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Measurements of third-order nonlinearity of inhomogeneous samples using nonlinear-imaging technique with a phase object

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ABSTRACT Using electrostatic self-assembly of a [CuPc-$(COOH)_4$]/polydiallyldimethylammonium chloride (PDDA) film, we demonstrate that signal fluctuation induced by a random surface inhomogeneity of less than 70 nm can be approximately resolved by a nonlinear-imaging technique with a phase object (NIT-PO) as opposed to Z-scan. In our NIT-PO simulation the sample is regarded as perfectly parallel, while the incident intensity distribution is modified to mimic that of an extremely weak laser beam traversing the sample, which is detected by a charge-coupled-device (CCD) camera. However, the original phase in the simulations is maintained, since phase distortions caused by the sample are not measurable at the CCD plane.

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For optical limiting applications, nonlinear absorption and refraction of various organic films, either single- or multilayered, are currently investigated to look for materials with large nonlinearities. Because of abrasion, sample instability, and slow chemical reaction with air or water vapor, uniform thickness or concentration of these materials is hard to achieve or maintain. Therefore, it is urgent to find a method to resolve the random surface inhomogeneity induced signal fluctuation from that of a perfectly smooth and parallel sample. In this letter, we illustrate that third-order nonlinearity of [CuPc$(COOH)_4$]/polydiallyldimethylammonium chloride (PDDA) with random surface inhomogeneity can be closely resolved by a nonlinear-imaging technique with a phase object (NIT-PO) [1], as opposed to Z-scan [2, 3]. NIT-PO is essentially a measurement technique that uses a phase object (PO) at the entry of a $4f$ coherent imaging system to characterize the value of the nonlinear refractive index of a material placed in the Fourier plane of the setup.

In both Z-scan and NIT-PO techniques, we need to integrate, with incident intensity and phase I_{in} and φ_{in} given, the differentials of intensity and phase with respect to the penetration depth ($\mathrm{d}I/\mathrm{d}z'$ and $\mathrm{d}\varphi/\mathrm{d}z'$, with z' being the sample penetration) over the sample thickness (L) to yield the intensity (I_L) and phase (φ_L) (i.e. the electric field E_L) at the exit surface of the sample. Afterwards, E_L is applied to the Huygens–Fresnel formalism to obtain the intensity I_{a} at the aperture for Z-scan. Or, E_L is applied to the Huygens–Fresnel formalism, the lens transmittance function and another Huygens–Fresnel formalism, which can be represented as a Fourier transform as a whole, to obtain the intensity I_{c} on the charge-coupled-device (CCD) plane. When surface inhomogeneity exists, I_L, φ_L, and the experimental observables I_{a} or I_{c} fluctuate from those obtained with a perfectly uniform and parallel sample. That is, when the random surface inhomogeneity cannot be quantitatively described, the experimental observables I_{a} or I_{c} cannot be simply fitted with given I_{in} and φ_{in} by adjusting the nonlinear coefficients. To deal with this deficiency, an approach with NIT-PO is proposed to fit surface inhomogeneity induced signal fluctuation. We first send a laser beam with a phase φ_{in} and an intensity I_{in}^{l} too weak to induce nonlinearities in the sample and then record the transmitted intensity distribution (I_{c}^{l}) on the CCD. The fluence distribution of the linear image contains the information of the imperfection of the sample. Note that the phase on the CCD (φ_{c}^{l}) cannot be recorded. Secondly, we send a laser beam with the same phase φ_{in} and an intensity (I_{in}^{h}) high enough to produce nonlinearities in the sample and record the intensity distribution (I_{c}^{h}) on the CCD camera. Because of nonlinear absorption and refraction, I_{c}^{h} differs from I_{in}^{h}. Given I_{in}^{h}, φ_{in}, and a sample with random inhomogeneity, I_{c}^{h} on the CCD camera cannot be theoretically calculated. To theoretically simulate I_{c}^{h}, we modify I_{in}^{h} mimicking I_{c}^{l} with pulse energy unchanged and maintain φ_{in} to evaluate I_{c}^{h}. As a result, our simulated I_{c}^{h} reveals a slight difference from that obtained experimentally. If φ_{c}^{l} can be retrieved somehow, it is believed that use of it to replace φ_{in} will more significantly reduce the discrepancy between experimental and theoretical results.

