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Environmentally persistent free radicals in bismuth-based metal–organic layers derivatives: Photodegradation of pollutants and mechanism unravelling

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ABSTRACT

Formation of environmentally persistent free radicals (EPFRs) on carbonaceous material has aroused increasing research attentions. In terms of metal organic frameworks (MOFs) derivatives, however, scarce studies have dedicated to the relevant aspects. Herein, EPFRs have been detected in Bi-metal organic layers (Bi-MOLs) derivatives. The corresponding g-factors and concentrations of EPFRs on Bi₂O₃@C by pyrolyzed at different temperatures were 2.0041–2.0046 and 7.04 $\times 10^{19}$ -1.77 $\times 10^{20}$ spins/g, respectively. Interestingly, similar EPFRs signals were also monitored in HKUST-1 based and UiO-66 based derivatives. We observed that Bi₂O₃@C system with the highest EPFRs concentration exhibited superior degradation and mineralization efficiency for phenol and tetracycline. Its excellent photocatalytic performance was mainly attributed to the interaction between the internal EPFRs and photoinduced active species, which promoted more generation of reactive oxygen species (ROS) radicals. This hypothesis was supported by line correlations for EPFRs concentration vs. degradation kinetics in samples pyrolyzed at different temperatures ($R^2 = 0.946$). Most significantly, mechanism investigation combined with DFT calculation indicated that the EPFRs not only promote the generation of ¹O₂ and •OH via molecular oxygen activation pathway but also provided a possibility of enhancing water oxidation by holes. These findings pave the way for MOFs derivative's implication and insight into the role of EPFRs in photocatalysis.

1. Introduction

Environmentally persistent free radicals (EPFRs) with a lone pair of electrons have been detected by electron-spin resonance spectroscopy (EPR) in biochar [1], ambient atmospheric particles [2], microplastics [3,4], etc. In general, their formation process contains the electron transport between aromatic organic compounds and transition metals or breakdown of chemical bonds under pyrolysis or light irradiation [5]. Compared with other free radicals, EPFRs can exist under ambient conditions (room temperature and atmospheric pressure) for hours to

months [6]. Recent studies demonstrated that EPFRs are active and can facilitate the generation of reactive oxygen species (ROS) in advanced oxidation process [7,8]. Our group has reported that EPFRs can promote •OH formation in a biochar-based Fenton-like system [9].

Metal-organic frameworks (MOFs) are crystalline porous materials with defined structural units, which are constructed by combining metal ions with organic linkers [10]. Given the remarkable properties, such as high surface area and tailorable structures, MOFs provide a variable platform to design nanomaterials [10,11]. MOFs derivatives, particularly, inheriting morphology and frameworks from parent MOFs, have

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attracted wide attention in the field of energy [12], environment [13], and catalysis [14]. Several typical MOFs, such as CAU-17 (Bi), HKUST-1 (Cu), and UiO-66 (Zr) also contain carboxylate ligands [15–17]. Pyrolysis is recognized as one of the main methods to synthesize MOFs derivatives [18]. Considering the instinctive thermal stability of MOFs, the pyrolysis at low temperature may be accompanied by incomplete combustion and carbonization [19]. These residues may gradually form EPFRs, thus it is reasonable to hypothesize that EPFRs can be produced during the pyrolysis of several MOFs with aromatic ligands. However, the properties and formation of EPFRs in these MOFs derivatives has not been explored, which could be one of the important missing links in the practical application of MOFs derivatives.

Various efforts have been made to document the potential application of MOFs derivatives on environmental remediation [11]. Among these fields, photocatalysis process has attracted increasing attentions due to the potential prospects for converting solar energy to chemical energy. Bismuth (Bi)-based semiconductor photocatalysts have been proved to be capable of degrading various organic pollutants, while the exploration on Bi-based MOFs derivatives is rare. In our previous work, the as-synthesized Bi₂O₂CO₃/g-C₃N₄ derived from CAU-17/melamine precursors exhibited great photocatalytic activity for the removal of sulfamethazine and tetracycline [20,21]. Nevertheless, most of the studies on Bi-MOFs derivatives are lack of refined control over morphologies [13]. Recently, metal-organic layers (MOLs) as an emerging two-dimension materials have been deeply investigated because of their superior flexibility and ultrahigh atomic utilization for catalysis [22]. Therefore, further investigation on Bi-metal organic layers (MOLs) derivatives for promoted visible-light-driven photocatalysis is promising.

The in-situ generated EPFRs has been recognized as novel radicalactivators to generate more active species to enhance photocatalytic pollutants degradation [23]. Based on the existing studies, the reaction mechanism is proposed that EPFRs could transfer electrons to dissolved oxygen to induce $\bullet O_2^- / \bullet HO_2$, which reacts with H⁺ or dismutate to H₂O₂. Subsequently, H₂O₂ is activated by EPFRs or possibly with the help/aid of UV light to produce •OH, which possesses a strong oxidation ability for various pollutants [1,8,24]. However, this mechanism picture cannot illustrate the whole reaction. Although the contribution of EPFRs for •OH formation has been proved, the important role of •OH for pollutants degradation is not clear [23]. Besides, the above mechanism is a highly O2 or H2O2-dependent pathway, the reaction process in an anaerobic environment is not clear [7,25]. While EPFRs are known to react with abstracted hydrogen of H₂O, whether they can promote/ facilitate the oxidation of H₂O in photocatalysis remains a mystery [7,26]. Answers to these questions are critical, as they relate to the original nature of EPFRs enhanced photocatalysis and the practical applications of MOFs derivatives in environmental remediation.

