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Sustainable impacts of electron shuttles on hierarchical Iron incorporated biochar in environmental decontamination: metal leaching, activation energy, and recyclability

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Abstract

Metal biochar is generally considered as an alternative candidate for future carbocatalysis and frequently participates in environmental decontamination, *i.e.*, AOPs., Nevertheless, the inevitable metal leaching still impedes its scaling-up application and poses the critical concern in the present scientific progress. New insights centred on its environmental sustainability are urgently needed. Herein, a hierarchical Fe biochar derived from cellulose fabricated *via* facile hydrothermal carbonization coupled with microwave irradiation was selected as the representative metal biochar. Several exterior organic electron shuttles (*i.e.*, ascorbic acid, oxalic acid, tartaric acid, and hydroquinone) were accommodated on the surface of the prepared hierarchical Fe biochar (Fe/CBC) to introduce more electroactive functionalities (*i.e.*, C-O and C=O). The synergies of inherent hierarchical structure, well-developed carbon π-electron network, and accommodated electron shuttle were for the first time unveiled to dramatically mitigate the metal leaching (from 2.436 to 0.578 mg L^{-1}) in specified AOPs, *i.e.*, Oxone (PMS) activation system. With the help of several characterisation methods including, XRD, SEM-EDS, TEM, Raman, XPS, *etc.*, the physicochemical properties (*i.e.*, morphology, elemental compositions, defective and graphitic degrees, *etc.*) of the prepared catalyst (Fe/CBC@TA) were also carefully elucidated. According to scavenging experiments and EPR analysis, catalytic mechanisms were successfully changed from one-phase pathway (mainly ·OH) to two-phase pathway with different predominant reactive species (first phase: $^1O_2$, second phase: ·OH). Besides, the increased activation energy and improved catalyst recyclability in redox reaction further coincided with its elevated environmental sustainability. Overall, this work provides new strategies to improve the sustainability, electrocatalysis, and mechanistic route of metal incorporated biochar in green and environmental remediation.

Keywords: metal biochar, electron shuttles, AOPs, sustainable catalyst, metal leaching

1. Introduction

In recent decades, the disposal of increasing biomass waste has been one of the most longstanding issues associated with population growth and anthropogenic activities in modern era [1, 2]. Specifically, the tremendous amounts of discarded agricultural and forestry waste each year remarkably exceed the natural degradation capacity and remain as big challenges to human [3, 4]. These biological wastes mainly consist of stable lignocellulosic substances (*i.e.*, hemicellulose, cellulose, and lignin) which are difficult to undergo biological activities to transform into soil nutrients due to the relatively slow activity of ubiquitous microbes [5].

Traditional methods like direct incineration would cause severe secondary pollution (*i.e.*, atmospheric contamination, green gas emission) and might lead to uncontrollable wildfires threatening to human lives [3, 6]. With the emergence of new demands for environmental sustainability in resource recycle bioeconomy, these agricultural and forestry wastes are more desired to be applied in various conversion technologies to produce value-added products [7, 8]. For instance, the green and sustainable technologies (*i.e.*, composting, anaerobic digestion, catalytic depolymerization, *etc.*) are triggering elevating attention in scientific communities because they can alternatively convert biomass into useful bioenergy (*i.e.*, biooil, syngas, chemical precursors) and organic fertilizer [1, 9]. Amongst all these sustainable techniques, utilizing biomass waste *via* thermal heating treatment to fabricate porous carbonaceous material, namely biochar, is holding great promise in environmental fields including energy storage [10], soil amendment [11-14], environmental decontamination [15-17], *etc.*

