Communications to the Editor

Large Optical Limiting from Novel Metal−Dendrimer Nanocomposite Materials

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Nanostructured materials have attracted substantial attention[1,2] due to their possible applications in optoelectronics and their anticipated versatility in providing a deeper understanding of size-sealed structure−function relationships. Nanostructured materials can be fabricated by a variety of methods, one of which involves the use of synthetic dendrimers as host container or scaffolding molecules.[3] Dendrimer nanostructures have been suggested as prime candidates for drug delivery systems, quantum-confined structures, and nanolevel storage units.[4,5] The rapid progress in the synthetic chemistry of organic dendrimers has also led to the fabrication of metal−dendrimer nanocomposites.[6,7] For example, it has been demonstrated that zerovalent transition metals can be encapsulated inside poly(amidoamine) (PAMAM) dendrimers in a variety of architectures.[7−9] While there has been great success in the fabrication of many new types of dendrimer nanocomposites (DNC), the nonlinear optical properties of these novel materials are still relatively unexplored.

In this contribution we report the new findings of large optical limiting effects from silver−dendrimer nanocomposites, here denoted as {Ag(0)}. The average size of the metal domains in these nanocomposites was estimated by transmission electron microscopy to be of the order of 5−25 nm,[7] depending on the template used. Two types of architectures are possible with respect to the positions of the metal domains within the PAMAM dendrimer matrix: external (E) and internal (I).[7]

The optical properties of nanoscale metal domains are strongly influenced by the surface plasmon (SP) resonance.[10] This is relevant for the case of optical limiting where the material's absorption is dependent upon the intensity of the input beam. The results we are reporting in this work were obtained with the external (E) type {Ag(0)}−dendrimer architecture, structure known as $\{Ag(0)\}_E$: ({$(Ag(0)_{96.97}$−PAMAM_E5.5COOAg}). The metal−dendrimer nanocomposites under investigation were prepared in water (aqueous) solutions.[7,8]

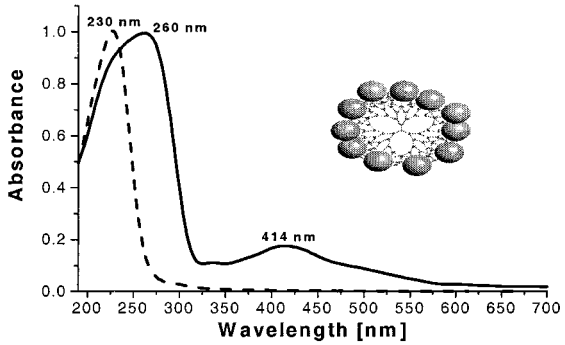

Figure 1. Absorption spectra of $\{Ag(0)\}_E$ (solid line) and of the pure dendrimer host (dashed line), both in aqueous solutions. A schematic representation of the $\{Ag(0)\}_E$ architecture is shown in the inset.

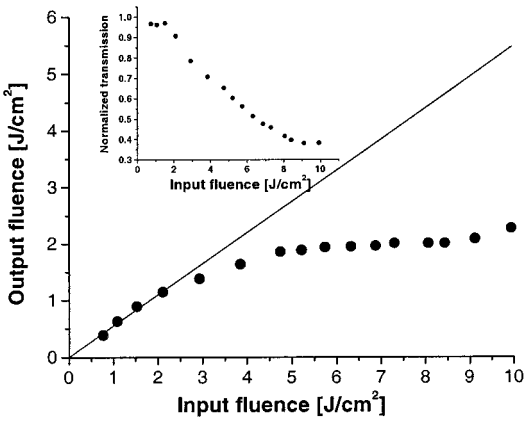

Figure 2. Optical limiting behavior of the $\{Ag(0)\}_E$ nanocomposite at 532 nm, for a 10 Hz pulse repetition rate. The solid line illustrates the case of a constant transmission of ∼60% (the transmission value at low fluence). The inset shows the corresponding transmission variation with the input fluence.

The linear absorption spectra of $\{Ag(0)\}_E$ and the pure dendrimer host are shown in Figure 1. The $\{Ag(0)\}_E$ structure exhibits an SP resonance absorption peak in the visible region at around 414 nm. The pure dendrimer absorption consists mainly of a strong peak at around 230 nm.

The nonlinear optical properties of these novel compounds were investigated with 6.5 ns laser pulses from a frequency doubled Nd:YAG laser at 532 nm, within their SP resonance spectral range. The repetition rate of the laser pulses was varied between 2 and 10 Hz. The optical setup consisted of an f/8 lens, focusing the Gaussian beam (initial radius of 2.2 mm) to a spot radius of ∼40 μm, and a power-meter positioned close to the output facet of the 1 mm-thick sample cell. The control of the input energy was obtained by a combination of quarter-wave plates and polarizers.

