A near-infrared-II light-response BODIPY-based conjugated microporous polymer for enhanced photocatalytic degradation of cationic dyes and H₂O₂ production†

Xiaobo Luo,‡a Yan Zhang,‡a Shiyuan Zhou,†a Peng Wang,*b Danfeng Wangac and Peiyang Gu†a

A BODIPY-containing conjugated microporous polymer (CMP, LBFD-1) was modified with calixarene to develop a hydrophilic CMP (LBFD-2) with broader absorption extending to the near-infrared-II region. LBFD-2 exhibited an H₂O₂ production rate of 2.14 mmol g⁻¹ h⁻¹ in the air without any sacrificial agents. The removal efficiency (η) of LBFD-2 towards methylene blue and rhodamine B reached >99.5% within 20 and 40 min in light. LBFD-2 can withstand diverse environmental changes, showing excellent reusability and potential for practical applications in real-water systems.

In recent decades, due to the rapid growth of global industry and agriculture, a significant volume of industrial wastewater has been discharged without proper consideration, resulting in numerous pollutants that have caused irreversible damage to aquatic environments. These pollutants pose a severe risk to human health and safety.1,2 Organic dyes are among the most prevalent pollutants in various industries, such as papermaking,3 food processing,4 plastics manufacturing,5 cosmetics production,6 and textile production.7 They exhibit potent biological toxicity and carcinogenic properties, damaging aquatic organisms and humans via the food chain.8,9 To address these challenging and hazardous organic pollutants, there is an urgent need to develop innovative and energy-efficient wastewater treatment technologies to regenerate and reuse water resources.10–12 Photocatalytic treatment technology stands out as an effective approach compared to conventional methods, utilizing eco-friendly solar radiation to activate catalysts that produce highly reactive species (such as ·OH, ·O₂, ·O₂⁻ and h⁺), ultimately achieving the oxidation and degradation of organic pollutants.13,14 The key to photocatalytic treatment technology is developing efficient photocatalysts with multiple surface reaction sites and surface reaction activity.

Conjugated microporous polymers (CMPs) are widely used in various fields such as gas capture and conversion, energy production, biomedical engineering, environmental remediation, sensing, and photocatalytic degradation due to their outstanding features including chemical/thermal stability, tunable pore structure, high surface area, and cost-effectiveness.15 However, the dispersion of most CMPs in water is usually poor due to their hydrophobic and rigid skeletons, which hinders their surface reactions.16 To overcome this challenge, post-synthetic modification of CMPs is an efficient method to control the surface functionality and microporosity of CMPs, thereby facilitating the development of efficient photocatalysts through the synergistic effect of adsorption and photocatalysis.17–19

Herein, an efficient CMP photocatalyst (denoted as LBFD-1) was successfully prepared by connecting difluoroboron-dipyrromethene (BODIPY) with 1,3,5-trifluoro-2,4,6-triiodobenzene via a Sonogashira coupling reaction. Specifically, BODIPY was introduced as an active photocatalytic center due to its remarkable reactive oxygen species (ROS) generation capability.20,21 The 1,3,5-trifluoro group was introduced as a connecting and post-synthetic site that enables interaction with a calixarene moiety to develop hydrophilic CMPs (denoted as LBFD-2). Such modification not only imparts hydrophilicity to LBFD-2 due to the introduction of calixarene fragments, thereby enhancing its adsorption efficiency towards dyes, but also enhances its inherent photoelectrical properties including broadening the absorption range for more efficient utilization of visible light, increasing photocurrent, and enhancing electrical conductivity.22 To evaluate the synergistic effect of adsorption and degradation, methylene blue (MB) and rhodamine B (RhB) were selected as two model pollutants to investigate the photocatalytic performance of LBFD-1 and LBFD-2. For LBFD-1, the removal efficiency (η) of MB...
showed a broader absorption range, which expanded from the reflectance spectroscopy. Compared with LBFD-1, the LBFD-2 in the absorbance spectra determined by UV-visible diffuse reflectance spectroscopy. The photocatalytic degradation performance of LBFD-1 and LBFD-2 was calculated according to the Tauc’s equation and measured to be 1.29 and 1.20 eV, respectively (Fig. S8a, ESI†). The narrower band gap of LBFD-2 indicated that it possessed better ability to produce photogenerated charges. Thirdly, the flat band potentials of LBFD-1 and LBFD-2 were determined to be −0.85 and −0.52 eV (vs. NHE) according to the Mott–Schottky curves (Fig. 1b and Fig. S8b, ESI†). Therefore, the valence band (VB) potentials of LBFD-1 and LBFD-2 were 0.44 eV and 0.68 eV, respectively, according to eqn (S1) (ESI†). Lastly, the photocurrent and electrochemical impedance of the photocatalysts were analyzed to characterize their photoelectrochemical properties. As shown in Fig. 1c, the photocurrent response of LBFD-2 was significantly stronger than that of LBFD-1, indicating that LBFD-2 could rapidly generate electrons and holes under visible light irradiation, resulting in better charge carrier migration and separation efficiency, which provided more charges for surface reactions. Moreover, the electrochemical impedance radius of LBFD-2 was much smaller than that of LBFD-1, further highlighting the better conductivity and superior photogenerated charge carrier migration ability of LBFD-2 (Fig. 1d and Fig. S8c, ESI†). These observations indicated that the post-modification of calixarene moieties not only endowed LBFD-2 with improved hydrophilicity and excellent swelling ability but also amplified its inherent photoelectrical properties. Compared to our previous work, a photocatalyst named CABP with two charge transfer channels,19 LBFD-2 exhibited enhanced photocurrent and smaller radius of electrochemical impedance (Fig. S9, ESI†) owing to three charge transfer channels, highlighting that increased channels are beneficial for the separation and transport of carriers.