As a hierarchically porous black carbon, biochar usually possesses favourable adsorption capacity, surface electronegativity, hydrophobicity, biological compatibility, and high pH value, which make it suitable and effective in soil amelioration (*i.e.*, heavy metals complexation/solidification, reduction of soil acidity, retention of nutrients, enhancement of biological activities, *etc.*) and wastewater treatment (*i.e.*, contaminant adsorption, catalytic degradation of organics) [18-24]. Apart from these applications, biochar was also utilized as economical catalyst in environmental remediations, *e.g.*, advanced oxidation processes (AOPs), to catalyse the generation of highly reactive radicals for pollutant degradation [25-28]. Compared with conventional carbocatalysis using nanocarbons such as graphene, reduced graphene oxide, carbon nanotubes, nanodiamond, *etc.*, raw biochar still exhibits relatively low surface area and deficient electroactive sites without further chemical/physical activation or modification [29]. Nevertheless, those expensive catalytic nanocarbons are generally associated with cost-intensive fabrication procedures, high energy/chemical inputs, and low yields [30]. Comparatively, low-cost biochar derived from wasted biomass demonstrates its preponderance as a cost-effective and tunable carbonaceous scaffold subject to different modification methods during preparation processes (*i.e.*, pyrolysis and hydrothermal carbonization) [31, 32].

Typically, biochar modification strategies incorporate diverse chemical and physical methods [33]. Most of recent studies focus on metal incorporation to generate metal/biochar assembled structure to modify inherent chemical inertness and electrochemical properties of biochar [28, 33-37]. It is well acknowledged that biochar carbon framework can readily enhance electron mobility over its conductive matrices and distribute exterior metal catalytic sites owing to its rich surface oxygen containing functionalities [26, 27, 38].

The direct utilization of raw metal/oxides in decontamination activities inevitably suffered from severe metal dissolution which might cause secondary contamination. Besides, the other irrevocable shortcomings such as poor affinity towards reactants (*i.e.*, peroxides or pollutants) originated from their intrinsic surface chemistry (*i.e.*, low specific surface areas (SSAs) and pore volume, uncontrollable surface energy, *etc.*) and thermal sintering behaviour also inhibit their wider application [39]. In this regard, the evolvement of metal biochar can provide promising candidate in AOPs with the harbouring of different toxic transition metals, *i.e.*, Iron

(Fe), Cobalt (Co), Copper (Cu), and so forth, because biochar can not only improve the reactivity (*i.e.*, high SSAs and pore volume, stability, affinity towards pollutants, *etc.*) but also form hierarchical structure to mitigate release of metals [15, 27, 28, 34, 35, 40-42]. The most common metal combined with biochar is Fe and its iron oxides, as iron-based contents can provide sufficient free-flowing electrons and endow magnetization to the resultant composite for easy separation. Besides, Fe^{2+}/Fe^{3+} redox circle was also conducive to the activation of peroxides, which would promise higher recyclability and versatile redox roles. A myriad of researches has been reported to employed Fe biochar in various applications due to its extraordinary electrochemical properties. Nevertheless, the inevitable metal leaching of Fe ions into water body still impedes its scaling-up application [39]. Also, the heterogeneous redox systems based on iron oxides are limited by the sluggish recovering rate from Fe^{3+} to Fe^{2+} in crystal lattice (solid phase), not to mention the generation of excessive sludge for post-treatment.

Recently, exterior organic electron shuttles (*e.g.*, CH_3COO^-, humic acid, quinone, *etc.*) were introduced into homogeneous Fe/persulfate activation system and exerted positive influence on Fe^{2+}/Fe^{3+} redox cycling [43, 44]. Xu et al. also found the absorbed low molecular weight organic acids (LMWOAs) on biochar surface could enhance Cr(VI) reduction with biochar as electron shuttle [45]. Intriguingly, these phenomena showcase an alternative prospect to reduce the metal leaching in metal/biochar-based AOPs to confine Fe-based redox circle in crystal phase. It is hypothesized and then proven in this work that proper electron shuttles could reach complementary coupling with hierarchical metal biochar to achieve better sustainability.

Herein, hierarchical Fe biochar was synthesized *via* hydrothermal carbonization (HTC) using cellulose and specified Fe salt as precursors, and then underwent NH_3 activation to tailor its surface properties to reach better affinity towards electron shuttles. The as-prepared hierarchical Fe biochar was employed as high-efficient metal-incorporated catalyst in aqueous decontamination. Different concomitant organic electron shuttles were introduced to investigate the changes of its surface chemistry, catalytic performance, and metal leaching in the degradation of various pollutants. The objectives of this research were to (i) exhaustively characterize the prepared hierarchical Fe biochar with various techniques and evaluate its feasibility to act as an effective catalyst in AOPs, (ii) explore the synergies between electron shuttles and hierarchical Fe biochar, and investigate their environmental sustainability using metal leaching, activation energy, and recyclability as indicators, (iii) and identify the plausible mechanisms in both theoretical and experimental manners. For the first time, exterior electron shuttles were introduced onto metal biochar surface to critically explore the environmental sustainability of metal biochar in AOPs. This research will unveil the correlations between metal biochar and electron shuttles, deepen the understanding of electron transfer regime in metal biochar, and then facilitate the application of hierarchical Fe biochar and its commensurate metal/carbon frameworks in future.