To explore some of these issues, we synthesized several MOFs derivatives and undertook a detailed study about the EPFRs in Bi-MOLs derivatives. The properties, concentration and formation process of EPFRs were investigated. The correlation among EPFRs, optical property and photocatalytic activity were discussed. Through mechanism investigation and DFT simulation, it was a possibility to unveil the full roles of EPFRs in the photocatalytic system. Herein, the study not only addressed the photodegradation mechanisms of phenol and TC with the assistance of EPFRs but also stimulated some possibilities about the roles of EPFRs on MOFs derivatives.

2. Experimental

2.1. Synthesis

The Bi-MOLs were prepared under solvothermal conditions according to the previous study [27,28]. The synthesis was carried out under solvothermal conditions in 100 mL or 500 mL Teflon lined steel reactor. Then sealed the reactor and heated it to 120 °C for 24 h. In large-scale synthesis (500 mL), Bi(NO₃)₃·5H₂O (750 mg) was added in 300 mL

MeOH at room temperature, and H₃BTC (3750 mg) was added to the solution after 2 min. The transparent mixtures were transferred into the reactor after the powder was dissolved. Yield vs. H₃BTC 17.1% \pm 0.1. The obtained white powder was washed with ethanol, MeOH and DMF three times, respectively. After drying in an oven (60 °C, 6 h), the product was identified by XRD as pure Bi-MOLs.

Synthesis of Bi-MOLs derivatives. The as-prepared Bi-MOLs precursor (300 mg) was placed in a porcelain boat and heated to different temperatures (450 °C, 550 °C, 650 °C heating rate 5 °C/min, named Bi₂O₃@C-450, Bi₂O₃@C-550, Bi₂O₃@C-650) for 1 h in a stream of N₂. After cooling to 450 °C at 2 °C/min, a flowing nitrogen atmosphere was turn off to yield Bi₂O₃@C. The chemicals and the more details of synthesis are listed in the Supplementary Information (SI).

2.2. Characterization methods

The structure, morphology and composition of as-synthesized samples were measured by X-ray diffraction (XRD, BrukerAXS D8), X-ray photoelectron spectrometer (XPS, Escalab 250Xi spectrometer), Micromeritics ASAP2460 (BET), JEOL 2100F transmission electron microscopy (TEM) and JSM-7800F scanning electron microscopy (SEM). The Fourier transform infrared (FT-IR) spectra were recorded on a Bruker spectrometer, scanning from 4000 – 400 cm⁻¹. Detailly, 4 mg assynthesized samples and 200 mg dried KBr was added into agate mortar and ground to achieve complete homogeneity. Then, the obtained products (80 mg) went through a transmission infrared ray test. The optical properties of as-prepared samples were performed by UV–vis diffuse reflectance spectroscopy (DRS, CARY 300 spectrophotometer) and the steady-state fluorescence spectra (PL, Hitachi F7000). Photoelectrochemical measurement are listed in the SI.

2.3. EPR measurement

The EPR spectrum for the identification of EPFRs on as-prepared samples was measured using Bruker MS 5000. Typically, 10 mg of asprepared samples were added in EPR tubes (60 mm height, 1 mm diameter) in a cavity using modulation and microwave frequencies of 100 kHz and 9.516 GHz, respectively. The detailed Parameters were as follows: 10 mW micropower; modulation 2 G: center field, 3380 G; sweep width 200 G; sweep time 60 s and 5 scans. Radical quantification was evaluated using Bruker's Xenon program according to the quantitative theory of spin calculation. The ROS signals and holes signals of the radicals were performed on Bruker a300.

2.4. Photocatalytic activity

The light source was a 300 W Xe lamp with a 420 nm cut-off filter. The photocatalytic performance of the as-synthesized products was evaluated by monitoring the decomposition of TC (20 mg/L, 50 mL, 25 mg catalysts) and phenol (10 mg/L, 50 mL, 50 mg catalysts) under visible light irradiation. Before the photocatalysis reaction, the mixture solutions were stirred in the dark for 60 min in order to ascertain adsorption equilibrium (Fig. S1a, b). The residual concentration of the pollutant was filtered and detected by high-performance liquid chromatography (Agilent 1260 Infinity II, USA). The total organic carbon (TOC) remaining in the solution of phenol and TC was studied by a TOC analyzer (Analytikjena multiple N/C 2100). Furthermore, the degradation intermediates of TC were detected by HPLC-MS (UPLC-MS, Agilent 1290/6460, Triple Quad MS, USA). The analysis methods of HPLC and HPLC-MS were illustrated in the SI.

