

Optical data storage in a tetraphenylethene-doped photopolymer

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We propose an application in optical data storage of tetraphenylethene-doped photopolymer, which has the attribute of aggregation-induced emission. We added some divinylbenzene in the photopolymer matrix in order to increase the fluorescence signal contrast. The photopolymer host was induced photochemical reaction at the focal point of a high-numerical-aperture lens. Thus, we could record binary data points inside the TPE-doped photopolymer matrix through two-photon absorption effect experiment. We got strong signal contrast between the exposure regions and the non-exposure regions. This attribute paves a new way for optical data storage and opens the way to exploring the possibility of utilizing the TPE-doped photopolymer as chemical sensors and components of organic light-emitting diodes.

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1. Introduction

In the era of “big data”, the problem of how to store the exponential increase in data is a troublesome issue. In 2011, a report from the International Data Corporation (IDC) claimed that the total amount of data generated globally would reach 35 ZB (1 ZB=10³ EB=10⁶ PB=10¹² GB) by 2020 [1]. Mainstream storage methods currently comprise hard disk drives (HDDs) and magnetic tapes, however, the bit-by-bit optical data storage (ODS) approach, may be more likely to be adopted in the future because the advantages such as ultralow energy consumption, ultra-long lifespans and higher storage capacity. Development of more

efficient ODS has attracted considerable attention from research groups [2-6].

For two-photon absorption (TPA) technology, the probability of a TPA transition depends upon the squared intensity of the beam used in the experiment. It is therefore advantageous to employ short pulses such as a picosecond or femtosecond laser source [7]. This excellent nonlinear property results in the excitation efficiency of the TPA process having a strong spatial constraint effect. There is also a higher resolution at the focal plane than that in single-photon absorption in the transverse and radial directions if we compare single-photon absorption in the infrared (IR) to two-photon absorption at the same wavelength. Even more

important than the laser source, however, the storage techniques are critically dependent on the performance of the storage media [8]. Based on a TPA localized-bit volumetric approach, ODS has been verified using two-photon fluorescence [7, 9], by refractive changes in photochromic [10, 11], phase-change material [12], and surface plasmons technology [13].

Since the Tang research group found unusual AIE phenomenon in 2001 [14], a number of AIE molecules with different structures have subsequently been developed by many research groups [15-22]. In normal aggregation-caused quenching (ACQ) phenomenon, in which light emissions from conventional fluorophores in dilute solution are often quenched at high concentrations or in an aggregate state. By contrast, fluorescence is induced in AIE dyes by aggregate formation because the restriction of intramolecular rotations in the aggregates blocks the π - π stacking interactions channel, hence, they just only release energy through strong fluorescence [23]. In 2016, the Han research group [24] used AIE materials to develop a method of realizing ODS. It is not suitable for ODS in practice because of its poor fatigue resistance and photostability. In this paper, we propose the application of TPE dye-doped photopolymer film in optical data storage through a different channel.

2. Experiments about AIE verification

The TPE material was used as purchased from Sigma without any treatments. Initially, we placed some TPE powder onto a piece of filter paper in order to exclude fluorescence from other objects. Fig. 1(a) shows a fluorescence photography of TPE powder under 365 nm UV light. We observed strong blue fluorescence. Fig. 1(b) shows the fluorescence emission spectrum of TPE powder with the maximum emission wavelength at 450 nm. The inset in Fig. 1(b) shows the TPE molecule structure that we used in the experiment.