In our experiments, the ultra-thin [CuPc$(COOH)_4$]/PDDA film was fabricated from anionic tetracarboxylic copper phthalocyanine [CuPc$(COONa)_4$] and cationic polydiallyldimethylammonium chloride (PDDA) by an electrostatic layer-by-layer self-assembled technique [4]. The whole thick-

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ness of the film used in our experiment is 1.0 μm. Nonlinearities of [CuPc(COOH)$_4$]/PDDA were first measured using the Z-scan technique with a frequency-doubled, Q-switched, and mode-locked Nd:YAG laser, which delivers 532-nm laser pulses with a width of $\tau = 22$ ps (FWHM) and a repetition rate of 1 Hz. Focusing the beam to have a beam radius at the waist of $w_0 = 30$ μm (HWe^{-2}M) and adjusting the incident pulse energy to be $\varepsilon = 0.5$ μJ, we obtained a peak-on-axis intensity of $I_{00} = 1.45\,\mathrm{GW/cm^2}$. At each sample position z, the total transmittance (the total transmitted energy divided by the incident energy) and the axial transmittance (the energy transmitted through an aperture in front of the detector, allowing 15% energy around the axis through) were measured. A plot of the former as a function of z, the open-aperture Z-scan curve, was obtained that reveals nonlinear absorption alone. On the other hand, a plot of the latter as a function of z, the closed-aperture curve, was obtained that exhibits nonlinear refraction in addition to nonlinear absorption if present. In the presence of nonlinear absorption, by division of the closed-aperture curve by the open-aperture one, the nonlinear absorption was effectively eliminated and the nonlinear refraction was retained alone. Figure 1 shows the divided Z-scan curves taken at equal input energy but at different sample positions. Although they all show a positive lensing effect, they yield different magnitudes and none of them can be fitted satisfactorily to theory. To clarify why different sample points yield different Z-scan curves, firstly a NT-MDT Solver P47-PRO scanning probe microscope (SPM) was operated in the contact atomic force microscope (AFM) mode to investigate the surface morphology of [CuPc(COOH)$_4$]/PDDA. As shown in Fig. 2, a three-dimensional AFM image in a $50 \times 50\,\mu\mathrm{m}^2$ region, approximately the size of a laser beam irradiated on the sample, shows a difference between the maximum and the minimum thicknesses of ~ 35 nm. The maximum thickness difference is therefore ~ 70 nm because the measured sample is a double-sided film. The thickness difference (ΔL) produces a $\sim 5\%$ intensity instability ($\{\exp[-\alpha(L-\Delta L)] - \exp(-\alpha L)\}/\exp(-\alpha L) \simeq 0.05$, where

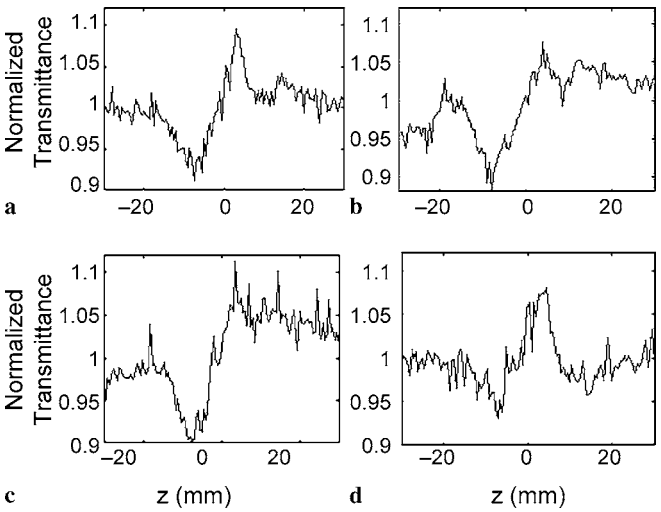

FIGURE 1 The curve of the division of closed-aperture Z-scan and open-aperture Z-scan for four respective measurements at different points of the [CuPc(COOH)$_4$]/PDDA film

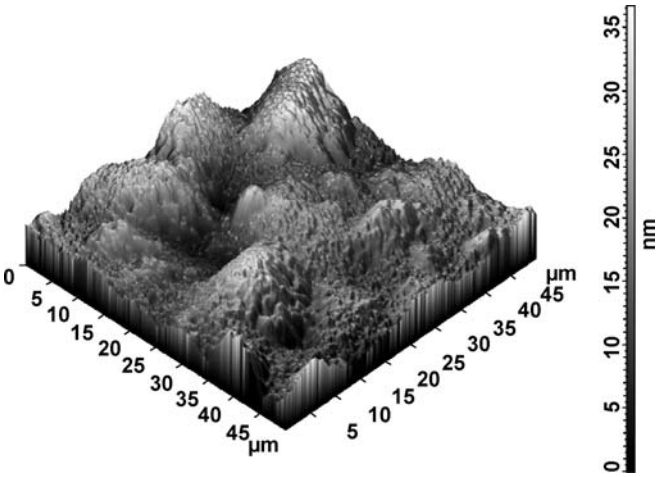

FIGURE 2 The three-dimensional AFM image of the [CuPc(COOH)$_4$]/PDDA film in a $50 \times 50\,\mu\mathrm{m}^2$ region