2.5. Theoretical calculation

The calculations were conducted by using Vienna Ab initio Simulation Package (VASP) at a version of 5.4.4 with the projector augmented wave (PAW) method. The method was density functional theory (DFT) with generalized gradient approximations (GGA) of Perdew-Burke-Ernzerhof (PBE) functional. The Bi₂O₃ slab structure was based on a double-layer Bi₂O₃ model. For Bi₂O₃-EPFRs simulation, we adopted an analogous heterojunction structure composed of EPFRs and single-layer Bi₂O₃. The charge density differences can be defined as $\Delta \rho = \rho_{\text{Bi}_2\text{O}_3-\text{EPFRs}} - \rho_{\text{Bi}_2\text{O}_3} - \rho_{\text{BTC}}$, where $\rho_{\text{Bi}_2\text{O}_3-\text{EPFRs}}$, $\rho_{\text{Bi}_2\text{O}_3}$, and ρ_{EPFRs} are the electron densities of the Bi₂O₃ slab with the adsorbed EPFRs molecule, isolated Bi₂O₃ slab, and isolated EPFRs molecule, respectively. More details are listed in the SI.

3. Results and discussion

3.1. The synthesis of catalysts

The Bi-MOLs precursors were synthesized under solvothermal conditions inspired by previous studies (Fig. 1a) [27,28]. Characterization of SEM, TEM and AFM confirmed the ultrathin MOLs possessed a lamellar-stacked structure with an average height of 1.8 nm (Fig. 1b-d; Fig. S3a, b). According to the PXRD (Fig. S2a), the MOLs possessed a similar topology structure of CAU-17 with accessible edge-sharing helical BiO₉ polyhedra (Fig. S2b) [17]. These precursors were pyrolysis in the N2 atmosphere followed by an oxidation process. After pyrolysis at 450 °C, the MOLs were transformed into Bi₂O₃ nanoparticles anchored in the microporous carbon layers (Fig. 1e, f; Fig. S3 c-e). Due to the atomically thin precursors, some melted Bi atoms were seeped out and transform into Bi2O3 nanoparticles attached on the surface of carbon layers [27]. Meanwhile, EDS mapping spectra indicated that the Bi and O elements were uniformly distributed in carbon layers (Fig. 1e, f, j). As the temperature increased from 450 °C to 650 °C, these samples possessed similar morphology but Bi2O3 nanoparticles located at the carbon networks distributed more uniform with smaller sizes (Fig. S4) [28].

3.2. Chemical and structural characterization

The chemical structure of Bi₂O₃@C synthesized at different temperatures was firstly investigated by XRD and FT-IR. As displayed in Fig. 2a, the PXRD patterns of Bi₂O₃@C-450, Bi₂O₃@C-550, and Bi₂O₃@C-650 were similar, suggesting the general structure of Bi₂O₃ was successfully maintained and possessed high phase purity (ICDC No. 27–0050) [29]. The FT-IR spectroscopy of Bi-MOLs exhibited obvious characteristic absorption peaks at 1619, 1541, 1436, 1358, 736 cm⁻¹ (Fig. 2b) [17]. The typical variation band in the region of 1358–1619 cm⁻¹ was ascribed to the asymmetric and symmetric stretching vibrations of carboxylic acid function [30]. Moreover, the spectrum showed the v(C–H) stretching vibration of a benzene ring at 736 cm⁻¹ and the vibration of the Bi-oxo cluster at 456 cm⁻¹ [31]. For the Bi₂O₃@C samples, the peaks ranging from 525 cm⁻¹ to 630 cm⁻¹ were corresponding to Bi-O bonds. Four obvious variations could be observed in this spectrum with the increasing temperature, emphasized by differently shaded regions in Fig. 2b. The peaks in 736 cm⁻¹, 1034 cm⁻¹, 1240 cm⁻¹ and 1660 cm⁻¹ displayed progressively decreases in the intensity, corresponding to the v(C - H) stretching vibration, the v(C - O) stretching vibration [32]. According to previous reports, the formation of oxygen-containing functional groups (OFGs) was mainly ascribed to incomplete combustion at low temperature [1]. This result indicated that the increase of pyrolysis temperature decreased the concentration of OFGs accompanied by dehydrogenation.

XPS analysis was further performed to elucidate detailed surface elemental composition and chemical states. As displayed in Fig. 3a, the full survey scanning spectra verified the main existed elements in the derived samples (Bi, C, O). For the C 1 s spectrum, four peaks located at 284.8 eV, 286.4 eV, 288.8 eV and 291.2 eV are related to C - C, C - O bonds, C = O bonds, and C = O - O functions, respectively. Interestingly, the 291.2 eV signals of Bi₂O₃-550 and Bi₂O₃-650 were attenuated compared to that of Bi2O3-450, which could prove that increasing pyrolysis temperature could reduce the concentrations of OFGs (Fig. 3b). This was further confirmed by the O 1 s spectrum.1 In Fig. 3c, the fitting peaks at 529.9 eV, 531.5 eV, 532.4 eV, and 533.8 eV were assigned to Bi - O bonds, Bi-OH bonds, H₂O, C = O functions of ketones or carboxyl groups, respectively [3,27]. With the increasing calcination temperature, the peaks intensity of C = O functions decreased obviously, indicating that fewer OFGs were produced. Furthermore, the signal of Bi -O bonds was intensified from 529.9 eV to 530.5 eV and meanwhile, the intensity of C - O - OH peaks was significantly reduced from 533.8 eV to 533.7 eV. Fig. 3d also showed that the binding energy of Bi(III) cation was enhanced with the increase of temperature, indicating that Bi atoms might obtain more electrons from oxygen-containing functional groups at low temperature, thus altering the binding energies of Bi atoms and Bi O bonds in Bi₂O₃.