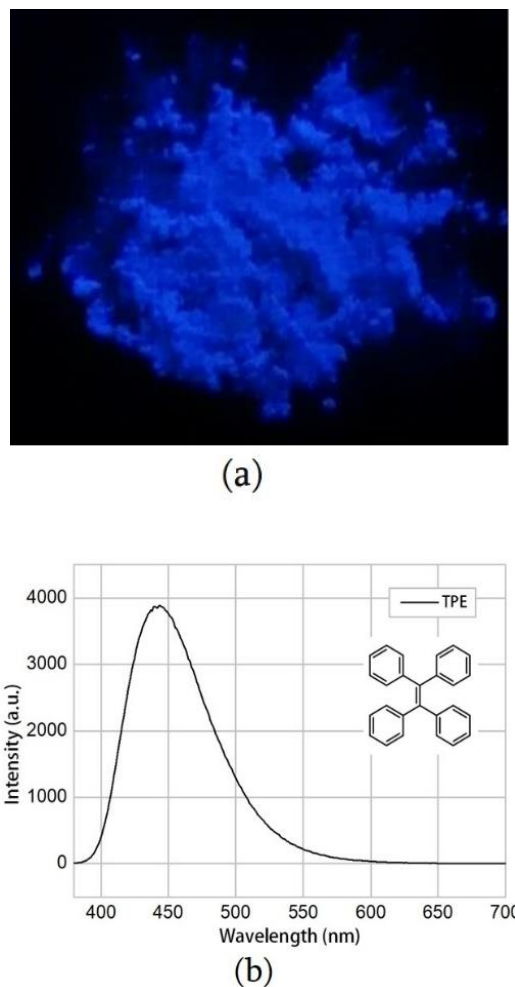


Fig. 1. (a) Fluorescence picture of TPE powder and (b) corresponding fluorescence spectrum under 365 nm UV excitation. The inset shows the TPE molecule structure (color online)

In recent years, bit-by-bit ODS based on photopolymerization has been the most popular method. The key to the success of this method is the monomer host material [25-27]. Large TPA cross-section and high mechanical strength are the fundamental requirements for optical beam recording [27]. In this experiment we used the five-functional monomer dipentaerythritol pentaacrylate (DTPA), which many research groups [27-29] had used to realize binary ODS through different optical channels. The Gan research groups reached a 9 nm feature size and 52 nm feature resolution in 2013 [27], which is still the world record.

We first created two groups A and B to verify that TPE dye still has the AIE attribute in the photoresist film. To prepare the photoresist group A, monomer DTPA and

photoinitiator 1173 which are both transparent and thermostable, were dissolved in acetone. To prepare the photoresist group B, the monomer DTPA, photoinitiator 1173, TPE powder were dissolved in acetone. Both groups were kept in the oven at a temperature of 50°C for 12 h to remove the acetone [26]. The final composition of group A and group B photoresists consisted of monomer 98 wt% and photoinitiator 2 wt% and monomer 98.68 wt%, photoinitiator 0.99 wt% and TPE 0.33 wt%, respectively.

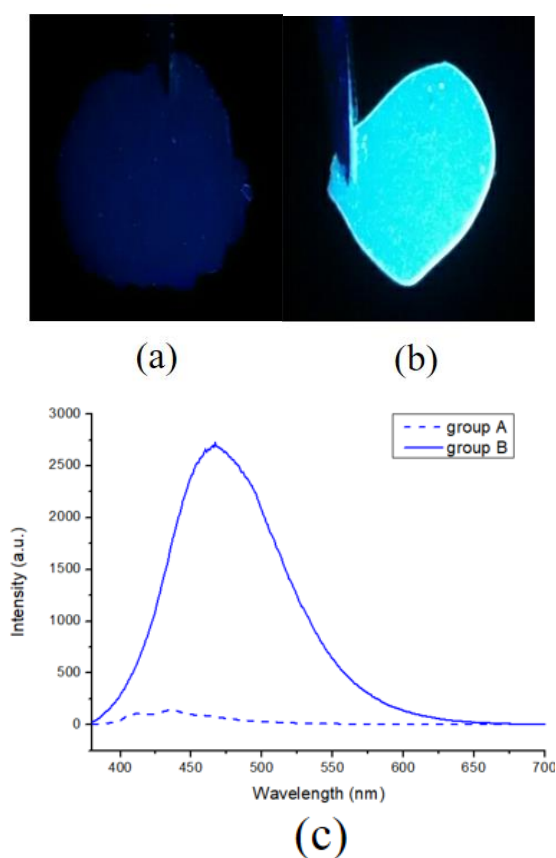


Fig. 2. Picture of solid photoresist of (a) group A and (b) B under 365 nm UV light. (c) Shows the fluorescence spectrum of group A and B at solid state (color online)

We put both kinds of 0.5 mL liquid photoresists under 365 nm high-power UV light for about 1 min to make two completely solid films, as shown in Fig. 2(a) and Fig. 2(b),

respectively. Group B shows stronger fluorescence intensity than group A under a 365 nm lamp light. We can see from Fig. 2(c) that the fluorescence intensity of group B is several hundred times than group A at the same test condition and the position of the maximum emission wavelength is at about 475 nm. In comparison to the TPE powder, the position of maximum fluorescence emission of the suspension solution and solid photoresist film are both slightly redshifted. The reason for this redshift is still unknown and further analysis is necessary to find the cause.