2. Experimental

2.1. Chemicals

Cellulose, as the main content in plant and wood biomass waste, was purchased from Sigma-Aldrich and employed as biochar precursor without further treatment. All chemicals used in this study were of analytical reagent grade and solvents were of high-performance liquid chromatography (HPLC) grade, including $FeCl_3$, bisphenol A (BPA, $C_{15}H_{16}O_2$), Oxone (PMS precursor, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), ascorbic acid (AA, $C_6H_8O_6$) from Sigma-Aldrich, oxalic acid (OA, $C_2H_2O_4$), methanol (MeOH, CH_3OH), ethanol (EtOH, C_2H_5OH), tartaric acid (TA, $C_4H_6O_6$), hydroquinone (HQ, $C_6H_6O_2$), NaN3 from Aladdin, China., *etc*. Ultrapure water (UW, 18.2 MΩ cm^{-1}) obtained from a Millipore Milli-Q Water Purification System (Milford, USA) was adopted for configuration of all experimental solutions if not specified.

2.2. Preparation of hierarchical Fe biochar

Cellulose feedstock was sieved through 120-mesh (particle size < 0.125 mm) prior to carbonization. The prepared cellulose powders were put in a Teflon-lined autoclave and underwent HTC at 180°C for 16 h. Then, the black carbons were impregnated with potassium hydroxide (KOH) and transition metal salt (*i.e.*, $FeCl_3$) in UW contained in beakers and the solvent was evaporated overnight. Subsequently, 10 min microwave radiation with 800 W was employed for further graphitization. Also, a post-treatment was performed by irradiating obtained biochar sample with 800 W microwave under NH_3 atmosphere for 8 min to tailor the surface chemistry. Subsequently, the obtained biochar composite was washed with 0.5 M HCl and deionized water (DI) until the eluent reached neutral pH. The obtained biochars were denoted as Fe/CBC. The metal-free biochar sample was also produced and set as control group without metal incorporation and post treatment, denoted as CBC. The biochar pre-treated with electron shuttles, exemplified by TA, was designated as Fe/CBC@TA.

Hierarchical Fe biochar bonded with various electron shuttles was prepared *via* a facile bonding process without adding any chemical cross-linking agent. Briefly, 200 mg L^{-1} Fe/CBC and a certain amount of organic electron shuttle were added in 100 mL UW contained in a conical flask with a poly tetra fluoroethylene (PTFE) paddle to reach homogeneous mixing for 24 H. The system was maintained at 80 ± 1 °C using a water bath to achieve higher collision occurrence. After reaction, the mixed system underwent infiltration and the separated solids were transferred to vacuum dryer after several-time washing using DI and EtOH, respectively. The extracted supernatant was used for measurement of accommodation efficiency, and the dried samples were stored in a desiccator for future use.

2.3. Characterisation

The surface morphology and approximate surface elemental analysis of obtained biochar were investigated using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS, Hitachi, Japan). The crystallographic structure was examined by obtaining X-ray diffraction (XRD, Bruker D8A, Germany) patterns equipped with high intensity monochromatic Cu-Kα source (λ=1.5218 Å). Scanning rate and 2θ collection range were set at 50 ° min^{-1} and 10-90 °, respectively. Fourier transform infrared (FTIR Nexus, Thermo Nicolet, USA) spectroscopy was adopted to investigate the surface functionalities on biochar with the wavelength range at 400-4000 cm^{-1}. Raman spectrometer (Raman spectra, Renishaw, UK) was employed to investigate the defective level and graphitization degree with 532 nm excitation. The textural characteristics were determined by using N_2 adsorption-desorption isotherms obtained from surface area analyser at 77 K (BET, Quantachrome Autosorb, USA). The ultimate elemental analysis (EA, Vario EL cube, Germany) was used to estimate the CHONS elemental ratio in biochar. The weight ratio of oxygen was quantitatively calculated using **Eq.1** below. X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, USA) with Al Kα radiation was used to investigate the composition and chemical state of the elements on the sample surfaces. The binding energy of all characteristic peaks were calibrated with carbon C1s core level at 284.8 eV. Devolution of XPS data was conducted using Shirley background associated with Gaussian-Lorentzian model in XPSPEAK41, and the component peaks were identified by comparison of their binding energies (BEs) with the reported literature values. The electron paramagnetic resonance (EPR, Bruker, Germany) spectra was performed with different spin-trapping agent including 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) or 2,2,6,6-tetramethyl-4-piperidone (TEMP), and the specific experimental conditions are described in Text S1. (Supporting information). pH of solution was adjusted with diluted NaOH or HNO_3 without buffer, and measured using a digital pH meter (Thermo, USA).