It has been well established that the presence of metal oxides and incomplete combustion in the thermal decomposition of organic compounds favor the formation of EPFRs [24,33]. To further investigate the OFGs in $Bi_2O_3@C$ samples, the EPR spectra were employed. The pristine Bi-MOLs didn't show any distinct signals, while a distinct singlet peak



Fig. 1. (a) Process of the formation of Bi-MOLs and Bi₂O₃@C, (b) SEM of Bi-MOLs, (c) TEM of Bi-MOLs, (d) AFM of Bi-MOLs, (e) SEM of Bi₂O₃@C-450, (f) TEM of Bi₂O₃@C-450, (g-i) SEM-EDS element mapping for Bi₂O₃@C-450, (j) HRTEM image of Bi₂O₃@C-450.



Fig. 2. (a) XRD patterns of Bi₂O₃@C-450, Bi₂O₃@C-550 and Bi₂O₃@C-650, (b) FT-IR spectra of Bi-MOLs, Bi₂O₃@C-450, Bi₂O₃@C-550 and Bi₂O₃@C-650.



Fig. 3. (a) XPS full spectra of $Bi_2O_3@C-450$, $Bi_2O_3@C-550$, $Bi_2O_3@C-650$. (b-c) XPS spectra full survey of $Bi_2O_3@C-450$, $Bi_2O_3@C-550$ and $Bi_2O_3@C-650$: (a) C, (b) O, (c) Bi, (d) Room-temperature EPR signals spectra of Bi-MOLs, $Bi_2O_3@C-450$, $Bi_2O_3@C-550$ and $Bi_2O_3@C-650$.

was observed with pyrolysis temperature at 450 °C (Fig. 4a). By detecting these free radicals at different time, their signals were stable with a less than 18.6% decrease after six months (Fig. 4b), suggesting the persistent nature of these free radicals. Furthermore, the intensity of EPFRs decayed with an increase in pyrolysis temperature. As shown in Table S1, the detected EPFRs concentration in Bi-MOLs derivatives during the pyrolysis process were in the range of 7.04×10^{19} - 1.77×10^{20} spins/g and the Bi₂O₃@C-450 possessed the highest concentration of EPFRs with 1.77×10^{20} spins/g. The decreased concentration of EPFRs in high pyrolysis temperature might be ascribed to the

decomposition of radical structure. To identify the types of EPFRs, the gfactors are generally considered crucial parameters. As depicted in Table S1, the g-factors of all derivatives were in the range of 2.0041–2.0046. Previous studies suggested that g-factors > 2.0040 are belong to oxygen-centered radicals. Moreover, the decrease in the concentration of oxygen-centered EPFRs was in line with the amount of surface OFGs (especially for ketone or carboxyl groups) detected in Bi-MOLs derivatives by FT-IR and XPS analysis, confirming that the detected signal could be assigned to the organic free radicals (Table S2) [34]. More interestingly, these EPFRs signals were also observed in



Fig. 4. (a) Room-temperature EPR signals spectra of Bi-MOLs, $Bi_2O_3@C-450$, $Bi_2O_3@C-550$ and $Bi_2O_3@C-650$. (b) Room-temperature EPR signals spectra for fresh $Bi_2O_3@C-450$ samples and after six months under ambient conditions. (b) Room-temperature EPR signals spectra for HKUST-1 and pyrolyzed at 450 °C. (c) Room-temperature EPR signals spectra for UiO-66 and pyrolyzed at 500 °C. (e) Room-temperature EPR signals spectra for nanosheets-like $Bi_2O_3@C-450$ pyrolyzed at N_2 atmosphere and N_2 followed by oxidation process. (f) Room-temperature EPR signals spectra for nanosheets-like $Bi_2O_3@C-450$ under different cycle experiments.

HKUST-1 based and UiO-66 based derivatives (Fig. 4c, d), which further supported our hypothesis that EPFRs could be produced during the pyrolysis of MOFs with aromatic ligands.

