Semiconducting Polymer Dots as Saturable Absorbers for Mode-Locked Thulium-Doped Fiber Lasers

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ABSTRACT We demonstrated an all-fiber passively mode-locked thulium-doped fiber laser (TDFL) using organic semiconducting polymer dots (Pdots) based saturable absorber (SA). The Pdots are prepared by methods of donor-acceptor moieties and reprecipitation, which possess a broadband absorption from 400 to 2200 nm and nonlinear saturable absorption property at 2 μm. By depositing the Pdots onto the microfiber as an SA, long nonlinear interaction length of evanescent wave and Pots can be achieved. An ultrafast fiber laser operating at 1926 nm was observed. The output power could reach to 76.2 mW at the maximum pump power of 2.1 W. Compared with Pdot-film SAs in our previous work, these experimental results verify that Pdot-SAs functioned with evanescent field interaction are promising nonlinear optical modulators for ultrafast and high-power pulse generation.

INDEX TERMS Semiconducting polymer dots, microfiber, saturable absorber, mode-locked.

I. INTRODUCTION

Passively mode-locked thulium-doped fiber lasers (TDFLs) generating ultrafast optical pulses around 2 μm are always extensively applied in diverse fields including fundamental research [1], [2], nonlinear optics [3], [4], biomedical research [5], and material processing [6], [7]. Ultrafast fiber lasers possess many desirable advantages of compactness, low cost, efficient heat dissipation, and good reliability under harsh environments compared to the bulk solid-state lasers. In mode-locked fiber lasers, a saturable absorber (SA) was used as the nonlinear optical switch for mode-locked operation. Therefore, many efforts have been dedicated to develop SAs with high performance. Transition metal dichalcogenides, black phosphorus, carbon nanotube, and graphene have been widely researched as the SAs to construct the mode-locked TDFLs [8]–[15]. The above-mentioned SAs all have large intrinsic third-order optical nonlinear

susceptibility, ultrafast response time, wide absorption band and good compatibility. Although great progress has been made in the research of SAs, only few studies of organic semiconducting polymer dots (Pdots) used as SAs for ultrafast pulse generation are reported, which possess several unique features such as photophysical properties, biocompatibility, good processability, low cost, and versatility of functionalization [16]–[18].

Pdots are defined to be a small nanoparticle composed of semiconducting polymers. Semiconducting polymers are formed by a backbone chain of alternating double- and single-bonds. Their overlapping p-orbitals create a system of delocalized π-electron. Therefore, the Pdots display very strong molecular polarizability and third-order optical nonlinearities due to the high delocalization of π-electrons and hence exhibit the nonlinear absorption [19], [20]. The current Pdots only possess good absorption from 400 to 1400 nm, which limits the broadband application at 1.56 and 2 μm. Few studies have been exploited to explore the new organic SAs that can display saturable absorption extending to the middle

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infrared region. Therefore, designing and synthesizing the Pdots with broadband absorption is of great significance. Moreover, in our previous work, the Pdot SAs were fabricated by the filmy method [21]. Then the SA films were sandwiched between two fiber ferrules to prepare the optical modulator device and inserted into the laser cavities. Although the filmy method was simple to carry out, the nonlinear absorption length was limited by the film thickness and it was easy to cause damage induced by the direct physical contact or the photothermal effect, which constrained the wider application of the Pdot-SA films in the pulsed lasers, especially for the high-power lasers. To overcome the above-mentioned restrictions and study whether the Pdot SAs could apply for the high-power pulsed lasers operating at 2 μm or not, we proposed an indirect interaction scheme through employing the microfiber coated with Pdots (MCP) as the SA.

In this paper, we report an all-fiber passively mode-locked TDFL based on the MCP SA with evanescent field interaction. The synthesized Pdots display a broadband absorption from 400 to 2200 nm and nonlinear saturable absorption property at 2 μm. By depositing the Pdots onto the microfiber as an SA, long nonlinear interaction length of evanescent wave and Pots can be achieved. An ultrafast fiber laser operating at 1926 nm was realized with a pulse width of 602 fs. The output power could reach to 76.2 mW at the maximum pump power of 2.1 W. Our results verify that MCP SA functioned with evanescent field interaction are promising nonlinear optical materials for ultrafast and high-power pulse generation.

