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Nonlinear Optical Properties of Poly (3, 4-ethylenedioxythiophene) Synthesized by Electropolymerization

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1. Introduction

Conjugated polymers with strong delocalization of π-electrons in the polymeric backbone are considered as promising candidates due to their wide-ranging applications [1-4], such as supercapacitors, light-emitting diodes, and nonlinear optical devices. Conjugated polymers are usually chemically synthesized and dissolved in organic solvents or fabricated into films on various substrates via spin-coating to study their NLO properties [5, 6]. However, such chemical polymerizations involve many processes and the films obtained are inhomogeneous. In contrast, the films integrated by electrochemical polymerization are more compact and possesses higher conductivity. The process is simple and controllable. Among the numerous nonlinear organic polymers, thiophene based polymers [4, 7] are currently under intensive investigation for nonlinear optics because of their large third-order response, high chemical stability, and readiness of functionalization.

In this study, Poly (3, 4-ethylenedioxythiophene) (PEDOT) was synthesized by the galvanostatic electropolymerization method. The microstructure and third-order optical nonlinearities properties of PEDOT films on ITO and PEDOT solution were investigated.

2. Experimental

EDOT monomer (Baytron, 99%), was distilled. For the electrochemical polymerization, propylene carbonate (PC 99.5%) was used as electrolytes in this experiment, toluene-p-sulfonic acid (TOSH) as surfactant and supporting salt, ITO as working electrode and tantalum sheet as counter electrode. ITO and tantalum sheet were cleaned using the method as described by Hass [8].

0.19g TOSH was added into 20ml PC solution and stirred for 5 minutes for better dissolution. Next, 0.2ml EDOT monomer was dripped into the solution by burette. By applying currents of different magnitudes, different PEDOT films and PEDOT solution samples (part of PEDOT floc from positive plate dispersed in PC) were fabricated. All the experiments were carried out at room temperature.

The morphology of PEDOT dispersed on PC electrolyte was measured by JEM-3010 high-resolution transmission electron microscope (HR-TEM). The surface morphology of the PEDOT films was observed by JSM-6700F field emission scanning electron microscopy (FESEM) and atomic force microscope (AFM). The optical transmittance of PEDOT solution and PEDOT films on the ITO electrode were investigated using JASCO-570 UV/VIS spectrophotometer. The nonlinear optical properties of PEDOT solution and PEDOT films were characterized using a modified Z-scan technique [9, 10]. A Q-switched Nd: YAG laser frequency-doubled at 532nm and characterized by pulse duration of 7ns was employed as the light source. The light beam was a TEM_{00}-mode optical Gaussian spatial profile, and it was focused by the lens with focal length of 160mm. The radius at beam waist, ω_0 was 10μm. The transmitted beam energy, the reference beam energy, and their ratio were measured by an energy ratio meter simultaneously. The linear transmittance of the pulse energy passing the aperture to the total pulse energy was measured to be 0.10 (S=0.10) without sample loaded. The measurement system was using CS_2 as standard calibration. To avoid cumulative thermal effects, data were collected in single shot mode. The Z scan experimental setup is shown in Fig.1.

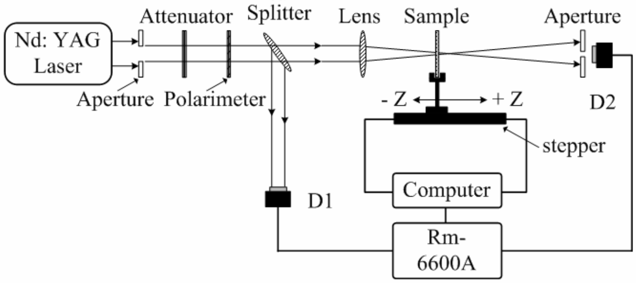

FIG.1. Schematic illustration of Z-scan experimental setup

3. Results and discussion

3.1 PEDOT films on ITO glass electrode

The PEDOT films on ITO substrate are transparent and their color is light blue. Fig.2 shows the optical transmittance of the PEDOT film (synthesized with 0.5mA/cm^2 current density for 5 minutes) on ITO glass substrate. The sample shows good transparency from 350nm to 800nm. The transmittance is about 71% at 532nm.

Fig.3 (a) and (b) show the FESEM and AFM images on the surface of the sample. It could be observed that the film is compact and smooth. Film roughness represented by root-mean-square value in 10×10μm^2 is only 9.4nm. The thickness of PEDOT film on ITO substrate was determined to be about 200nm by α-stepper profiler.