In previous studies, EPFRs are usually formed by the electrontransfer from aromatic compounds to transition metals or cleavage of chemical bonds under combustion conditions [5,6]. Such a phenomenon is usually observed on biochar, metal oxides and clay minerals [34]. Compared to these materials, MOFs derivatives possess some natural advantages. Firstly, the breakdown of the moderately strong coordinate bonds between metal center and organic ligands possibly generates free radicals. Then, the well-defined structure and reticular chemistry of metal-containing units and organic ligands may enhance the chemisorption of organic compounds on metal surfaces. Based on the ESR spectra of Bi-MOFs derivatives at different synthesized conditions (Fig. 4e), the formation of EPFRs was more likely to be ascribed to the breakdown of coordinate bonds and subsequent generation of persistent surface bound radicals on the bismuth surface [35]. The proposed formation process was depicted in Fig. 5. The first step was attributed to the framework collapses and the generation of corresponding radicals. Then these radicals were inclined to abstract hydrogen from other molecules to form hydroxyl functional groups or quinone moieties during pyrolysis [34]. Furthermore, the bismuth surface could also actively dissociate linker molecules, produced quinone moieties or phenolate species, and subsequently resulting in the formation of surface bunded EPFRs [36]. The planar-averaged charge density of Bi_2O_3 -EPFRs was also in favor of this process. As shown in Fig. 5b, the yellow and blue regions were corresponding to the electron accumulation and depletion. The calculation results indicated that the electrons transferred from C-O bonds in EPFRs to Bi atoms in Bi_2O_3 [37].



Fig. 5. (a) Simplified model of EPFRs formation from the pyrolysis of Bi-MOLs via chemisorption and electron transfer (b) Planar-averaged electron density difference of Bi₂O₃-EPFRs based on the DFT methods.



Fig. 6. (a) Photocatalytic degradation curves of phenol under visible light irradiation ($\lambda > 420$ nm) for different samples, (b) pseudo-first-order kinetic fitting curves and the corresponding apparent rate constants *k*, (c) photocatalytic degradation curves of tetracycline under visible light irradiation ($\lambda > 420$ nm) for different samples, (d) the photodegradation and TOC removal curves of phenol and tetracycline on Bi₂O₃@C-450 and Bi₂O₃@C-650.

3.3. Photocatalytic activities

Phenol and TC were selected as model pollutants to evaluate the photocatalytic performance of Bi₂O₃@C. Fig. S1c showed the decomposition efficiency of single light irradiation or catalysts with the addition of H₂O₂ for phenol degradation. It could be observed that nearly no phenol decomposition occurs in the absence of photocatalysts or with the direct addition of H₂O₂. This was probably because these EPFRs in Bi₂O₃@C-450 were internal and encapsulated by a carbon layer, which have limited interaction with H₂O₂ [25]. However, under visible light irradiation, the derived Bi2O3@C displayed much superior photocatalytic performance compared with Bi-MOLs. The Bi2O3@C-450 showed the best catalytic activity and the removal efficiency of phenol is 100% within 50 min (Fig. 6a). Furthermore, we used the pseudo-firstorder kinetic model to simulate the degradation of experimental data (Table S3). Under this circumstance, the Bi₂O₃@C-450 exhibited the highest rate constant about 0.066 min^{-1} , which was 2.4 and 5.2 times higher than that of Bi₂O₃@C-550 and Bi₂O₃@C-650, respectively (Fig. 6b). Given that the surface area of photocatalyst had a distinct impact on the photocatalytic activity, we also normalized the corresponding rate constant k. As shown in Table S3, the $Bi_2O_3@C-450$ still displayed the highest normalized apparent rate constants with 7.15 g/ $m^2 \cdot min \times 10^{-4}$. Furthermore, for the degradation of TC, Bi₂O₃-450 still exhibited superior photocatalytic activity and the degradation efficiency was 100% within 50 min visible light illumination (Fig. 6c). The Bi₂O₃@C-450 with the highest EPFRs concentrations displayed the best photocatalytic performance could be ascribed to the assumption that EPRs could in-situ reacted with photoinduced species to generate more ROS radicals [8,35].

To further assess the catalytic activity, the removal of total organic carbon (TOC) was identified after the adsorption and degradation. As displayed in Fig. 6d, the Bi₂O₃@C-450 system displayed promoted mineralization ability. Nearly 32.4% and 75.4% of TOC were removed after 120 min TC and phenol photocatalytic reaction in the Bi₂O₃@C-450, while 31.6% and 39.9% were removed after 120 min photocatalytic reaction in the Bi₂O₃@C-650, respectively. Although two catalysts exhibited similar TOC removal efficiency for TC, Bi₂O₃@C-650 possessed a higher adsorption efficiency. These results indicated that Bi₂O₃@C-450 catalysts were more inclined to mineralize the pollutants over Bi₂O₃@C-650. The degradation undergoes possible two steps: (1) the scission of pollutants and (2) subsequent oxidation of intermediates [38].

To deeply explore the degradation pathway of phenol and TC over Bi₂O₃@C-450, the degradation intermediates were identified by HPLC and LC/MS-MS analysis. As shown in Fig. S6 a, b, both intensities of TC peak (4.07 min) and phenol peak (7.32 min) decreased obviously with photocatalytic reaction proceed, showing the superior catalytic activity. The degradation intermediates of phenol were monitored by HPLC along with irradiation time (Fig S6 c and d). Fig S6 c showed the retention time of different degradation species of phenol. The peaks at 1.6 min, 1.8 min, 2.3 min, 3.0 min and 3.9 min were assigned to oxalic acid, maleic acid, catechol, benzoquinone and resorcinol, respectively. As the photocatalysis reaction proceeded, the intensity of the phenol signal decayed gradually, whereas the intensity of the intermediate intermediates became stronger. The proposed degradation pathways was: phenol \rightarrow hydroquinone or catechol \rightarrow benzoquinone \rightarrow oxalic acid or maleic acid \rightarrow CO₂ or H₂O (Fig. S9) [39]. The degradation products of TC were investigated by HPLC/MS spectrometry. Fig S7 and Fig S8 showed the MS spectra and possible chemical structure of several intermediates that were discovered during the degradation process. The peaks with m/z =445 at retention time 4-5 min were ascribed to TC, which finally decreased 98% within 60 min of degradation. Subsequently, three TC degradation pathways were proposed in Fig S10 [39–42]. In pathway I, intermediate with m/z of 475 was produced due to the oxidation of TC by ¹O₂. Pathways II and III were a hydroxylation reaction. TC was firstly oxidized to intermediate with m/z of 431 due to the demethylation.