The result of the nonlinear transmission measurement with a pulse repetition rate of 10 Hz for a solution in a relatively low concentration of 2.0×10^{-4} mol/L is shown in Figure 2. When the input fluence varies from 0.7 to 10.0 J/cm^2 (equivalent to the increase of the peak irradiance from 0.2 to 1.3 GW/cm^2) the transmission decreases by 62%. The threshold fluence for optical limiting is around 2.0 J/cm^2. The optical limiting performance of

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(1) Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. *Science* **1996**, *272*, 1924.
(2) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226.
(3) Balogh, L.; Swanson, D. R.; Spindler, R.; Tomalia, D. A. *Proc. ACS PMSE* **1997**, *77*, 118.
(4) Sooklal, K.; Hanus, L. H.; Ploehn, H. L.; Murphy, C. J. *Adv. Mater.* **1998**, *10*, 1083.
(5) Chechik, V.; Crooks, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 1243.
(6) Balogh L.; Tomalia D. A. *J. Am. Chem. Soc*. **1998**, *120*, 7355.
(7) Balogh, L.; Valluzzi, R.; Hagnauer, G. L.; Laverdure, K. S.; Gido, S. P.; Tomalia, D. A. *J. Nanoparticle Res*. **1999**, *1(3)*, 353.
(8) Balogh, L.; Laverdure, K. S.; Gido, S. P.; Mott, A. G.; Miller, M. J.; Ketchel, B. P.; Tomalia, D. A. *Mater. Res. Soc. Symp. Proc*. **1999**, *756*, 69.
(9) He, J. A.; Valluzzi, R.; Yang, K.; Dolukhanyan, T.; Sung, C. M.; Kumar, J.; Tripathy, S. K.; Samuelson, L.; Balogh, L.; Tomalia, D. A. *Chem. Mater*. **1999**, *11*, 3268.
(10) Link, S.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 8410.

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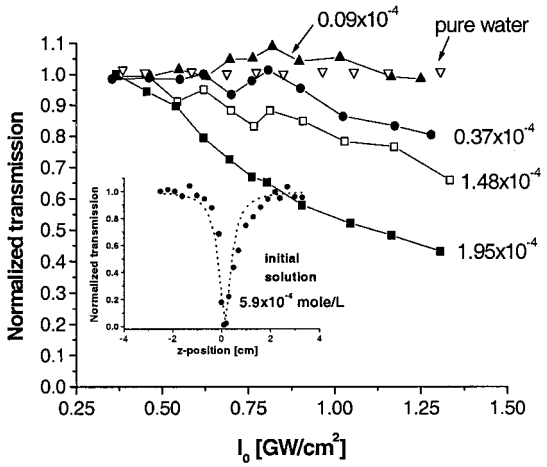

Figure 3. Nonlinear transmission result for the external type $\{Ag(0)\}_E$ structure at 532 nm, with the relative variation of the concentration indicated in mol/L units. The open z-scan trace for initial concentrated solution, at 532 nm and $I_0 = 0.42$ GW/cm^2, is shown in the inset. The dotted lines are guides to the eye.

$\{Ag(0)\}_E$ compares well to the results obtained with novel organic structures such as: EHO−OPPE[11] (where a transmission drop of 65% was obtained between 0 and 0.6 GW/cm^2), the AF-380 dye[12] (exhibiting a threshold fluence of ∼2 J/cm^2 and a transmission loss of 60% for an input fluence increase up to 13 J/cm^2), and single-walled carbon nanotube suspensions[13] (showing a threshold fluence of ∼2 J/cm^2 and transmission decrease of 70% for fluence increasing up to 6 J/cm^2).

We also carried out an investigation of the influence of the solution concentration on the nonlinear transmission behavior. As expected, the transmission decrease was less effective with the reduction of the solution concentration, as indicated in Figure 3. We performed several cycles of increasing and decreasing the peak irradiance between 0 and ∼1.3 GW/cm^2, and the results gave the same nonlinear transmission behavior as seen in Figure 3. Further information about the optical limiting processes occurring in the $\{Ag(0)\}_E$ structure at 532 nm was obtained by utilizing the open z-scan technique[14] in the same optical setup configuration, with 10 Hz pulse repetition rate. From the open z-scan result shown in the inset to Figure 2 it can be noticed that drastic optical extinction, by a factor of 115, occurs for a concentrated solution (5.9×10^{-4} mol/L) of $\{Ag(0)\}_E$ at the laser beam focus for a fluence of 3.3 J/cm^2 (relatively moderate input irradiance of 0.42 GW/cm^2).