II. PREPARATION AND CHARACTERIZATION OF MATERIALS

The Pdots were synthesized through a combination of donor-acceptor moieties and the reprecipitation method [22], [23]. Firstly, the polymer PIDT-BBT was prepared by donor-acceptor moieties through Stille cross-coupling polymerization. Figure 1a represented the synthetic route and chemical structure of the conjugated polymer PIDT-BBT. In general, a flask was charged with 4,8-bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)benzo [1,2-c:4,5-c']bis[1,2,5] thiadiazole (0.25 mmol), 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b'] dithiophene (0.25 mmol) and toluene (10 mL). After adding the palladium catalyst Pd(PPh3)4 (0.004 mmol), the flask was degassed with three freeze-pump-thaw cycles to remove air. Under nitrogen protection, the mixture was stirred under 100 °C for 48 hours. Then the reaction was stopped by adding the (4, 4, 5, 5-Tetramethyl-1, 3, 2-dioxaborolan-2-yl) benzene (20 mg) and bromobenzene (0.2 mL) to the mixture separately. The crude product was cooled down to room temperature and washed with deionized water. The organic layer was concentrated and dropped into excess methanol. And the precipitates were collected by filtration and then purified through Soxhlet extraction. The obtained product was then dried in a vacuum. The reprecipitation method was adopted to prepare the Pdots.
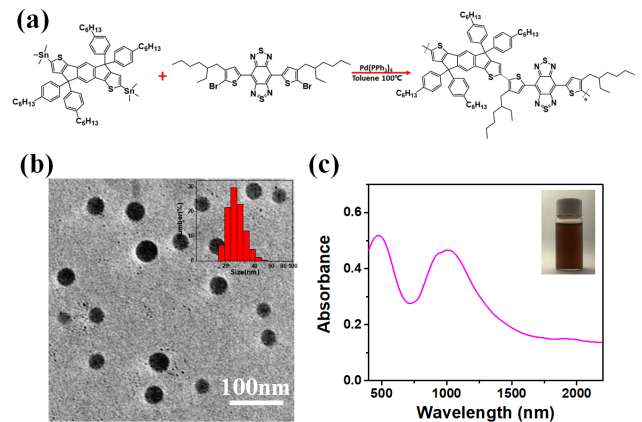

FIGURE 1. (a) Synthetic pathway and structure of the conjugated polymer PIDT-BBT. (b) TEM image of PIDT-BBT nanoparticles. Inset: DLS results of the PIDT-BBT Pdots. (c) Absorption spectrum of the Pdots. Inset: photograph of the stable Pdots solution.

Briefly, a tetrahydrofuran (THF) solution (1 mL) of polymer PIDT-BBT and PSMA (20 wt%) was quickly injected to deionized water (10 mL) with vigorous ultrasonication. The THF was removed by blowing nitrogen into the solution under ~90 °C. A 0.45 μm membrane filter was adopted to remove the fraction of aggregates.

The obtained Pdots were examined by the transmission electron microscopy (TEM). In Figure 1b, it was worth noting that the Pdots were spherical and their surface was smooth. It could be seen from the illustration of Figure 1b that the particle size of Pdots measured by dynamic light scattering (DLS) was between 20-40 nm. The absorption spectrum of the synthesized Pdots was characterized through a spectrophotometer (UV-3600 Shimadzu) as presented in Figure 1c, which showed that prepared Pdots had a broad absorption bandwidth in the range of 400~>2200 nm. As shown in the inset of Figure 1c, a stable Pdots solution was obtained, and there was no aggregation after 24 hours.

Figure 2a shows the process of the fabrication for the MCP SA, which is made by depositing the Pdots onto a microfiber. The microfiber is fabricated from a single mode fiber (SMF-28) by using a method of standard flame brushing. It can be seen that the microfiber was immersed into the Pdots solution droplet. Then we employed the photodeposition method for making the Pdots arrange along the fiber direction by using a 1980 nm laser as the injecting light. In order to confirm the initial position of Pdots deposition and control the deposition time, a power meter was used to monitor the laser out. When the Pdots deposition loss was up to 2 dB and the total loss was ~4.2 dB, the incident lights were turn off. Then the fabricated SA was dried at room temperature.