Then, the intermediates with m/z of 388, 417, 327 and 362 were produced due to the loss of certain functional groups. Owing to ringopening reaction, these intermediates would be broken down into some small molecular compounds and be further mineralized into CO_2 and H_2O .

3.4. The relationships among EPFRs, optical property and catalytic activity

UV-DRS was performed to explore the optical absorption. As shown in Fig. 7a, a progressive extension in the optical absorption edge was observed with the temperature increasing. The photoelectric experiments were further applied to investigate the transportability of photogenerated charge carriers. Commonly, photocatalysts displaying higher photocurrent response, lower PL intensity and smaller radius of Nyquist plots possess a stronger ability to separate electron-hole pairs under the visible light irradiation [20,43,44]. But it seemed not to be the cases for Bi₂O₃@C-450, Bi₂O₃@C-550 and Bi₂O₃@C-650. In contrast, these samples showed similar transient photocurrent response curves (Fig. 7b). And the Bi₂O₃@C-450 had the biggest arc radius triggers and highest PL intensity but displayed the best photocatalytic activity (Fig. 7c, d). Such a situation motivated us to conduct further detailed investigations to unravel the reaction mechanism on the photodegradation of organic pollutants over the Bi-MOLs derived Bi₂O₃@C and the origin of catalytic ability difference bearing different temperatures [45].

It has been well established that EPFRs and abundant surface OFGs could accelerate the production of ROS (e.g. •OH and ¹O₂) in the carbonbased photocatalytic system for organic pollutions decomposition [1,8]. To identify the relationships between EPFRs and catalytic activity, we performed regression analyses among the phenol degradation (k_{obs}) , EPFRs concentration and the amounts of surface oxygenated functional groups. As shown in Fig. 7e, the catalytic performance was increased with the increased concentration of EPFRs, and the correlation coefficient was 0.946. This result demonstrated that the enhanced photocatalytic activity under different pyrolysis temperatures was greatly dependent upon the concentration of EPFRs [46]. Besides, the concentration of EPFRs obviously decreased after photocatalysis reaction also verified this hypothecation (Fig. 4 f, Table S1). Given the controls which pollutants treated by single light irradiation or catalysts showed negligible decomposition efficiency, the photocatalytic performance of Bi₂O₃@C was mainly attributed to the ROS generated through the synergistic effect between photoinduced active species and EPFRs. We further confirmed the correlation coefficient between the rate constant and the amounts of OFGs (Fig. 7e). The high correlation coefficient (0.961) indicated the catalytic performance was in line with the changes in the OFGs. As depicted in Fig. 7f, the generation of EPFRs was accompanied by the production of OFGs, and the correlation coefficient for -COOH groups and -C = O-O groups were 0.943 and 0.830, respectively. Therefore, OFGs in EPFRs could presume to be the interaction active sites between photoinduced active species and EPFRs, which also has been observed in other experiments [3,47].

3.5. The role of EPFRs in photocatalysis

Understanding the reaction mechanism of EPFRs-enhanced photocatalysis, including the types of active species and their generation pathway will broaden the photocatalytic applications of Bi-MOLs derived materials [48]. Based on this, we conducted the quenching experiments with the presence of different scavengers to uncover the predominant active radicals produced in photocatalytic reaction. As indicated in Fig. 8a, nearly 100% deactivation of Bi₂O₃@C-450 was observed with the addition of EDTA-2Na, suggesting the holes played a vital role during the photocatalytic degradation reaction. Moreover, the degradation efficiency was suppressed with the presence of mannitol, about 82.19% phenol degradation was reduced. The phenomenon Z. Wang et al.



Fig. 7. (a) UV–vis DRS of pristine Bi-MOLs, $Bi_2O_3@C-450$, $Bi_2O_3@C-550$, $Bi_2O_3@C-650$, (b) Transient photocurrent response curves, (c) Steady-state PF spectra for $Bi_2O_3@C-450$, $Bi_2O_3@C-550$, $Bi_2O_3@C-550$, $Bi_2O_3@C-550$, $Bi_2O_3@C-550$, $Bi_2O_3@C-550$, $Bi_2O_3@C-550$, $Bi_2O_3@C-650$ (d) Nyquist plots of electro-chemical impedance spectroscopy. (e) Relationships between EPFRs concentrations and k_{obs} of phenol degradation (green line), and relationships between OFGs concentrations and k_{obs} of phenol degradation (blue line). (f) Relationships between EPFRs concentrations and the amounts of OFGs (green line), and relationships between EPFRs concentrations and the amounts of -C = O-O groups (orange line).