For optical excitation close to the linear absorption band, such as at 532 nm for $\{Ag(0)\}_E$, the cross sections for reverse saturable absorption (RSA) and nonlinear scattering should be much higher than the cross section for two-photon absorption.[15] Time-resolved photoluminescence measurements on $\{Ag(0)\}_E$ showed that the excited-state lifetimes in this compound are very short, of the order of picoseconds.[16] RSA processes were seen to develop on the time scale of the excited-state lifetime. As in the case of pthalocyanine complexes, this is usually in the nanosecond range.[17] Therefore, we can suggest that the contribution of RSA is small for the $\{Ag(0)\}_E$ since the lifetime of the excited state is extremely short. To explain the slow optical limiting effect we observed we focus on absorption-induced nonlinear scattering.[13]

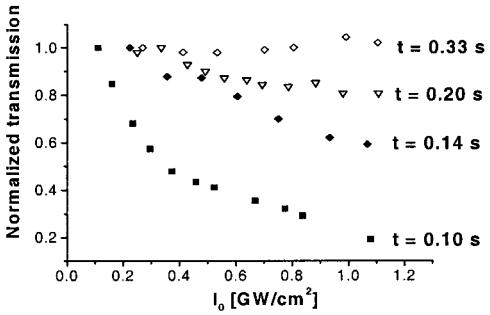

Figure 4. Nonlinear transmission results for $\{Ag(0)\}_E$ in a concentration of 2.95×10^{-4} mol/L at 532 nm, with the variation of the pulse repetition rate; *t* indicates the specific repetition periods.

To gain insight into the relative time scale of the optical limiting mechanism we investigated the dependence of the nonlinear transmission on the pulse repetition rate. The results of this investigation are shown in Figure 4 where the specific pulse repetition periods are indicated. The transition from actual optical limiting behavior, for repetition rates higher than 5 Hz, to the transparency regime seen at a repetition rate of 3 Hz indicates that the mechanism governing the optical limiting is slow. The strong absorption at 532 nm can lead to local heating of the aqueous solution at the focal spot which is then followed by the reversible creation of scattering centers, most probably microbubbles, when approaching boiling temperatures.[13,18] Increased beam scattering at large angles could be observed with the naked eye at the power-meter aperture. Such thermally assisted scattering processes are indeed expected to occur on a millisecond time scale and to be very sensitive to solvent boiling point.[13,15] Measurements were performed also on the internal type of Ag−dendrimer nanocomposites which did not exhibit any optical limiting behavior at 532 nm.

In this work we have demonstrated that a metal−dendrimer nanocomposite topology can exhibit large optical limiting at 532 nm by factors up to 115. The mechanism governing the optical limiting observed is nonlinear scattering, most probably due to bubble formation at the small laser spot. This important finding indicates the feasibility of using novel metal−dendrimer nanocomposites for applications in optical limiting devices and medicine.

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(11) He, G. S.; Weder, C.; Smith, P.; Prasad, P. *IEEE J. Quantum Electron.* **1998**, *34*, 2279.
(12) Joshi, M. P.; Swiatkiewicz, J.; Xu, F.; Prasad, P.; Reinhardt, B. A.; Kannan, R. *Opt. Lett.* **1998**, *23*, 1742.
(13) Mishra, S. R.; Rawat, H. S.; Mehendale, S. C.; Rustagi, K. C.; Sood, A. K.; Bandyopadhyay, R.; Govindaraj, A.; Rao, C. N. R. *Chem. Phys. Lett.* **2000**, *317*, 510.
(14) Sheik-Bahae, M.; Said, A. A.; Wei, T. M.; Hagan, D. J.; Van Stryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760.
(15) Tutt, L. W.; Boggess, T. F. *Prog. Quantum Electron*. **1993**, *17*, 299.
(16) Varnavski, O.; Ispasoiu, R. G.; Balogh, L.; Tomalia, D. A.; Goodson, T., III. *Phys. Rev. Lett.* Manuscript submitted.
(17) Perry, J. W. Organic and metal-containing reverse saturable absorbers for optical limiting. In *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S., Miyata, S., Eds.; CRC Press: Boca Raton, FL, 1997.
(18) Khoo, I. C.; Wood, M. V.; Guenther, B. D.; Shih, M.; Chen, P. H. *J. Opt. Soc. Am. B* **1998**, *15*, 1533.