Nonlinear optical properties of polyaniline composite materials

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The nonlinear optical properties of polyaniline composite materials (PANI/Au) were studied using the single-beam Z-scan technique. These molecules exhibited a strong reverse saturable absorption and an interesting optical limiting performance with a nanosecond Nd:YAG laser pulses at 532 nm.

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Since the development of laser technology, the research on materials and devices for protection of optical sensors and human eyes from intense laser beams generated much interest in the development of optical limiting materials[1,2]. Amongst the new classes of materials, conjugated polymers (CPs) are especially interesting, because they combine the optical and electronic properties of semiconductors with the processing advantages and mechanical properties of polymers[3]. The most studied CP, polyaniline (PANI), is a unique example since its electrical properties can be reversibly controlled both by changing the oxidation state of the main chain and by protonation of the imine nitrogen atoms. In addition to a wide range of desirable electrical, electrochemical, and optical properties, PANI exhibits excellent environmental and thermal stability[4,5].

Polyaniline composite materials (PANI/Au) have been demonstrated to be a new kind of the excellent molecules due to their efficiency and highly conjugated framework. They have special kinds of architectures, which may enhance the optical nonlinearities and thus can be utilized in photonic applications[6,7].

In this letter, we study the nonlinear optical properties of a PANI/Au with nanosecond Nd:YAG laser pulses at 532 nm, which shows large nonlinear absorption coefficient and strong reverse saturated absorption. This material is especially convenient for nonlinear investigstions because of its high durability, simple processability, and low linear absorption.

The single-beam Z-scan technique[8] was used to measure the nonlinear optical properties, which shows great advantages due to its simplicity and high sensitivity. Nonlinear absorption coefficient can be obtained by measuring its transmissivity at various positions near focal point.

The experimental setup is shown as Fig. 1. A frequency-doubled Nd:YAG laser with a pulse width of 6.8 ns at 532 nm was used as the light source in the Z-scan experiment. A lens with focal length of 30 cm was used to focus the laser pulses into a 2-mm quartz cuvette, which contained the PANI/Au sample solution. The optical nonlinear absorption of the PANI/Au was measured by the open-aperture Z-scan technique using 532-nm Nd:YAG laser pulses with a repetition rate of 10 Hz.

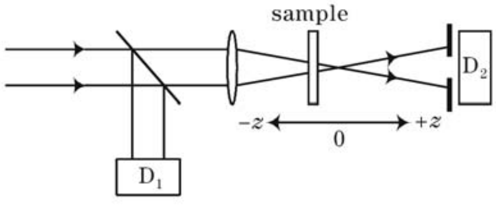

Fig. 1. Experimental setup.

Figure 2 shows the linear absorption spectrum of PANI/Au at room temperature, from which we can get linear absorption coefficient α_0. The absorption band edge E_g is determined by

$$\alpha h\nu = A(h\nu - E_g)^{1/2}, \quad (1)$$

where $h\nu$ is the incident photon energy, and A is a constant.

Nonlinear absorption is a phenomenon that absorption coefficient changes with high intensity. For the open-aperture Z-scan, the normalized energy transmittance $T(z)$ can be expressed in terms of the peak irradiance in a summation form, which is more suitable for numerical evaluation

$$T(z, S=1) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}} \quad \text{for } |q_0| < 1, \quad (2)$$

where $q_0(z,t) = \beta I_0(t) L_{\mathrm{eff}} / \left(1 + z^2/z_0^2\right)$, β is the nonlinear absorption coefficient of the sample, I_0 is the intensity of laser beam at focus ($z = 0$), $L_{\mathrm{eff}} = \left(1 - \mathrm{e}^{-\alpha_0 L}\right)/\alpha_0$ is the effective length with α_0 the linear