Fig. 8. (a) Effect of different quench agents on photocatalytic degradation of phenol by Bi_2O_3 @C-450. EPR spectra of radical adducts trapped by TEMPO (h⁺), TEMP (¹O₂), DMPO ($\bullet O_2^-$ and $\bullet OH$) in different sample dispersion in the dark and under visible-light irradiation: (b) in methanol dispersion for DMPO- $\bullet OH$, (c) in aqueous dispersion for TEMPO- h⁺, (d) in aqueous dispersion for DMPO- $\bullet O_2^-$, (e) in aqueous dispersion for TEMP-¹O₂. (f) photocatalytic degradation curves of phenol under visible light irradiation ($\lambda > 420$ nm) under continuous O₂/Air/Ar purge.

suggested that •OH was another main active species in the degradation process. As for the NaN₃ and TEMPOL, their effects on the degradation efficiency were considerably low, suggesting the mild contribution of $\bullet O_2^-$ and 1O_2 to the phenol removal. Such a situation was further proved by EPR spin-trapping technology. The production of active species was monitored under dark and visible light illumination of 5 and 10 min. No obvious peaks were observed in the dark, whereas the significant signal peak of DMPO- $\bullet O_2^-$, DMOP- $\bullet OH$ and TEMP- 1O_2 appeared after the visible light illumination (Fig. 8b, d, e). With the increase of the reaction time, the intensity of characteristic peaks became stronger, suggesting that $\bullet O_2^-$, $\bullet OH$ and 1O_2 all worked in the photocatalytic process. It should be noted that the enhanced intensity of characteristic peaks of $\bullet OH$ was much higher than that of $\bullet O_2^-$ and 1O_2 . Meanwhile, the remarkably decreased intensity of the characteristic peaks of TEMPO-h⁺ unambiguously demonstrated that holes play a crucial role in the reaction process (Fig. 8c).

Based on the reported Bi₂O₃-related photodegradation process, the generation of •OH and ¹O₂ in PFR-enhanced photocatalysis was mainly discussed [49–51]. It has been proved that quinones or quinone-like composites could promote ¹O₂ production via the energy transfer

process [52]. Besides, Huang et al. [53] have reported the heavy atom effect of Bi³⁺ cations could promote ${}^{3}O_{2} \rightarrow {}^{1}O_{2}$ intersystem crossing, thus improving the formation of singlet oxygen. Since a number of quinones or quinone-like moieties were fabricated on the surface of Bi₂O₃@C-450 (on the basis of FTIR and XPS analysis, named Bi₂O₃@C-450-Q), it was reasonable to hypothesize that the quinone-like moieties of Bi₂O₃@C-450 would promote ${}^{1}O_{2}$ harvesting. In this pathway, Bi₂O₃@C-450-Q firstly reached excited triplet states due to heavy atom effect under visible light irradiation, and then the excited 1 [Bi₂O₃@C-450-Q]* further reacted with oxygen to yield ${}^{1}O_{2}$ via ${}^{3}O_{2} \rightarrow {}^{1}O_{2}$ intersystem crossing.

Commonly, two possible pathways for the generation of •OH have been widely accepted in photocatalysis [54]. The first way to produce •OH radicals was via H₂O₂ mediates [55]. This process seemed feasible, on the one hand the CB band edge potential of Bi₂O₃@C (-0.82 eV) was negative enough for the generation of $\bullet O_2^-(O_2/\bullet O_2^-, -0.33 \text{ eV vs NHE})$ Fig. S11). On the other hand, EPFRs have been proved to directly activate molecular oxygen to $\bullet HO_2/\bullet O_2^-$ via electron transfer, which could further disproportionately form H₂O₂ Subsequently, the generated H_2O_2 was decomposed to produce •OH by $Bi_2O_3@C-450-EPFRs$ or photoinduced electrons and holes. To confirm the O2-dependent reaction pathways, the photodegradation of phenol was performed under continuous O₂/Ar purge (Fig. 8f, Table S4). The corresponding degradation efficiency was 100% within 40 min illumination, suggesting molecular oxygen activation pathway played an important role in this reaction. Although EPFRs in our system had limited reactivity for the generation of ROS, the in-situ photogenerated active species possibly provided another reaction pathway for the interaction with EPFRs [47]. As a result, they were usually passive and "non-reactivity" in ambient conditions, while can in-situ accelerate the generation of •OH radicals under visible light irradiation.

