Appl. Phys. B 76, 761–763 (2003)
DOI: 10.1007/s00340-003-1207-6

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Large optical limiting of [60]fullerene-substituted terpyridine palladium nanoparticles

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Received: 16 September 2002/Revised version: 25 April 2003
Published online: 24 June 2003 • © Springer-Verlag 2003

ABSTRACT The optical-limiting (OL) properties of new palladium nanoparticles based on a C_{60} derivative are investigated using nanosecond laser pulses at 532 nm wavelength. The nanoparticles in chloroform solution exhibit better OL performances than C_{60}in toluene. The main origins concerning the OL are discussed.

PACS 42.70.Nq; 42.65.Hw; 42.65.Sf; 78.66.Tr; 78.67.Bf

1 Introduction

Optical limiters are devices that strongly attenuate intense laser beams while exhibiting high transmittance for low-intensity ambient light levels. These devices are indispensable for the protection of human eyes and optical sensors against intense laser threat. In the last few years, numerous materials used in optical limiters have generated great scientific and technological interest. For example, fullerenes, metallophthalocyanines and metal clusters have been investigated extensively for their strong optical limiting performances [1–6]. Recently, nanomaterials [7–10] such as carbon nanotubes and metal and semiconductor nanoparticles have emerged as new class of optical limiting materials. We have prepared a novel C_{60} derivative containing the terpyridine group self-assembled on the surface of palladium nanoparticles. In this present work, we would like to report the studies of OL responses and origins at 532 nm wavelength of the nanoparticles.

2 Materials and experiments

The material measured in our experiments was metal palladium nanoparticles, protected by a ligand. The ligand is C_{60} derivative with a substitute group of terpyridine, denoted as C_{60}tpy. The molecular structure of the ligand is illustrated in Fig. 1. The average size of the palladium nanoparticles was estimated by transmission electron microscopy (TEM) to be of the order of 5–15 nm. Here, we name the nanocomposite as C_{60}tpy-Pd for simplicity. It was dissolved in chloroform at a concentration of 0.25 mg/ml. The linear absorption spectra for C_{60}tpy-Pd, C_{60}tpy in chloroform and C_{60} in toluene are provided in Fig. 2. Compared with C_{60}tpy and C_{60}, C_{60}tpy-Pd exhibits a different linear absorption, especially in the short-wavelength region. This may result from the interaction between C_{60}tpy and the palladium nanoparticle.

The investigation of the OL properties of the nanocomposite was conducted at a wavelength of 532 nm. For comparison, we also performed the same experiment for C_{60} in toluene, which has been reported as a representative material

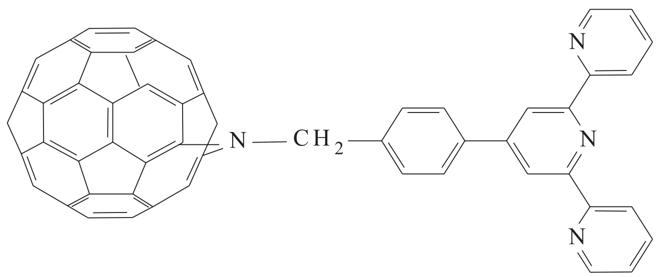

FIGURE 1 Structure of C_{60}tpy

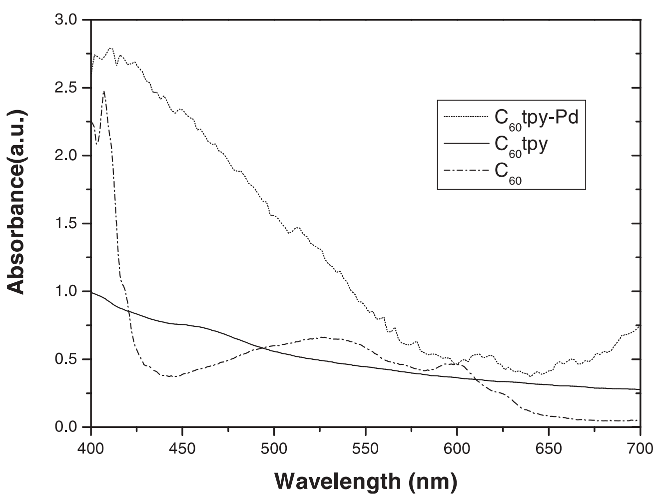

FIGURE 2 Linear absorption spectra of C_{60}tpy-Pd, C_{60}tpy in chloroform and C_{60} in toluene

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with good OL performance. Both C_{60}tpy-Pd and C_{60} solutions were housed in quartz cells with a path 2 mm long. They had the same linear transmittance of 80%. The laser pulses used in the experiments were supplied by a frequency-doubled, Q-switched, mode-locked Continuum ns/ps Nd:YAG laser system, which provided linearly polarized 8 ns (FWHM) optical pulses at 532 nm with a repetition of 1 Hz. The transverse mode of the laser pulses was nearly Gaussian. The input laser pulses adjusted by an attenuator were split into two beams. One was employed as reference to monitor the incident laser energy, and the other was focused onto the sample cell by using a lens of 30 cm focal length. The sample was positioned at the focus. The incident and transmitting laser pulses were monitored by utilizing two energy detectors (Rjp-735 energy probes, Laser Precision). OL was studied by measuring the non-linear fluence transmittance change with input fluence.