The photocatalytic degradation performance of LBFD-1 and LBFD-2 towards MB and RhB was evaluated to validate the reasonability of the post-modification strategy and a well-known photocatalyst, g-C₃N₄, was also employed for comparison. As shown in Fig. 2a and b, the η of LBFD-2 was significantly higher than that of LBFD-1 and g-C₃N₄. After being stirred in the dark for 15 min, the UV-visible region to the near-infrared region due to the strong charge transfer in its structure. Secondly, the band gaps of LBFD-1 and LBFD-2 were 2.14 mmol g⁻¹ h⁻¹ and 1.70 mmol g⁻¹ h⁻¹, respectively, resulting in better charge carrier migration and separation efficiency. Therefore, the valence band (VB) potentials of LBFD-1 and LBFD-2 were calculated according to the Tauc’s equation and measured to be 1.29 and 1.20 eV, respectively (Fig. S8a, ESI†). The narrower band gap of LBFD-2 indicated that it possessed better ability to produce photogenerated charges. Thirdly, the flat band potentials of LBFD-1 and LBFD-2 were determined to be −0.85 and −0.52 eV (vs. NHE) according to the Mott–Schottky curves (Fig. 1b and Fig. S8b, ESI†). Therefore, the valence band (VB) potentials of LBFD-1 and LBFD-2 were 0.44 eV and 0.68 eV, respectively, according to eqn (S1) (ESI†). Lastly, the photocurrent and electrochemical impedance of the photocatalysts were analyzed to characterize their photoelectrochemical properties. As shown in Fig. 1c, the photocurrent response of LBFD-2 was significantly stronger than that of LBFD-1, indicating that LBFD-2 could rapidly generate electrons and holes under visible light irradiation, resulting in better charge carrier migration and separation efficiency, which provided more charges for surface reactions. Moreover, the electrochemical impedance radius of LBFD-2 was much smaller than that of LBFD-1, further highlighting the better conductivity and superior photogenerated charge carrier migration ability of LBFD-2 (Fig. 1d and Fig. S8c, ESI†). These observations indicated that the post-modification of calixarene moieties not only endowed LBFD-2 with improved hydrophilicity and excellent swelling ability but also amplified its inherent photoelectrical properties. Compared to our previous work, a photocatalyst named CABP with two charge transfer channels,19 LBFD-2 exhibited enhanced photocurrent and smaller radius of electrochemical impedance (Fig. S9, ESI†) owing to three charge transfer channels, highlighting that increased channels are beneficial for the separation and transport of carriers.

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Considering the fact that the residual concentration of dyes was generally low in real-water treatment scenarios, the feasibility of removing dyes with low concentrations was investigated. Here, the concentration of MB and the dosage of LBFD-2 were 10 ppm and 0.1 mg mL⁻¹. As shown in Fig. S13 (ESI†), after 4 min of visible light irradiation, the η of MB reached >99%, approaching complete removal, which indicated that LBFD-2 can be potentially applied in practical scenarios to address the issue of environmental water pollution. In addition, the reusability of LBFD-2 towards MB and RhB was also investigated (Fig. S14, ESI†). LBFD-2 still maintained an η value of 99.5% after 5 cycles, demonstrating its excellent recyclability and reusability, and the FT-IR spectrum and SEM images after 5 cycles showed no obvious differences from those of original LBFD-2 (Fig. S15 and S16, ESI†), further highlighting its excellent structural stability. Moreover, the desorption experiments showed that LBFD-2 can degrade most of the anionic dyes in light compared to that in darkness (Fig. S17, details are provided in the ESI†).