Although the oxygen promoted the catalysis activation, the degradation efficiency of phenol was slightly decreased 6.4% within 40 min illumination under Ar conditions. It indicated that there might exist another possible pathway for the production of •OH. In the second route, H₂O directly reacted with the photogenerated holes [56]. Nevertheless, compared to the standard redox potential (OH-/•OH or H₂O/•OH, 1.99 and 2.37 eV respectively), the more negative valence band edge potential of Bi2O3@C (1.82 eV for Bi2O3, 1.02 eV for $Bi_2O_3@C$) was infeasible to oxidize H_2O/OH^- to generate •OH radicals (Fig. S11, including calculated details). A reasonable hypothesis was that the presence of EPFRs accelerated the second route. Density functional theory calculation was performed to elucidate this photocatalytic reaction pathway. Here we examined the reaction mechanism by using single-layer tetragonal Bi2O3 bounded with CmOO• radicals. The free energy diagrams for the photocatalytic H₂O to H* and OH* with or without the assistance of EPFRs were shown in Fig. 9a, Fig. S12. Both Bi_2O_3 and Bi_2O_3 -EPFRs displayed the largest activation energy (ΔEa) for the formation of activated water, suggesting the initial absorption and

activation could limit the whole reaction [57]. Encouragingly, with the assistance of EPFRs, the activation energy (Δ Ea) for the formation of transition states decreased from 0.35 eV to 0.24 eV. This result indicated the introduction of EPFRs facilitated the activation of absorbed H₂O [58]. Furthermore, Bi₂O₃-EPFRs-H* has a much lower Gibbs free energy for OH* formation, indicating its higher activity for photocatalytic H₂O to H* and OH*. Therefore, with the assistance of PFRs, the free energy of water oxidation on Bi₂O₃ towards the generation of OH* radicals was decreased from 1.47 eV to 0.9 eV. Moreover, the previous Bader charge analysis indicated that the charge accumulation might promote the construction of a built-in electric field at Bi₂O₃-EPFRs, which accelerated the separation of photoinduced electrons and holes [38]. The above results indicated the presence of EPFRs not only reduced the free energy of water oxidation but enhanced the possibility of the generation of OH* radicals by holes via the formation of built-in electric field.

In summary, the proposed whole reaction process was demonstrated in Fig. 9b. When the Bi₂O₃ nanoparticles bounded with EPFRs were under visible light irradiation, three possible reaction processes might occur in the whole system: (I) the energy transfer pathway for ${}^{1}O_{2}$ generation, (II) with the assistance of EPFRs, the two-single-electron participated O_2 reduction pathway to give $\bullet O_2^-$ and $\bullet OH$, (III) the EPFRs accelerated hole-mediated H₂O oxidation pathway for •OH production. The EPFRs in this process was not only account for enhancement of the decomposition of photoinduced H2O2 but also accelerated the activation of H₂O by holes [59]. However, the constant consumption of EPFRs in photocatalysis reaction resulting in a poor cycle ability. Furthermore, the abstraction of hydrogen could react with Bi2O3 to form Bi₂O₃-OH or react with EPFRs to form hydroperoxide groups (-C -OOH) during the reaction process. These hydroperoxide groups were extremely unstable and easily cleaved to generate CO• (tertiary alkoxy radicals) and •OH [3,60]. Furthermore, the produced tertiary alkoxy radicals were inclined to further react with Bi₂O₃ and transform into Bi₂O₂CO₃, resulting in a decreased catalysis ability. As a result, after four-cycle experiments, the degradation of phenol was decreased to 58.3% within 60 min visible light irradiation (Fig. S13, Table S4). This hypothesis was also examined by XRD and FT-IR. As presented in Fig. S14a, the additional peaks in the fourth used samples corresponded to the Bi₂O₂CO₃ phase. Furthermore, the new FTIR peaks of 844 cm⁻¹ 1440 cm⁻¹ and 1660 cm⁻¹ in the fourth cycle samples also confirmed the introduction of Bi-O bonds, C = O and C-O groups of $Bi_2O_2CO_3$ (Fig. S14b).

4. Conclusion

EPFRs are emerging pollutants but also possess high reactivity, which can activate hydrogen peroxide or oxygen to generate reactive oxygen species. In this study, EPFRs have been detected in Bi-MOLs derivatives, in which the properties, concentrations, and formation process of EPFRs were proposed. More importantly, the EPFRs signals



Fig. 9. (a) Calculated free-energy diagram for the photocatalytic H₂O to H* and OH*, (e) A possible mechanism for pollutant degradation.

also have been observed in HKUST-1 and UiO-66 based derivatives. Then, the attention of this research focused on the catalysis activity. These EPFRs in Bi-MOLs derivatives were passive in ambient conditions, while can in situ react with photogenerated active species to enhance photocatalytic performance. Mechanism investigation and DFT calculation revealed that EPFRs not only enhanced the photoinduced O2 activation pathway but accelerated the reaction pathway for the photocatalytic H₂O to H^{*} and OH^{*} by decreasing water activation energy from 1.47 eV to 0.9 eV. As a result, Bi-MOLs derived ultrathin Bi₂O₃@C-EPFRs photocatalysts exhibited great catalytic capacity and mineralization efficiency towards phenol degradation, even though under continuous Ar purge. Although the EPFR-enhanced photocatalytic performance has been well proved in this study, the detailed reaction pathway of how EPFRs react with electrons and holes is not perspicuous. Further exploration about the effects of EPFRs in photocatalysis relied on in-situ characterization and time-resolved technologies are recommended, especially for the detection of reaction intermediates. Furthermore, the environment risks and potential hazards of EPFRs formed by the pyrolysis of MOFs need to be carefully explored.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2021.133026.

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