For further investigation of optical non-linear properties and OL, a Z-scan experiment was carried out by using the same laser system as in the OL experiment. The experimental arrangement was similar to that in the literature [11]. The single pulse energy was about 150 μJ corresponding to a fluence of 663 mJ/cm^2 at the focus. The C_{60} toluene solution and the C_{60}tpy-Pd chloroform solution, both with linear transmittances of 80%, were placed in 2 mm thick quartz cells.

3 Results and discussion

The OL experimental results for C_{60}tpy-Pd and C_{60}, with linear transmittance of about 80%, are shown in Fig. 3. The non-linear transmittances as a function of incident fluence are illustrated in Fig. 4. At very low incident fluence, their optical responses obey Beer's law, and the transmittances are roughly constant. In contrast, at high fluence the transmittances decrease markedly. However, the detailed OL performance of C_{60}tpy-Pd is different from that of C_{60}. As shown in Fig. 3, at a given incident fluence of 1500 mJ/cm^2, output fluences are about 235 mJ/cm^2 and 257 mJ/cm^2 for C_{60}tpy-Pd and C_{60}, respectively, and the former is lower than the latter, indicating that the C_{60}tpy-Pd chloroform solution has stronger OL than the C_{60} toluene solution. Furthermore, it can be found in Fig. 4 that the transmittance begins to decrease at lower incident fluence for C_{60}tpy-Pd than for C_{60}, which implies further that C_{60}tpy-Pd has better OL performance than C_{60}.

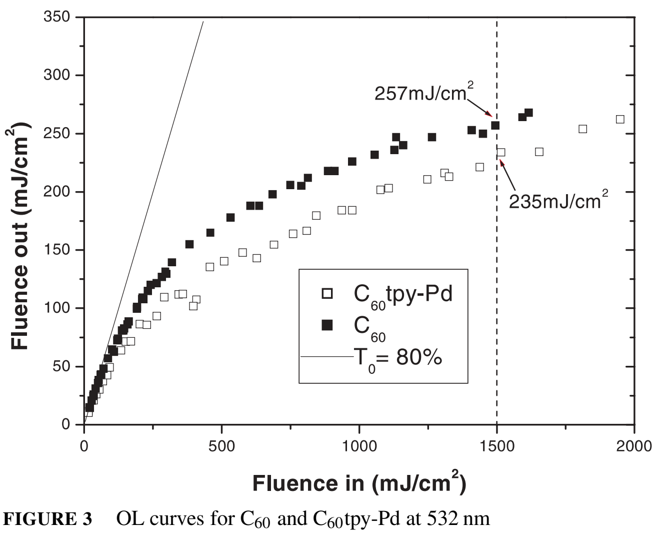

FIGURE 3 OL curves for C_{60} and C_{60}tpy-Pd at 532 nm

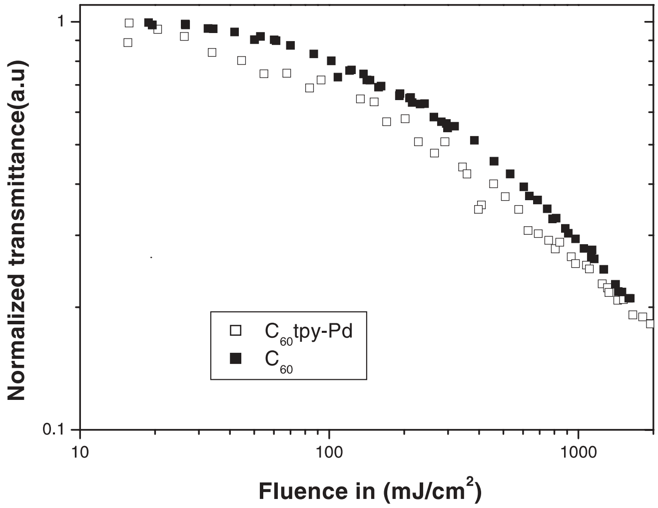

FIGURE 4 Non-linear transmission of C_{60} and C_{60}tpy-Pd at 532 nm

Mechanistically, the origins for OL responses of nanomaterials remains unclear. In general, the results can be evaluated in terms of the existing non-linear absorption and non-linear scattering mechanisms [12]. As reported by S.L. Qu and co-workers, the ligand of C_{60}tpy shows weaker excited-sate absorption and OL than C_{60} in toluene [13]. However, as investigated above, the OL for the C_{60}tpy-Pd chloroform solution is better than that for C_{60} in toluene. This indicates that the enhancement of OL in C_{60}tpy-Pd arises mainly from the palladium nanoparticles. In order to further study the origins of OL in C_{60}tpy-Pd, we conducted Z-scan experiments, and the results of the experiments are shown in Figs. 5 and 6. These are normalized open-aperture Z-scan curves and normalized transmission curves of Z-scan data with an aperture (linear transmission $S = 0.1$) divided by