$$\text{O}\,wt.\% = 100\% - \text{C}\,wt.\% - \text{H}\,wt.\% - \text{N}\,wt.\% - \text{S}\,wt.\% - \text{ash}\,wt.\% \qquad (1)$$

2.4. Batch experiments

The catalytic performance of all biochar samples was assessed using typical batch experiment procedure with PMS as activator for organics removal in aqueous solution. Specifically, 100 mL solution containing excess amount of BPA (*i.e.*, 100 mg L^{-1}) was put in a 250 mL conical flask sealed with foil. Then, 200 mg L^{-1} biochar and 1 g L^{-1} Oxone powder (corresponding to 3.25 mM PMS) were added sequentially to initiate the reaction. All experiments were carried out at 25 ± 1 °C (if not specified) with vigorous stirring of 200 rpm in a thermostat oscillator. At predetermined time interval, an aliquot of 1 mL solution was withdrawn from solutions and transferred in HPLC vials after passing through 0.45 μm mixed cellulose ester (MCE, Millipore) membrane filter, and 0.5 mL MeOH was then promptly mixed with the extracted solution to quench the excessive radicals in bulk solution. After reaction was terminated at the end, all solutions were centrifuged at 5000 rpm for 10 min to separate the catalyst for further regeneration, and the extracted supernatant was preserved for determination of PMS consumption. Scavenging experiments were conducted in a similar procedure. Specifically, different organic scavenging agents (*i.e.*, 2 M EtOH, 500 mM TBA, 15 mM NaN_3) were added in BPA solution to reach desired concentration. Then, catalysts and Oxone were added to initiate the catalytic reaction, and aqueous samples were also taken as aforementioned.

Pollutant concentrations were analysed with HPLC (limit of detection (LOD) at 0.1 mg L^{-1}, Hitachi) or Ultraviolet and visible spectrophotometry (UV-vis, LOD at 1 mg L^{-1}, PerkinElmer), and pollutant removal efficiency was calculated using **Eq. 2** as follows. The leaching amounts were quantified by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Scientific, LOD of 0.1 μg L^{-1}). The metal concentrations after wet digestion (0.1 g sample in 4 mL HNO_3 and 1 mL $HClO_4$ under 105 °C till total evaporation) were measured using atomic absorption spectroscopy (AAS, Jena, LOD of 0.1 μg L^{-1}). The bonding efficiency of electron shuttles (**Eq. 3**) on Fe/CBC and total organic removal were calculated using a TOC analyser (TOC, multi 3100, LOD of 1 μg L^{-1}). All experimental procedures were conducted at least in duplicate, and data were presented are presented as mean values ± standard deviations.

$$\text{Removal efficiency (\%)} = \frac{[\text{pollutant}]_{\text{initial}} - [\text{pollutant}]_{\text{final}}}{[\text{pollutant}]_{\text{initial}}} \quad (2)$$

$$\text{Accomodating efficiency (\%)} = \frac{[\text{Electron shuttle }]_{\text{initial}} - [\text{Electron shuttle }]_{\text{final}}}{[\text{Electron shuttle}]_{\text{initial}}} \quad (3)$$

2.4. Analytical methods

The concentrations of BPA were analysed by HPLC equipped with a C-18 column (Eclipse XDB-C18) and a UV-VIS Detector and UV wavelength was set at 280 nm. The mobile phase was a mixture of absolute methanol and phosphorus acid (0.5 vol.%) with volume ratio of 25/75 at a flow rate of 400 mL min^{-1}.