Shown in Figure 2b is the photograph of the fabricated MCP SA. It can be seen that the Pdots are deposited along the microfiber. In order to intuitively observe the evanescent field which passed through the MCP SA, a red light laser diode at 635 nm was injected into the MCP SA. The evanescent field scattered by Pdots was clearly seen in Figure 2c.
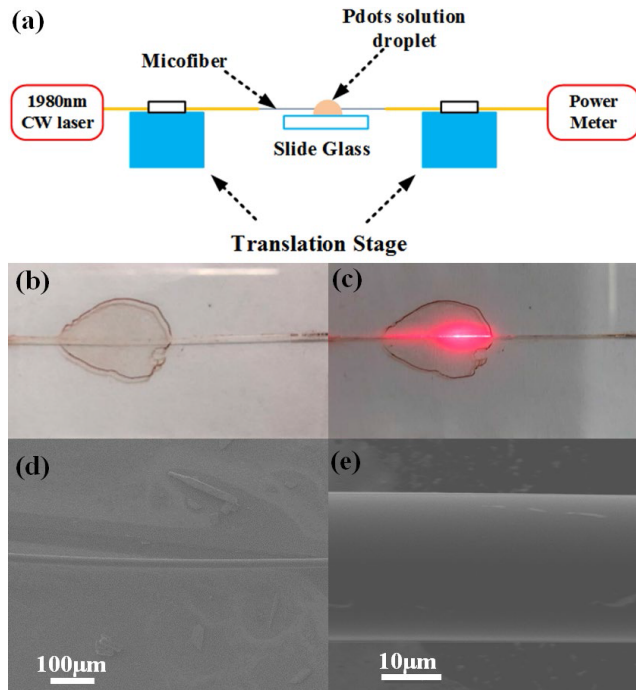
FIGURE 2. (a) Fabrication of the MCP SA. (b) Photograph of MCP SA. (c) The evanescent field Photograph of the MCP SA through launching the red light. (d, e) SEM images of the MCP SA at different scales.

To examine the characteristics of the fabricated MCP SA, the scanning electron microscope (SEM) of the MCP SA was first represented at a scale of 100 μm and 10 μm as shown in Figure 2(d, e). It is obvious that the waist diameter of the microfiber is ~25.7 μm.

Open-aperture Z-scan method is widely adopted to characterize the third-order nonlinear property of the SA. The large nonlinear absorption coefficient indicates that the proposed SA has a strong nonlinear modulation capability and a high potential for pulsed laser generation. To measure the nonlinear absorption coefficient β of PIDT-BBT Pdots at 2 μm, we employed the open aperture Z-scan measurement with the ultrafast laser operating at 1930 nm as the excitation light. Figure 3a displays the generated Z-scan test data. By using nonlinear absorption model to fit the Z-scan data of PIDT-BBT Pdots [24], the value of β was calculated to be ~-2.26 × 10^{-8} mW^{-1}. Such values indicate that MCP can be considered as the promising SA for pulse generation at 2 μm.

In addition, saturable absorption characteristic is also of great importance for pulsed laser generation. To analyze the saturable absorption properties of the MCP SA, the evolution of transmission ratio was studied as the increase of incident power density by employing a pulsed fiber laser (1980 nm, 1 ps) [25]. Figure 3b shows that the prepared MCP SA has obvious saturable absorption at 1980 nm. The modulation depth, saturation intensity and non-saturable loss were measured to be ~6.3%, ~11.3 MW/cm^2 and ~35.3%, respectively. As a comparison, the MCP SA showed a smaller modulation depth of 6.3% than the value (20%) of Pdot-SA film [21], which indicated that the MCP SA possessed an
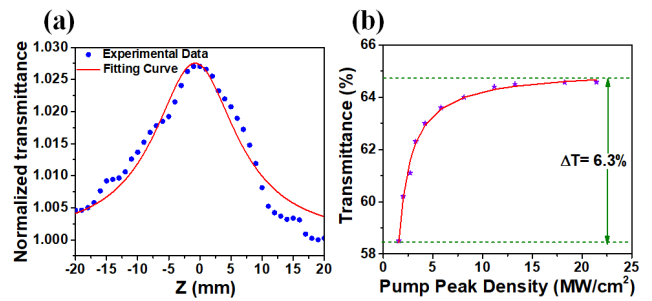

