell by using a lens with 30 cm focal length. The samples were positioned at the focus. The incident and transmitted laser pulses were monitored by utilizing two energy detectors (Rjp-735 energy probes, Laser Precision). Optical limiting was studied by measuring the output fluence change with input fluence. Firstly, we investigated optical limiting of C_{60}TPY-Pb dissolved in chloroform. Then, in order to determine the effect of the solvent on the optical limiting, we performed an optical limiting experiment of C_{60}TPY-Pb dissolved in ethanol and dimethylformamide (DMF). For comparison, we also performed the same experiment for C_{60} in toluene, which has been reported as a representative material with good optical limiting performance. When measured, four solutions were housed in identical quartz cells with a path 5-mm long. They have the same linear transmittance of 75% at 532-nm wavelength.

For the further investigation of the optical limiting mechanism, a *Z*-scan experiment was carried out by using the same laser system as in the optical limiting experiment. The experimental arrangement is similar to that in the literature [12]. The single-pulse energy is about 150 μJ, corresponding to a fluence of 663 mJ/cm^2 at the focus. When measured, C_{60} toluene solution and C_{60}TPY-Pb chloroform solution with linear transmittance of 80% were placed in 2-mm-thick quartz cells.

3 Results and discussion

Under 8-ns laser pulses, the changes of output fluence with input fluence are shown in Fig. 4, and the normalized transmission curves are illuminated in Fig. 5 to make results more clear. It can be found easily in Fig. 4 that, at low input fluence, the optical responses of C_{60}TPY-Pb in three different solvents and C_{60} in toluene obey Beer's law. Namely, the output fluence increases linearly with the increasing input fluence. When the input fluence increases further, the output fluence increases nonlinearly and slowly. Obviously, an optical limiting effect occurs. Especially, C_{60}TPY-Pb in chloroform exhibits the strongest optical limiting of the four samples, while C_{60}TPY-Pb in DMF gives the weakest optical limiting. Additionally, C_{60}TPY-Pb in both chloroform and ethanol exhibits stronger optical limiting than C_{60} in toluene, which indicates that C_{60}TPY-Pb is also a good optical limiting material. As shown in Fig. 5, the difference of optical limiting of C_{60}TPY-Pb in different solvents can also be found easily from the results of the normalized transmission. With the increase of the input fluence, the normalized transmission of C_{60}TPY-Pb in chloroform decreases fastest. The optical limiting threshold, defined as the input fluence at which the transmission decreases to half of the linear transmission, can be found to be 507 mJ/cm^2, 780 mJ/cm^2, 1300 mJ/cm^2 and 810 mJ/cm^2 for

C_{60}TPY-Pb in chloroform, ethanol, DMF and C_{60} in toluene, respectively. This further confirms that the optical limiting of C_{60}TPY-Pb nanowires is strong and strongly solvent dependent.

Mechanistically, the origins of optical limiting in nanomaterials remain unclear. In general, the results can be evaluated in terms of the existing nonlinear absorption and nonlinear scattering mechanisms. Compared with nonlinear absorption, nonlinear scattering could be influenced more easily and more strongly by the solvent. It has been found in carbon black suspensions and carbon nanotubes that the optical limiting results mainly from absorption-induced nonlinear scattering, and the effect shows a significant solvent effect [13–17]. In some metal nanoparticles such as gold, silver and palladium, absorption-induced nonlinear scattering was also found to be the main origin of optical limiting [18–22]. As a matter of fact, during our optical limiting experiment in C_{60}TPY-Pb nanowires, increased beam scattering has been observed with the naked eye at the power-meter aperture. Furthermore, the apparent sensitivity of the optical limiting performance in C_{60}TPY-Pb nanowires to the solvent implies that nonlinear scattering plays a dominant role in the optical limiting.