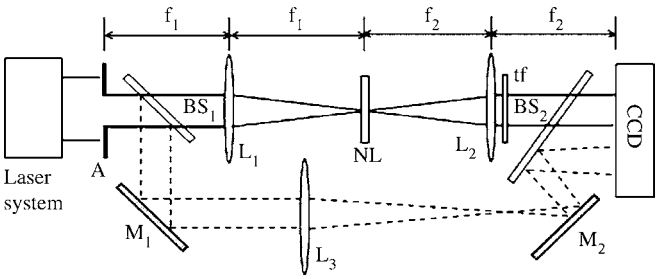

FIGURE 3 The schematic of the NIT-PO system. The $4f$ system consists of lenses L_1 and L_2, which have equal focal lengths. The nonlinear material (NL) is located in the Fourier plane. The aperture with PO (A) is on the front focal plane of L_1. The CCD camera is on the rear focal plane of L_2. L_3, lens; M_1, M_2, mirrors; BS_1, BS_2, beam splitters; tf, neutral filter

$L = 1.0$ μm is the sample thickness and $\alpha = 7.38 \times 10^5$ is the linear absorption index of the sample) and a 0.4 rad phase instability ($2\pi \times 70\,\mathrm{nm} \times (1.5 - 1.0)/532\,\mathrm{nm} = 0.4$, with 1.5 and 1.0 denoting the refractive indices of the sample and air, respectively) on the laser beam transmitted through the sample. Secondly, the same Z-scan measurements on CS_2 contained in a 1-mm-thick quartz cell were repeated. Knowing that the quartz cell has good surface homogeneity, the measurements at various sample positions were conducted and indistinguishable results were obtained. This indicates that surface inhomogeneity may cause signal fluctuation and different Z-scan curves at various points on [CuPc(COOH)$_4$]/PDDA.

Afterwards, NIT-PO was applied to [CuPc(COOH)$_4$]/PDDA to measure its nonlinear absorption and refraction coefficients. This technique, based on a $4f$ system (Fig. 3) with top-hat beams, was first devised by Boudebs et al. and its details can be seen in [1] and [5]. The experimental apparatus includes the same laser source as that used in Z-scan, two confocal lenses (L_1 and L_2) with equal focal lengths $f_1 = f_2 = 400$ mm (the magnification being $G = 1$), an aperture with a radius of $R_a = 1.7$ mm placed at the front focal plane of L_1, and a PO with a radius of $L_p = 0.5$ mm and a phase retardation of $\varphi_L = 0.40\pi$ placed in the middle of the aperture and a numerical aperture of $N_a = 0.1$. The Airy radius at the focal plane of L_1 is $\omega_0 = 1.22\lambda f_1/(2R_a) = 76$ μm. This yields a Rayleigh range of $z_0 = \pi\omega_0^2/\lambda \approx 3.4$ cm. The CCD camera (Imager QE, Lavision) has 1040×1376 pixels