FIGURE 3. (a) Z-scan measured results at 1930 nm, (b) Dependence of the transmittance on the incident power density at 1980 nm.
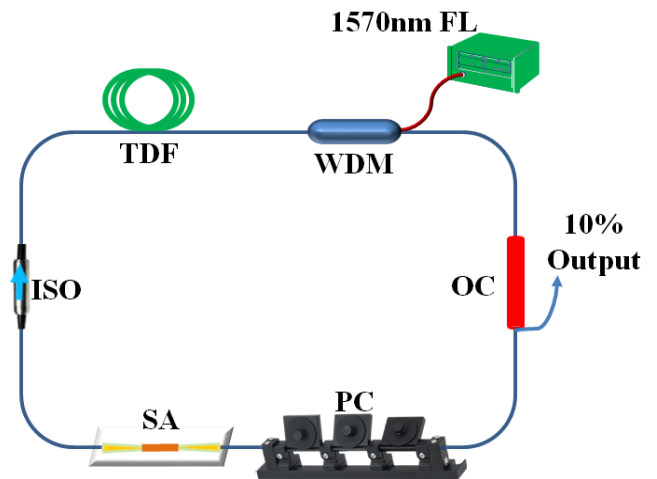

FIGURE 4. Schematic diagram of the TDFL.

adequate property for constructing femtosecond fiber lasers at 2 μm.

III. RESULTS AND DISCUSSION

In order to see whether the MCP SA can be used to induce mode-locking at 2 μm or not, the MCP SA was inserted into theTDFLs as shown in Figure 4. A 1570 nm fiber laser with a maximum output power of ~2.1 W was used as the pump source. Then the pump light could be launched into the cavity through a 1570/2000 nm wavelength-division multiplexing (WDM) coupler. The gain fiber was a 20 cm long TDF. An isolator (ISO) was adopted to maintain the laser operation unidirectional and stable. Polarization state was controlled by adding a polarization controller (PC). The running pulses in the cavity were extracted out through a 10 dB optical coupler (OC). Here, the used ISO, PC and OC all operated at 2000 nm. The MCP SA was integrated into the cavity to maintain the all-fiber structure and served as the optical modulator. The performance of output light was characterized by using an optical spectrum analyzer, an autocorrelator, and a digital oscilloscope together with a high speed photodetector, which all had been calibrated.

The TDFL operated in a passively mode-locked regime for a power threshold of 900 mW by adjusting PC condition. Figure 5a shows the lasing wavelength of the mode-locked
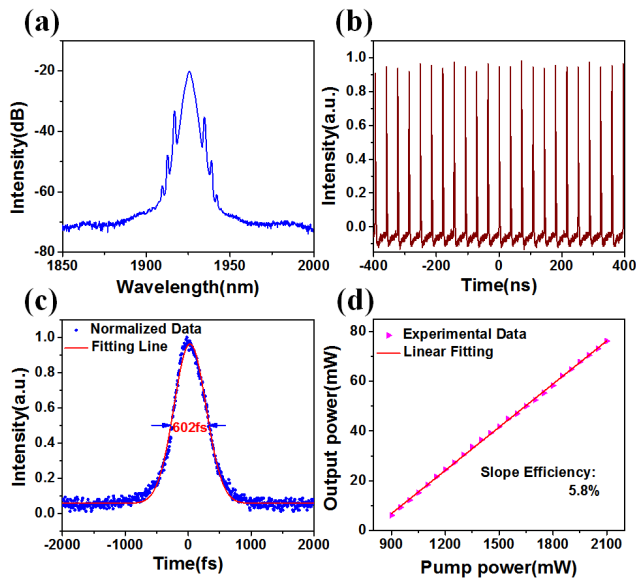
FIGURE 5. Mode-locked characteristics of TDFL: (a) emission spectrum, (b) pulse train, (c) single pulse profile, (d) Output power versus pump power.

TDFL with a pump power of 1.8 W, whose central wavelength located at 1926 nm. Apparently, the Kelly bands caused by dispersive wave interference were also noticed, which indicated the solitary laser operation [26], [27]. Figure 5b reveals that the time interval of sequential pulses was about ∼46.66 ns and corresponding repetition rate was ∼27.8 MHz. Figure 5c displays the monopulse of the above mode-locked operation, and the duration of which was 602 fs after amplification measured by the autocorrelator. Furthermore, the measured output power evolution as the increase of the pump power is represented in Figure 5d. By varying the 1570 nm laser power from 0.9 to 2.1 W, the output power increased linearly from 6.14 to 76.2 mW, and the resulting optical-to-optical efficiency was about ∼5.8%. Moreover, the maximum output power (76.2 mW) limit was determined by the maximum pump power (2.1 W). We will research the damage threshold of MCP SA in our following work. Therefore, compared with the Pdot-SA films, the MCP SA could greatly enhance the optical damage threshold due to a longer nonlinear interaction length between light and Pdots. This result verifies that the proposed MCP SA is appropriate for constructing high-power ultrafast TDFLs.