The PMS concentration was determined using a modified iodide oxidation method [46]. A chromogenic reagent containing 100 g L^{-1} KI and 0.5 g L^{-1} $NaHCO_3$ was prepared. The reagent was allowed to equilibrate for 15 min, and then 10 mL reagent was transferred into a 15 mL polypropylene centrifuge tube. An aliquot of 0.25 mL sample from reaction system was introduced, and then the mixture was thoroughly mixed for a few seconds and allowed to stand for 20 min. The solution was yellow and absorbance was measured at a wavelength of 352 nm using an Optizen Pop UV-Vis spectrometer.

The calculation of reaction stoichiometric efficiency (RSE) was conducted by **Eq. 4** as the ration of removed BPA to the consumed PMS, to verify the change of PMS consumption after the accommodation of electron shuttles.

$$\text{RSE} = \frac{\text{moles of degraded BPA}}{\text{moles of consumed PMS}} \quad (4)$$

The activation energy was performed using Arrhenius equation (**Eq. 5**) to evaluate the energy threshold in peroxide activation.

$$\text{k} = \text{Aexp}(-\frac{E_a}{RT}) \quad (5)$$

Where k, A, E_a, R, and T correspond to reaction rate constant (min^{-1}), prefactor, activation energy (kJ mol^{-1}), universal gas constant (J mol^{-1}), and temperature (K) obtained in experiments.

3. Results and discussion

3.1. Leaching Fe amount during catalysis under different pH values

The leaching of transition metals into aqueous solution is the critical factor that determines the sustainability of metal/biochar in redox-based processes. Besides, leaching amount of metal-involved AOPs are tightly subject to pH change due to the distinct forms of metal complexation under varied pH and passivation phenomenon [39]. In this regard, metal leaching amounts in reaction systems with different pH values was selected as the indicator to suggest the change of sustainability of Fe/CBC before and after electron shuttles introduction in AOPs.

First, 200 mg L^{-1} raw Fe/CBC was applied in the degradation of 100 mg L^{-1} BPA with the addition of 1 g L^{-1} Oxone powder under different pH values (2-10). As shown in **Fig. 1a**, the leaching amounts typically followed a unimodal trend with the peak amount (2.436 mg L^{-1}) centred at pH value of 6. Considering that legal limit of Fe ions released in solution imposed by European union is 2 mg L^{-1}, this peak amount apparently outnumbered the limit and posed environmental threat to human being. Intriguingly, the leaching amounts under alkaline conditions were found to be higher than those under acidic conditions. It might indicate the different mechanism from zero-valent iron (ZVI) biochar system in the similar activation system, whereby Fe^0 tends to undergo acidic dissociation with Fe^{2+} and Fe^{3+} acting as the desirable and intermediary products in peroxide activation [15, 16, 27]. Besides, the overall metal leaching amounts were relatively low compared with other researches based on Fe incorporated biochar [47, 48]. This indicates Fe/CBC might directly donate electrons to activate PMS without involving the phase transformation of Fe species.