In order to confirm our hypothesis mentioned above, we also conducted Z-scan experiments of C_{60}TPY-Pb in chloroform and C_{60} in toluene. The experimental results are shown in Figs. 6 and 7. They are normalized open-aperture Z-scan curves and normalized transmission curves of Z-scan data with an aperture (linear transmission of $S = 0.1$) divided by those without an aperture, respectively. From Fig. 6, it can be found that the valley of the curve for C_{60}TPY-Pb is relatively deeper than that for C_{60}. This indicates that C_{60}TPY-Pb exhibits stronger nonlinear absorption or nonlinear scattering than C_{60}. The peak–valley configurations in Fig. 7 indicate that C_{60} exhibits a self-defocusing effect. And, the symmetry of a closed-aperture Z-scan for C_{60} in Fig. 7 indicates that there is almost no nonlinear scattering in C_{60}, while C_{60}TPY-Pb shows a self-focusing effect at 532 nm. Furthermore, a noteworthy feature of the Z-scan for C_{60}TPY-Pb in Fig. 7 is its asymmetry with a larger valley and a smaller peak. This indicates that nonlinear scattering occurred in C_{60}TPY-Pb. The nonlinear scattering can reduce transmission of the Z-scan with aperture (closed-aperture Z-scan) as nonlinear absorption does, while, for the Z-scan without aperture, the data cannot be affected by small-angle nonlinear scattering when we use a beam collector over a large solid angle. As a result, the division of normalized transmission curves of the Z-scan with an aperture by those without an aperture cannot eliminate the influence of nonlinear scattering. Therefore, the data in Fig. 7 contain the contribution from both nonlinear refraction and scattering. It is the nonlinear scattering that influences the symmetry of the closed-aperture Z-scan curve for C_{60}TPY-Pb. A similar phenomenon was also found in gold and palladium nanoparticles [22, 23]. So, we can propose that nonlinear scattering also presented during optical limiting of C_{60}TPY-Pb nanowires, and it dominated the optical limiting in C_{60}TPY-Pb nanowires.

The nonlinear scattering from absorbing particles in liquids can result from two types of scattering centers [18, 19]. The fast mechanism, which reaches maximum amplitude in less than 1 ns, occurs at a relatively high fluence and for short pulses (ps) and is assigned to the vaporization of particles. The slow mechanism, which develops in a few nanoseconds, occurs at a relatively low fluence and for long pulses (ns) and is assigned to the energy transfer from the particles to the surrounding solvent and to the formation of solvent bubbles. Additionally, the slow-scattering mechanism is more strongly influenced by the solvent used than the fast one.

In the case of C_{60}TPY-Pb nanowires, because we used nanosecond laser pulses in our experiment, our observation of a strong solvent dependence of the optical limiting behavior can rule out microplasma formation (fast mechanism) as being an important mechanism. So, we can believe that the mechanism governing the optical limiting observed in C_{60}TPY-Pb nanowires is mainly the slow mechanism, that is, absorption-induced nonlinear scattering from solvent bubbles. The Pb nanowires, after they absorb incident light, can heat up and transfer immediately the heat they have accumulated to the surrounding solvent. Then, the solvent evaporates and gives rise to microbubbles around the initial nanowires. The solvent bubbles acting as scattering centers scatter the

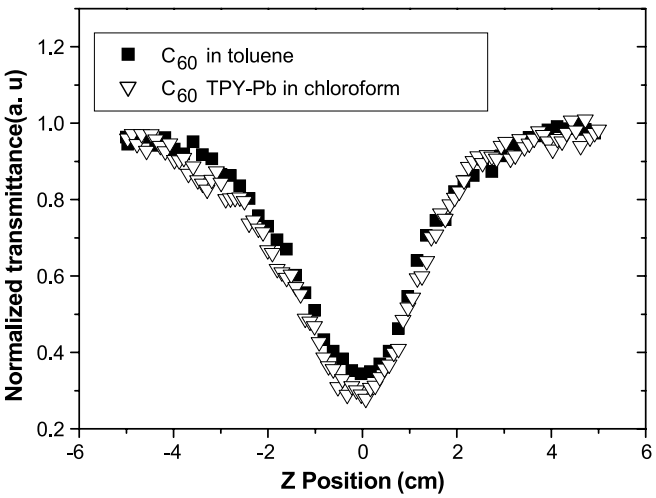

FIGURE 6 Normalized transmission curves of open-aperture Z-scan for C_{60}TPY-Pb in chloroform and C_{60} in toluene at 532 nm