Furthermore, long term stability is a key issue for mode-locked fiber lasers based on the SA. To test the stability of the mode-locked TDFL induced by the MCP SA, the spectra (Figure 5a) were recorded in a 20 min interval for 3 hours. As shown in Figure 6a, it is obvious that the spectra had no obvious change in wavelength or intensity. Besides that, the radio frequency (RF) property was also measured in Figure 6b. It can be seen that the fundamental peak was in accordance with the laser repetition rate (27.8 MHz) and the signal-to-noise ratio was ∼67 dB (about 10^7 contrast). Ultrafast carrier dynamics of this SA is responsible for the strong noise suppressing capability. These results confirm
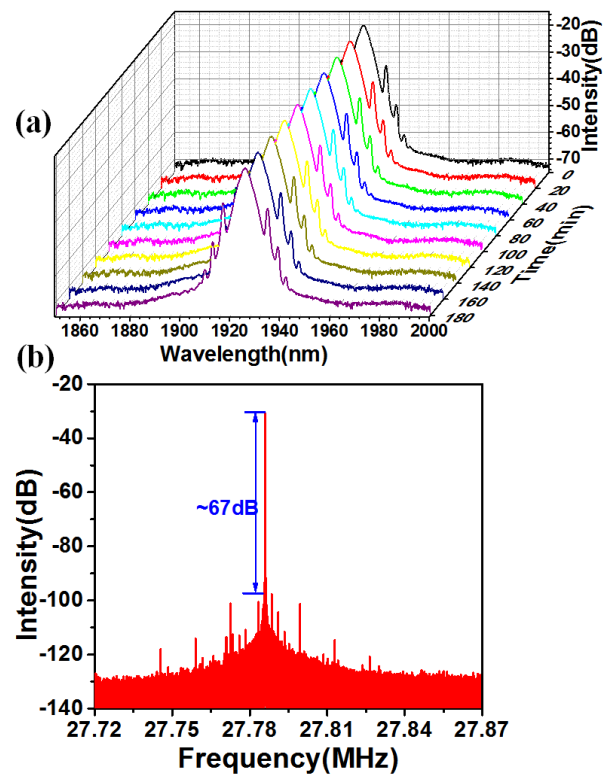

FIGURE 6. (a) Time-dependent emission spectra measured at 20 min interval. (b) RF spectrum of mode-locked TDFL.

that the mode-locked operation induced by the MCP SA possess good stability.

IV. CONCLUSION

In our previous work, we had adopted the PIDT-BBT Pdot films as the SA and realized the passively Q-switched operations at 1, 1.5, and 2 μm [2 1]. As a comparison, the MCP SA showed a smaller modulation depth of 6.3% than the value (20%) of Pdot-SA film, which indicated that the MCP SA possessed an adequate property for 2 μm mode-locked pulses generation. Moreover, the mode-locked operation induced by the MCP SA possessed the bigger damage threshold (>2.1 W), maximum output power (>76.2 mW) and conversion efficiency (5.8%) than Pdot-SA film's (905 mW, 3.61 mW, 2.05%). Therefore, the MCP SAs displayed more excellent performance in the pulsed laser generation.

In conclusion, we experimentally demonstrated an all-fiber passively mode-locked TDFL based on a MCP SA with evanescent field interaction. The synthesized Pdots possess a broadband absorption from 400 to 2200 nm and nonlinear saturable absorption property at 2 μm. By depositing the Pdots onto the microfiber as an SA, long nonlinear interaction length of evanescent wave and Pots can be achieved. A self-started mode-locked operation at 1926 nm was observed with a pulse width of 602 fs. The output power could reach to 76.2 mW at the maximum pump power of 2.1 W. Compared with Pdot-film SAs, these experimental results verify that Pdot-SAs functioned with evanescent field interaction are

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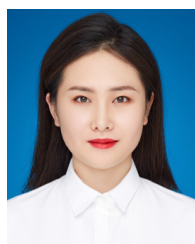
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