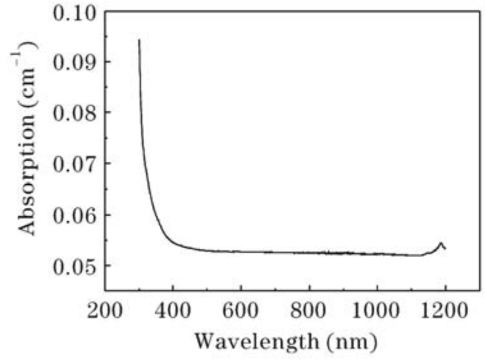

Fig. 2. Linear absorption spectrum of PANI/Au.

absorption coefficient and L the sample length, $z_0 = kw_0^2/2$ is the diffraction length of the beam. So the nonlinear absorption coefficient β (in unit of cm/GW) can be deduced.

Figure 3 shows the open-aperture Z-scan result of PANI/Au in ethanol solutions at the transmittance of 70%. The open-aperture transmittance is symmetric with respect to the focus ($z = 0$), where it has a minimum obviously, indicating that β is positive. Figure 2 is determined by Eq. (1) with the experiment parameters, and the PANI/Au nonlinear absorption coefficient is $\beta = 5.93$ cm/GW, excited state cross-section value of $\sigma_{ex} = 1.41 \times 10^{-18}$ cm^2 is obtained. Considering the ground state cross-section $\sigma_0 = 0.98 \times 10^{-18}$ cm^2 and $\sigma_{ex}/\sigma_0 > 1$, so the nonlinear absorption of PANI/Au composite material shows a reverse saturable absorption process.

Presently, the composition of inorganic matter and organic matter is a hotspot of material study[9], which provides a new content of choosing nonlinear optical material. As we know, inorganic matter has stable physicochemical property and high damage threshold, while organic matter has good tenacity. So it is significative to study the optical limiting of the nano-composites[10]. When laser excites the samples near the focal point, we make use of two polarized prisms to change incident power I_i in order to find out its relation with the transmitted power I_0. The experimental results are described in Fig. 4. In the beginning, I_0 increases rapidly and meets linear relationship with I_i under weak radiation. After I_i is above a threshold, I_0 changes slowly due to optical nonlinearity, and basically trends to a plain stage in the end, which is optical limiting.

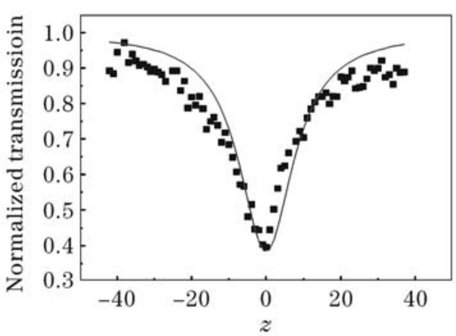

Fig. 3. Normalized open-aperture Z-scan transmittance of PANI/Au.

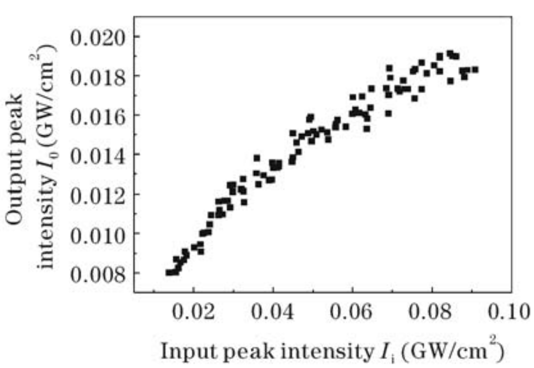

Fig. 4. Optical limiting behaviors of PANI/Au.

The optical nonlinear properties of the nanocomposites PANI/Au has been investigated by the Z-scan technique with 10-ns laser pulses at 532 nm, and the nonlinear absorption coefficient β of PANI/Au of 5.93 cm/GW was measured by using open-aperture Z-scan technique. The optical limiting performance has demonstrated to be attributed to the reverse saturable absorption, and the PANI/Au is proved a good nonlinear optical material for the further application.

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