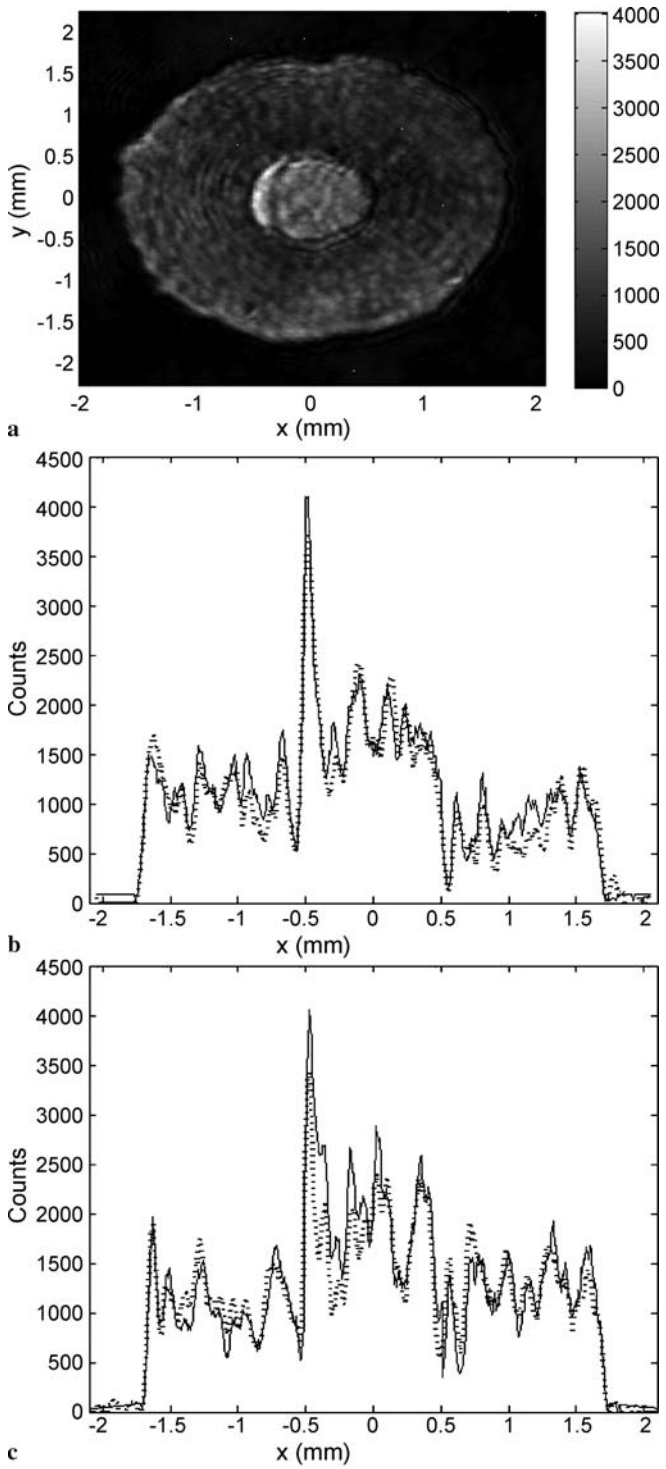

FIGURE 4 (**a**) The experimental result of the $[CuPc(COOH)_4]$/PDDA film obtained by using NIT-PO at a specific point of the sample. (**b**) The profile extracted from (**a**) at $y = 0$ (*dashed line*) and the theoretical fit curve (*solid line*). (**c**) The profile taken at another sample point (*dashed line*) and the theoretical fit curve (*solid line*)

and 4095 gray levels. The size of each pixel is $6.4 \times 6.4\,\mu m^2$. The branch consisting of mirror M_1, convex lens L_3, and mirror M_2 is used to monitor the energy fluctuation of the input laser pulse. During the measurement, the laser beam (usually an expanded Gaussian beam) first passes through the aperture with the PO and is then focused by lens L_1 onto the nonlinear sample at the focal plane, i.e. the Fourier plane. After traversing the sample, the diverging beam is collimated by lens L_2 and then recorded by the CCD camera at the rear focal plane of L_2. The same neutral density filter set is either placed before the sample to attenuate the intensity incident onto the sample or moved after L_2 to increase the intensity incident onto the sample but attenuate the intensity incident onto the CCD camera to avoid damage. Figure 4a shows the pattern of equifluence, recorded by the CCD camera, of a 2.85-μJ (the peak intensity being $2.3\,GW/cm^2$) laser pulse distorted by a specific point of the sample. Figure 4b shows the fluence as a function of the lateral distance (dashed line). This curve is extracted from Fig. 4a by plotting fluence as a function of x with $y = 0$. A theoretical curve (solid line) simulated in the manner mentioned above (the equations used in the simulation can be found in [1]) closely fits the experimental result. When the same measurements were repeated at various sample points, the patterns of equifluence (also the fluence vs. x graphs) differ from point to point but all lead to close nonlinear refractive coefficients ($n_2 = 5.5 \times 10^{-15}\,m^2/W$) and nonlinear absorption coefficients ($\beta = 1.7 \times 10^{-7}\,m/W$). See Fig. 4c for the fluence vs. x curve taken at another point as an example. We thus conclude from this series of experiments that NIT-PO is a suitable technique for the measurement of inhomogeneous samples.

After being invented in 1989, Z-scan has soon become a standard technique for nonlinear absorption and nonlinear refraction measurements because it is easy to operate, it is very sensitive, it can separate nonlinear absorption and nonlinear refraction, and it can determine the sign of nonlinear refraction. Since the measured samples are exposed to a laser beam of different sizes at different sample positions z, Z-scan signal fluctuations differ at each z. Moreover, since surface inhomogeneity differs from point to point, Z-scan curves obtained at different sample points deviate from each other and yield different nonlinear coefficients.

Later developed techniques, such as I-scan [6, 7], d-scan, r_a-scan, and ϱ-scan [8], all fix the samples at a specific position relative to the beam waist. This makes the samples exposed to the laser beam of the same size and thus avoids signal fluctuation induced by laser irradiation of different sizes. However, measurements performed at different sample points still inevitably deviate from each other because the inhomogeneity is different from point to point.

Similar to I-scan, d-scan, r_a-scan, and ϱ-scan, our NIT-PO technique fixes samples on the Fourier plane. This avoids signal fluctuation induced by laser irradiation of different sizes. Moreover, at different sample points, the surface inhomogeneity induced signal fluctuations at low input energy are recorded by the CCD camera. Using these fluctuations to interpret those obtained at high input energy at the same points, the patterns of equifluence obtained at various sample points are closely fitted using close nonlinear absorption and refraction coefficients.

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