3. Optical data storage experiment

To demonstrate the ODS capacity of our TPE-doped photoresist film, a custom-built fluorescence microscopy was used for recording data as shown in Fig. 3. A femtosecond (fs) laser with a wavelength of 515 nm at a repetition rate of 40 MHz with a 500-fs pulse width creates a diffraction limited Gauss spot, which traced the entire light path to reach a certain depth inside the recording media. A 100× 1.4 NA oil immersion objective (Olympus, Japan) that can compensate for the spherical aberrations was used to focus the light into the media. A filter was used to stop the back-scattered laser source from reaching the charge-coupled device (CCD). A Physik Instrument (P-563.3CD and E-712.3CDA, Germany) piezo stage was used to position and scan the sample. Half-wave and quarter-wave plates were used to change the polarization state of the laser beam to circular polarization. Samples used for recording data points were prepared by dropping about 10 μ l of group B photoresist, which contains TPE dye molecules onto a glass slide. A cover slip was used to sandwich the photoresist between two coverslips separated by a 40- μ m-thick sticky-tape spacer [30]. Using the nonlinear TPA effect, the viscous photopolymer matrix will be solidified at the focal region under 515 nm. The TPA effect accounts for the effect of photoinitiator 1173, which induced solidification inside the photopolymer host. We stored data points inside the medium when the exposed regions were solidified and could observe the recording process through CCD clearly, as shown in Fig. 4(a), because of the refractive difference.

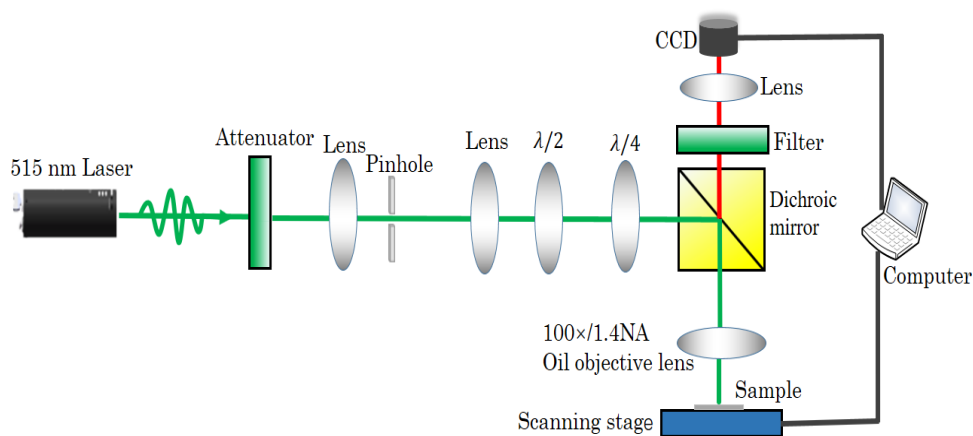


Fig. 3. Optical setup used for recording of the TPE-doped photopolymer medium (color online)

During the process of making points, the average exposure power was 10 mW and recording time 30 ms, respectively. Fig. 4(b) shows the SEM (FEI-Magellan 400) photograph of the array of points when the liquid material part was washed away by using acetone after the recording process. The exposure regions which were at the focal point of a high-numerical-aperture oil lens were solidified by the excitation laser source and not dissolved by the acetone. The feature size of our recording points is about 255 nm as shown in Fig. 4(c). As shown in Fig. 4(d), in order to obtain the smaller record feature size, we decrease the recording power and the smallest feature size is roughly about 175 nm while the average is 2 mW and exposure time is 30 ms, respectively.

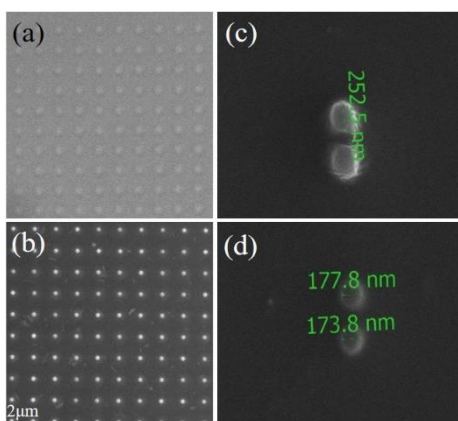


Fig. 4. The data points were recorded inside the storage medium. (a) is the CCD screenshot. (b) and (c) show the SEM result and indicate that the feature size of data points is about 255.7 nm while the average power is 10 mW and exposure time is 30 ms. (d) indicates that the feature size of data points is about 175 nm while the average power is 2 mW and exposure time is 30 ms (color online)