The Z-scan experimental curve of PEDOT film in PC is shown in Fig.4, in which the incident energy is 3μJ. The solid line shows the best theoretical fitting curve to the data. The signal profile with a peak-to-valley indicates a negative (self-defocusing) nonlinear refractive index. Since ITO substrate does not contribute to NLO properties, the result was from the PEDOT film. The laser-induced damage threshold of PEDOT films on ITO is around 6μJ. Thus the nonlinear effect is a third-order response rather than thermal effect. We made Z-scan measurements at several laser intensities and found that the relation of $\Delta n/I_0$ versus the peak input irradiance I_0 displayed a horizontal straight line. This indicates that the nonlinear effect is a third-order response.

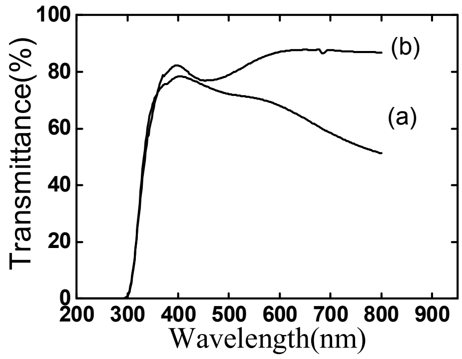

FIG.2. Optical transmittance of the PEDOT film synthesized at current density of 0.5mA/cm2 for 5 minutes (a) and ITO glass substrate (b).

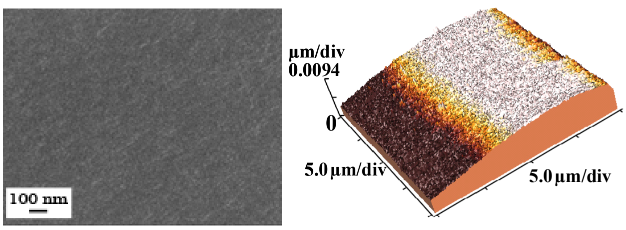

FIG.3. The surface morphology of the PEDOT film electropolymerization on ITO at 1mA/cm2 for 5 minutes, (a) FESEM image, (b) AFM image

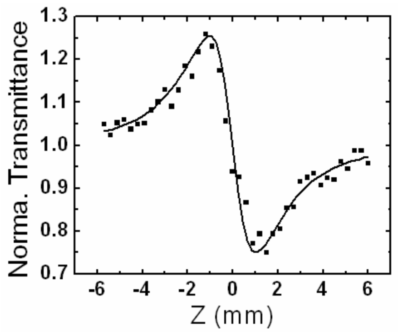

FIG.4. Measured Z-scan of PEDOT film using 7ns pulses at λ = 532nm, indicating a large negative nonlinearity (self-defocusing). Solid line is the best theoretical fitting obtained with equation (1).

According to the work reported by Chapple et al. [11] and Yin et al. [12], optical nonlinear refractive and absorptive parameters can be simultaneously estimated from the closed aperture. With the thin-sample approximation, the normalized transmittance (T) is given as $T(z)=1+\frac{4x}{(x^2+9)(x^2+1)}\Delta\phi-\frac{2(x^2+3)}{(x^2+9)(x^2+1)}\Delta\psi$ (1)

Where $x=z/z_0$, z is the position of the sample, while z_0 is the Rayleigh range of the lens; $\Delta\phi=k\gamma I_0 L_{eff}$ is the phase shifts due to refractive nonlinearity; $\Delta\Psi=\beta I_0 L_{eff}/2$ is the phase shifts due to absorptive nonlinearity. $k=2\pi/\lambda$ is the wave number, I_0 is the intensity of the incident laser beam, $L_{eff}=(1-e^{\alpha_0 L})/\alpha_0$ is the effective length of the sample, γ (m^2/W) is nonlinear refractive index, and β is the absorption coefficient.

The value of $\Delta\phi$ and $\Delta\psi$ can be obtained through the best theoretical fit from the Z-scan curve as shown in Fig.4. Then γ and β can be calculated. The real and imaginary part of the third-order nonlinear susceptibility can be deduced by the following equations: $\mathrm{Re}\chi^{(3)}=2n_0^2 c\varepsilon_0\gamma$ (2) $\mathrm{Im}\chi^{(3)}=n_0^2 c\varepsilon_0\lambda\beta/2\pi$ (3). The calculated value of nonlinear refractive index, γ(m^2/W), is $-9.25\times10^{-13}m^2W^{-1}$. The real and imaginary part of third-order optical susceptibility ($\mathrm{Re}\chi^{(3)}$(SI), $\mathrm{Im}\chi^{(3)}$(SI)) are $-9.63\times10^{-15}m^2V^{-2}$ and -4.01×10^{-17} m^2V^{-2}, respectively. Then, the third-order optical susceptibility $\chi_{SI}^{(3)}$ is $9.63\times10^{-15}m^2V^{-2}$ using $\chi^{(3)}=\sqrt{(\mathrm{Re}\chi^{(3)})^2+(\mathrm{Im}\chi^{(3)})^2}$. Converting into the Electro Static Unit (esu), the nonlinear refractive index, n_2 (esu), is -3.09×10^{-6} esu, and the third-order susceptibility $\chi^{(3)}(esu)$ is 6.90×10^{-7}esu. Compared to some representative organic polymer nonlinear materials and ferroelectric materials such as PLT30 films [13] and SBT films [14], PEDOT films show much higher nonlinear refractive index and the third-order susceptibility.