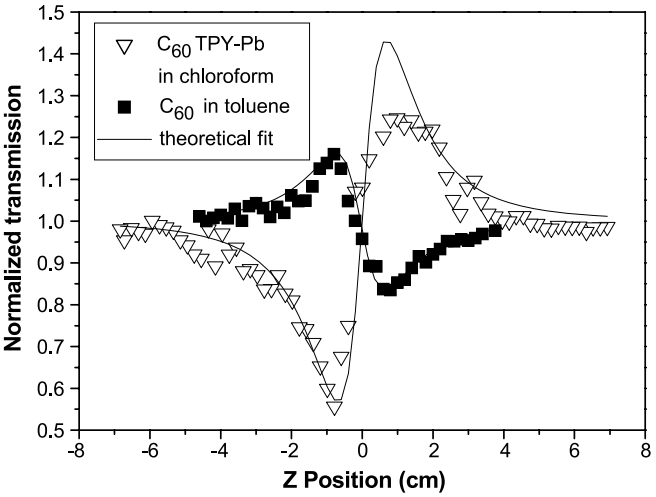

FIGURE 7 Normalized transmission curves of Z-scan data with an aperture (linear transmission of $S = 0.1$) divided by those without an aperture for C_{60}TPY-Pb in chloroform and C_{60} in toluene at 532 nm

TABLE 1 Thermodynamic parameters of the solvents[a]

Host solvent	Chloroform	Ethanol	DMF
Thermal conductivity (W/m/K)	0.117	0.169	0.166
Heat capacity (J/g/K)	0.96	2.44	2.14
Boiling point (°C)	61.15	78.32	150
Density (g/ml) (20 °C)	1.4892	0.7892	0.941
Surface tension (dyn/cm)	27.16	22.32	35.2
Viscosity (cp) (25 °C)	0.57 (20 °C)	1.1	0.796

[a] D.R. Lide, *CRC Handbook of Chemistry and Physics*, 76th edn. (1995)

laser beam away from the propagation direction, which leads to the strong optical limiting. Clearly, the easier the microbubbles form, the stronger the optical limiting performance is. To vaporize the interface solvent layer, we need to overcome the thermal conductivity in the solvent by depositing sufficiently high energy in the early part of the pulse duration and using a solvent with low thermal diffusivity. Note from Table 1 that chloroform has the lowest thermal conductivity, lowest heat capacity and lowest boiling point. It is the combination of these factors that leads to the quickest local superheating of the interface solvent layer to a critical temperature, at which bubbles form. As a result, C_{60}TPY-Pb nanowires in chloroform offer the strongest optical limiting. Compared with ethanol, DMF has relatively lower thermal conductivity and heat capacity, but C_{60}TPY-Pb nanowires in DMF exhibit the weakest optical limiting. That is because the boiling point of DMF is 150 °C, much higher than those of chloroform and ethanol. The apparent sensitivity of the optical limiting performance to the thermodynamic parameters of the solvent suggests that the observed optical limiting is mainly dominated by slow nonlinear scattering. Of course, the nonlinear absorption from C_{60}TPY can also contribute to the optical limiting, which enhanced the optical limiting in C_{60}TPY-Pb nanowires [21–23].

4 Conclusions

In summary, we investigated the optical limiting of C_{60}TPY-Pb nanowires in three different kinds of solvents (chloroform, ethanol, DMF). It was found that the optical limiting behavior in C_{60}TPY-Pb nanowires is strongly solvent dependent, and C_{60}TPY-Pb nanowires in chloroform and ethanol can offer even stronger optical limiting than C_{60}. The main role responsible for optical limiting is absorption-induced nonlinear scattering from solvent bubbles. Additionally, the thermodynamic properties such as thermal conductivity, heat capacity and boiling point which can cause quick local overheating of the interface solvent layer play an important role in optical limiting of C_{60}TPY-Pb nanowires.

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