To investigate the influence of electron shuttles on sustainability of Fe/CBC, exterior organic electron shuttles with distinct molecular structure and functionalities was selected to be deployed on Fe/CBC surface. Noteworthily, the Fe/CBC without ammonia activation was inert for electron shuttles accommodation due to the high graphitized surface and deficient oxygen-containing functionalities, which could barely provide anchoring sites to accommodate electron shuttles because of the electroneutrality of graphitized carbon surface [25, 49]. Compared with oxygen functional groups which are prone to lower reducibility, block pore volume, and impede electrocatalysis of biochar framework, the introduction of nitrogenous dopants has been well acknowledged for its versatile role in reallocating surface charges and spins to tailor the carbocatalysis of well-ordered crystalline carbon lattice [50, 51]. In this work, facile and economical ammonia post-treatment was employed to enhance polarity of biochar surface to increase its affinity towards electron-rich organic electron shuttles. Furthermore, the introduction of nitrogenous dopants might synergize with electron rich metal centres to accelerate the electron mobility owing to their high electronegativity compared with substituted carbon atoms (Pauling scale: $\chi_N=3.04 > \chi_C=2.55$) to promise faster electronics [28, 29]. As shown in **Fig. 1b**, four selected organics (*i.e.*, AA, OA, TA, and HQ) could be successfully accommodated on biochar surface after ammonia post-treatment, *i.e.*, all accommodation efficiencies transcended 50 % suggesting a good affinity of biochar surface after nitrogen incorporation. To investigate the relationship between accommodation efficiency and organic category, two inherent factors of electron shuttles including molecular weight and O/C ratio were plotted with linear fitting. The fitting results indicated molecular weight of organic exhibits weak correlation with accommodation efficiency ($R^2=0.6274$), while a linear correlation could be found for organics without benzene ring ($R^2=0.9194$). This indicated nitrogenous dopants tend to bond with oxygen-containing groups (*i.e.*, hydroxyl functional group) due to its stronger electronegativity. Besides, HQ showed the highest accommodation efficiency with complete adsorption, and this phenomenon resulted from the strong π-π interaction between its benzene ring and graphitized biochar matrices.

Subsequently, the sustainability of Fe/CBC accommodated with representative electron shuttle (TA, accommodation efficiency 79 %) was examined using same procedure. The metal leaching amounts were all reduced dramatically (between 2.9 ~ 6.84 times, reached undetectable level at pH=10) to lower than 0.1 mg L^{-1} even at around neutral condition (0.578 mg L^{-1} at pH=6, 4.21 times), indicating the favourable improvement of Fe/CBC sustainability after TA accommodation. Reduced metal leaching could not only mitigate the environmental concern but also preserve more active metal centres for redox cycling, thus promoting electrocatalysis of Fe/CBC.

3.2. Material characterization

The XRD patterns of Fe/CBC and Fe/CBCs accommodated with organic electron shuttles are presented in **Fig. 2a**. The pattern of raw Fe/CBC clearly demonstrated two sharp peaks at 26.64° and 44.99°, respectively assigned to (101) plane of SiO_2 (JCPDS PDF#46-1045, **Fig. S1**) and (031) plane of Fe_3C (JCPDS PDF#35-0772). The existence of SiO_2 was attributed to the residual ash content. Considering the inert properties of SiO_2 in redox reactions, the effect of ash content on electrocatalysis could be ruled out. As described in **Section 2.2**, Fe/CBC was prepared utilizing several graphitization protocols including hydrothermal carbonization and microwave irradiation. The appearance of Fe_3C indicated the successful incorporation of Fe content, and Fe metal centres could bond to carbon matrices *via* inner-sphere interaction (*i.e.*, covalent bonds) with stronger bonding force. A close view by TEM (**Fig. 3**) further unveiled bonding interaction of Fe/CBC, and a hierarchical porous structure with an outside layer of around 20 nm could be clearly observed. The outside layer with a crystalline spacing of 0.25 nm assigned to graphite was verified to be carbon layer. Correspondingly, the inner core surrounded by Fe_3C with a crystalline spacing of 0.20 nm was confirmed to consist of iron content. Therefore, Fe/CBC was implied to house Fe core with well-ordered graphitic carbon layer to form a well-developed hierarchical structure. Additionally, wet digestion was employed to determine the Fe content levels in Fe/CBCs (**Table 1**). Fe species accounted for 0.89 ± 0.12% for Fe/CBC, and its value was diluted to 0.71 ± 0.08 % after TA accommodation due to the introduction of electron shuttle layer.

After deploying four selected organics on Fe/CBC surface, two characteristic peaks corresponding to SiO_2 and Fe_3C decreased significantly, suggesting the washing-out of ash content and the cover of Fe_3C centre with organic layer, respectively. Noteworthily, the peak at around 26.64°was not completely erased and a small peak with a broader FWHM value still remained, which was plausible to be assigned to the overlapping peak of (111) plane of graphite [52]. This scenario further verified that the Fe/CBCs were highly graphitized. Furthermore, the broader peak at around 20-25° is usually employed to indicate the amorphous carbon level in carbonaceous materials. Compared with the narrow width of amorphous carbon peak of raw Fe/CBC, all Fe/CBCs accommodated with electron shuttles indicate a wider peak range, and the increments of peak range could roughly correspond to accommodation efficiencies (AA < TA < OA < HQ). These results confirmed the successful accommodation of electron shuttles on Fe/CBC surface. Besides, a restively sharp peak at 23.14°, assigned to (011) plane of oxalic acid (JCPDS PDF#20-1817), appeared on Fe/CBC@OA pattern. This might indicate OA was entrapped in porous structure *via* pore filling adsorption/partition rather than bonded onto Fe/CBC *via* chemical complexation. Comparatively, the other three organics were more probable to interact with Fe/CBC surface *via* chemical complexation due to the absence of crystalline peaks.