3.2 PEDOT solution

The color of PEDOT solution is light blue and its color becomes gradually deeper as polymerization time increases. Fig.5 shows the optical transmittance of PEDOT solution with 5 minutes' electropolymerization (current density: $0.5mA/cm^2$). The sample is tested in 1mm quartz cuvette and the transmittance is tested about 74% at 532nm.

The Z-scan experimental curve of PEDOT solution in PC is shown in Fig.6, in which the incident energy is 10μJ. Solid line shows the best theoretical fitting curve to the data. It is also a negative (self-defocusing) nonlinear refractive index. Since the quartz cuvette substrate has no NLO property at 532nm, the high NLO properties is attributed to the PEDOT solution. The measurement and calculation of NLO property of PEDOT films were the same as mentioned in section 3.1. The nonlinear refractive index, n_2 (esu), is -2.40×10^{-10} esu, and the third-order susceptibility $\chi^{(3)}(esu)$ is 5.35×10^{-11}esu. The results are more than one order of magnitude higher than that of other reported polymer solutions [4-6]. To study the reasons for this high optical nonlinearity, we further inspected our sample by TEM morphology. From Fig.7, it can be seen that PEDOT is rodlike grown under our process condition. Due to electropolymerization, the monomer grows up directly. This directional growth could increase the conductivity of the polymer, which accounts for the enhancement in the optical nonlinearity.

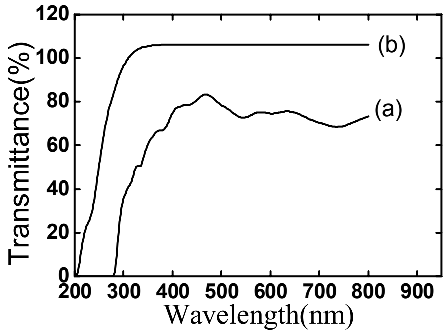

FIG.5. Optical transmittance of the PEDOT solution in PC at current density of $0.5mA/cm^2$ for 5 minutes (a) and PC pure solution (b)

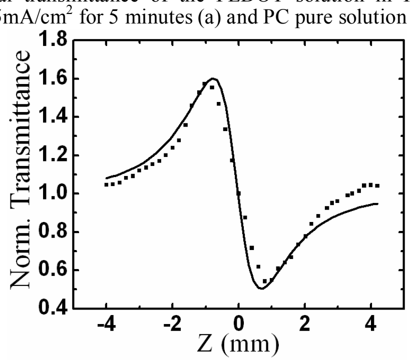

FIG.6. Measured Z-scan of PEDOT solution in PC using 7ns pulses at λ = 532 nm, indicating a high negative nonlinearity (self-defocusing). Solid line is the best theoretical fitting obtained with equation (1).

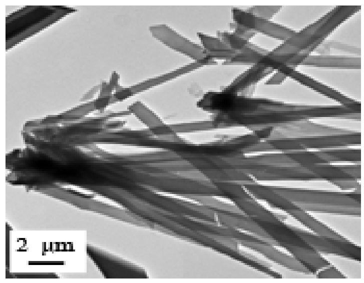

FIG.7. TEM morphology of PEDOT in PC solution

4. Conclusions

PEDOT films on ITO and PEDOT in PC solution were obtained by electropolymerization. Both of them have good transparency as measured by UV/VIS spectrophotometer. Their third-order optical nonlinearities were studied using Z-scan technique. The PEDOT films on ITO synthesized by electropolymerization are light blue, compact and smooth and its third-order nonlinear refractive index has shown to be the value as large as $10^{-13}m^2W^{-1}$. On the other hand, PEDOT in PC solution is rodlike as observed from the TEM morphology and its third-order nonlinear refractive index is found to be as large as $10^{-17}m^2W^{-1}$. Both PEDOT film and solution exhibit perfect stability and ultra-high third order nonlinear refractive indexes, indicating that the PEDOT as promising candidate for optical apparatus.

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