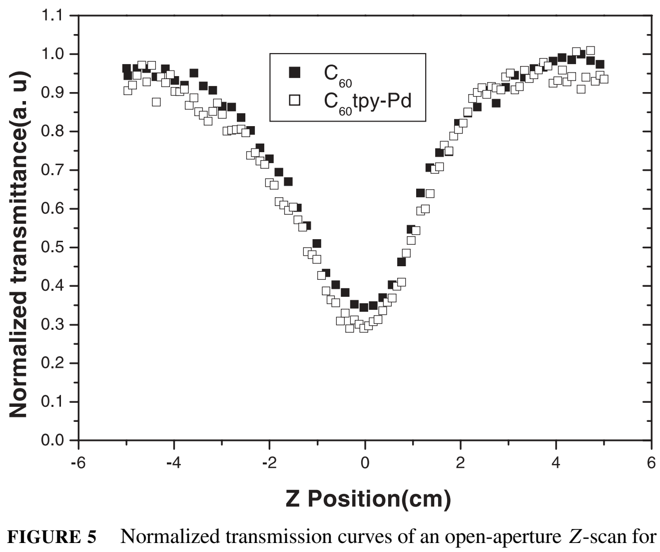

FIGURE 5 Normalized transmission curves of an open-aperture Z-scan for C_{60}tpy-Pd and C_{60} at 532 nm

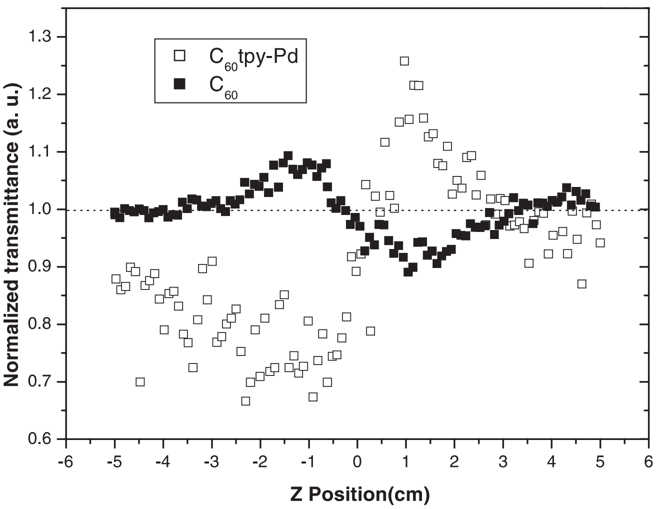

FIGURE 6 Normalized transmission curves of Z-scan data with an aperture (linear transmission of $S = 0.1$) divided by those without an aperture, for C_{60}tpy-Pd and C_{60} at 532 nm

those without an aperture, for C_{60}tpy-Pd and C_{60}, respectively. From Fig. 5, it can be found that the valley of the curve for C_{60}tpy-Pd is deeper than that for C_{60}. This indicates that C_{60}tpy-Pd exhibits stronger non-linear absorption and non-linear scattering. The peak–valley configurations in Fig. 6 indicate that C_{60} exhibits a self-defocusing effect, while C_{60}tpy-Pd shows a self-focusing effect at 532 nm. Furthermore, as for the C_{60}tpy-Pd, the smaller peak and larger valley may suggest that strong non-linear scattering occurs in the C_{60}tpy-Pd chloroform solution. A similar phenomenon was also found by S.L. Qu in gold nanoparticles [10]. In fact, we observed by naked eye increased beam scattering at large angles during the experiment with the C_{60}tpy-Pd chloroform solution. The non-linear scattering can be attributed to the palladium nanoparticles. It is the large light-scattering centers induced by excited-state absorption from C_{60}tpy that improves the OL performance of C_{60}tpy-Pd. Specifically, we propose to assign the scattering centers to the vaporization or fragmentation of the palladium nanoparticles. This is in agreement with the reported OL responses in gold nanoparticles by L. Francois and co-workers [9]. Both non-linear absorption and non-linear scattering are responsible for the strong OL in C_{60}tpy-Pd. Such cooperative non-linear effects produce good OL.

4 Conclusions

The OL effects of C_{60}tpy-Pd were investigated under irradiation with 8 ns laser pulses at 532 nm. The mechanism of the effects is believed to arise mainly from non-linear absorption and non-linear scattering. It is the non-linear scattering induced by absorption that strengthens the OL performance in the nanomaterial. Further research is needed to evaluate the relative magnitudes of the two effects.

ACKNOWLEDGEMENTS This work was supported by National Natural Science Foundation of China with Grant No. 50172013, the Major State Basic Research Development Program with Grant No. 20151002 and the Multidiscipline Scientific Research Foundation of Harbin Institute of Technology with Grant No. HIT. MD2001.25.

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