To further explore the photodegradation mechanism of LBFD-2, quenching experiments were conducted to determine the ROS generated during the photocatalytic degradation process. Various quenchers including isopropyl alcohol (IPA), β-carotene, 1,4-benzoquinone (p-BQ), and disodium edetate dihydrate (EDTA-2Na) were utilized in the photodegradation system to capture *OH, ·O₂⁻, *O₂⁻ and h⁺, respectively. As shown in Fig. 2c and Fig. S18 (ESI†), compared with p-BQ and EDTA-2Na, the introduction of β-carotene and IPA significantly inhibited the degradation of MB and RhB. Thus, the *OH and ·O₂⁻ were considered as the main ROS, meanwhile, the electron spin resonance (ESR) experiments were carried out to further confirm this assumption. As shown in Fig. 2d and e, the standard triplet signals belonging to ·O₂⁻ with an intensity ratio of 1:1:1 significantly enhanced as the irradiation time increased to 1 min, and the standard multiple signals attributed to *OH also dramatically enhanced with increasing irradiation time, indicating that LBFD-2 could generate ·O₂⁻ and *OH as the primary reactive species during the photodegradation process. Moreover, the H₂O₂ production performance was measured in air (Fig. 2f). The H₂O₂ production rate of LBFD-2 was calculated to be 2.14 mmol g⁻¹ h⁻¹ in air and in the absence of any sacrificial agents, demonstrating its excellent H₂O₂ generation ability, which primarily served as the source of *OH for efficient photodegradation. Compared to our previous work,† the photocatalytic H₂O₂ production of LBFD-2 and subsequent photodegradation efficiency towards MB were both improved likely due to a more suitable pore size and better photoelectrochemical performance by multiple charge transfer channels (Fig. S19, ESI†).

With the assistance of liquid chromatography–mass spectrometry (LC-MS) analysis, the degradation pathways of MB and RhB were proposed (Fig. 3 and Fig. S20, S21, ESI†). Two primary pathways were elucidated for the degradation of MB. The MB molecule was ionized in aqueous solution to produce the original signal (m/z = 284), which was further attacked by ROS to form intermediates 1 (m/z = 365) and 7 (m/z = 301). In pathway I, the cation in intermediate 1 was partially isomerized to form intermediate 2 (m/z = 354), then the intermediate 2 was attacked by ROS and underwent a decomposition process to form intermediates 3 (m/z = 168) and 4 (m/z = 126), which was further oxidized by ROS to form intermediates 5 (m/z = 98) and 6 (m/z = 104). In pathway II, the intermediate 7 was attacked by ROS to undergo demethylation and a ring opening process to generate intermediates 8 (m/z = 202) and 9 (m/z = 136), and then intermediate 9 was attacked by ROS to form intermediate 10 (m/z = 158). Finally, these small molecules were mineralized to CO₂ and H₂O. The contents of RhB’s degradation pathway are shown in the ESI†.

As shown in Fig. S22 (ESI†), a plausible photocatalytic degradation mechanism of LBFD-2 was illustrated. Under illumination, LBFD-2 generated electron–hole pairs (eqn (1)) and simultaneously reacted with O₂ to produce ·O₂⁻ through energy transfer (eqn (2)), which was feasible since the VB potential of LBFD-2 (0.68 eV) was higher than the oxidation potential of standard O₂/·O₂⁻ (0.67 eV vs. NHE). Moreover, the standard potentials of OH⁻/*OH (1.99 eV vs. NHE) and H₂O₂/*OH (2.68 eV vs. NHE) were both higher than the VB potential of
Visible light irradiation, the generated H$_2$O$_2$ by LBFD-2 produced *OH (eqn (4)–(6)). Finally, the model cationic dyes, including MB and RhB, were effectively degraded under the synergistic effect of 1 O$_2$ and *OH (eqn (7)).

In summary, an efficient CMP photocatalyst was synthesized via the post-synthetic modification of a hydrophobic photocatalyst (LBFD-1) to a hydrophilic photocatalyst (LBFD-2) by introducing a calixarene moiety. This strategy not only improved the water dispersibility and molecular polarization of LBFD-2 but also enhanced its optoelectronic properties. As a result, LBFD-2 exhibited strong photo-degradation capability, achieving η > 99.5% for MB (200 ppm) within 20 min and RhB (50 ppm) within 40 min under visible light irradiation. It also achieved an excellent H$_2$O$_2$ production rate of 2.14 mmol g$^{-1}$ h$^{-1}$ in air and in the absence of sacrificial agents, which primarily served as the source of *OH for efficient photodegradation. After 5 cycles of the photodegradation process, the morphology and structure of LBFD-2 remained unchanged with the η still reaching 99%. This work indicated that the calixarene-based CMP photocatalyst possesses excellent practicality and recyclability, and holds great potential for various applications.

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Data availability
The data supporting this article have been included as part of the ESI.

Conflicts of interest
There are no conflicts of interest.

Notes and references
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