For the sake of writing data points inside the photopolymer and verifying the fluorescence signal enhancement effect of divinylbenzene in the solid films, another group C was built. The composition of group C photoresist consists of monomer 82.42 wt%, photoinitiator 0.82 wt%, TPE 0.27 wt% and divinylbenzene 16.49 wt%, respectively. Using the same fabrication method what we mention above, we made two solid film samples of group B and C. After finishing the recording process, we tested the fluorescence signal of the recorded points under laser scanning confocal microscopy (Zeiss Observer SD) and the final results are shown in Fig. 5. Fig. 5(a) represents the result of the sample of group B. We randomly chose one of the ten horizontal lines and the gray value results are shown in Fig. 5(b) which we barely distinguish the recorded binary data points because they are completely overwhelmed by the background signal. In group C, the divinylbenzene reacted with TPE dye could increase the TPE conjugated degree under the effect of laser light and we further could get better SNR and the result is shown in Fig. 5(c). We also randomly choose one line and found that all the gray values exceed 70 and the signal contrast ratio rough reaches 2.33:1 which we could clearly distinguish the recorded data points from other areas because the very well signal contrast.

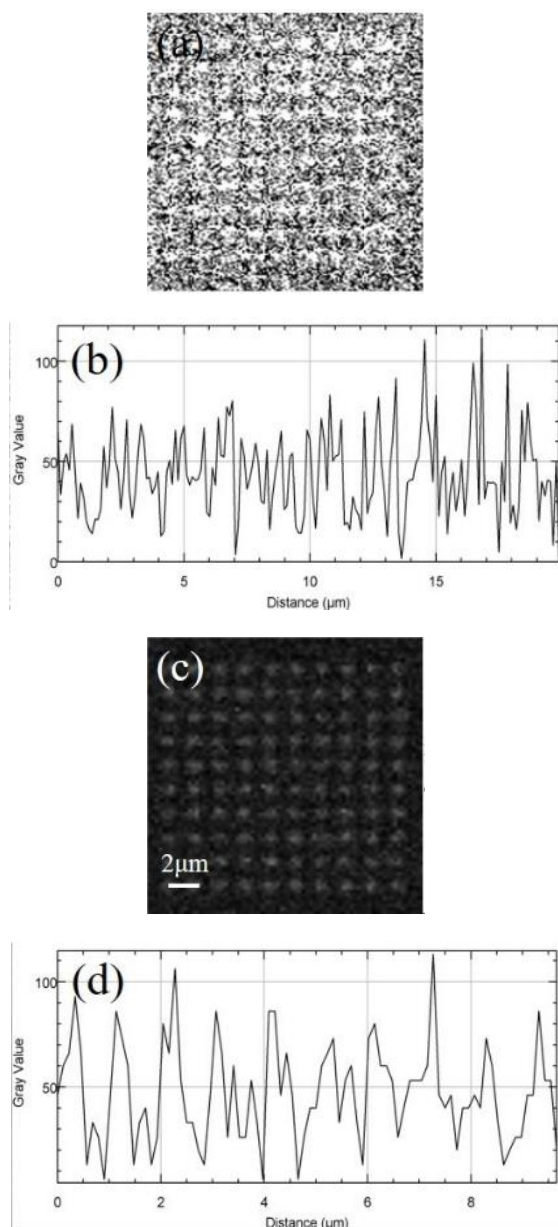


Fig. 5. Fluorescence maps with different divinylbenzene weight percentage. Photoresist host (a) without divinylbenzene and (b) is the corresponding gray value curve; Photoresist host (c) with 16.49 wt% divinylbenzene and (d) is the corresponding gray value curve and the signal contrast ratio rough reaches 2.33:1

4. Summary and conclusions

In conclusion, the main purpose of this letter is to prove the feasibility of TPE-doped photoresist in ODS. Utilizing the AIE characteristic of TPE material, we obtain a

fluorescence intensity difference between the points representing binary point “1” and “0” which can be used to create the ODS. The fluorescence intensity difference can be tuned by adjusting the amount of the TPE. Future possibilities include the design of a series of AIE molecules whose normal states have weak fluorescence or even non-fluorescence, but will emit very strong fluorescence when a photochemical reaction occurs that is excited by a particular wavelength of laser.

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