As shown in **Fig. S2**, the morphological images could be obtained using SEM. The prepared Fe/CBC (**Figs. S2a and b**) demonstrated an irregular granule with distinct porous structure and an average particle size smaller than 20 μm, indicating a typical morphological feature of char material. To investigate the surface compositions after electron shuttle incorporation, the images of Fe/CBCs accommodated with organics were also shown with **Figs. S2c, d, e, and f** corresponding to Fe/CBCs@AA, OA, TA, and HQ, respectively. SEM images revealed that accommodation of AA and HQ remarkably reduced the density of macro- (< 50 nm) and mesopores (2-50 nm). The deposition of organics might cover accessible active sites and account for unfavourable electrocatalysis (data shown later). With respect to Fe/CBCs@TA, winkled and corrugated layer-like structure could be found to form on biochar surface without compromising great porous density, which might suggest the optimal accommodation strategy. To further verify the textural properties of Fe/CBCs@TA, BJH porosity and BET surface area were identified and summarised in **Table 1**. Raw Fe/CBC possessed an ultrahigh SSA of 1139.76 m^2 g^{-1} owing to the generation of rich porous structure during graphitization and activation. Comparatively, SSA of Fe/CBC@TA significantly declined to 792.33 m^2 g^{-1} due to TA introduction, which was still considerable compared with other biochars produced from conventional pyrolysis [33]. Significant reduced external surface area of Fe/CBCs@TA (S_{ext}, 368.38 m^2 g^{-1} compared to 639.54 m^2 g^{-1} for Fe/CBC) indicated that TA mainly deploy on biochar surface to form an exterior layer, which could coincide with the morphological feature. Also, TA was found to mainly settle down in mesopores by comparison of reduced total pore volume (V_{total}, 0.53 cm^3 g^{-1} compared to 0.88 cm^3 g^{-1} for Fe/CBC) and micro pore volume (V_{micro}, 0.23 cm^3 g^{-1} compared to 0.28 cm^3 g^{-1} for Fe/CBC). Large fraction of micropores (< 2 nm) could be preserved and the V_{micro}/V_{total} notably increased from 31.8 % to 43.3 % after TA accommodation. Compared with mesopores associated with mass transfer in adsorption process, micropores mainly act as catalytic sites and electron-rich structural defects in AOPs. Thus, the preservation of micropores could be conducive to catalytic performance. As illustrated in **Fig. 2b**, the curve of Fe/CBC apparently demonstrated a type-IV isotherm with hysteresis loop located at 0.45-0.95 relative pressure (P/P_0), indicating a typical mesoporous feature [53]. After TA accommodation, Fe/CBC@TA curve levelled off below 0.2 P/P_0 and exhibited a smaller hysteresis loop. Also, the pore size distribution (PSD, **Fig. S4**) suggested the consumption of mesoporous structure with partial micropores remained. These results confirmed the critical role of mesopores in TA accommodation and further verified the preservation of catalytic micropores.

With the implementation of Raman spectroscopy technique, two crucial parameters including defective level and graphitization degree that determines carbocatalysis can be quantitatively explored. As shown in **Fig. 2c**, two apparent peaks at 1350 and 1580 cm^{-1} could be clearly observed. Specifically, the characteristic peak at 1350 cm^{-1} (D band) indicates the defects and A_{1g} atomic arrangement of carbon atoms, while the peak at 1580 cm^{-1} ^{1} (G band) corresponds to E_{2g} mode vibration of graphitic carbon [54]. The ratio of their peak intensities, namely I_D/I_G, is generally employed to indicate either defective level or graphitization degree. For Raman spectra of Fe/CBCs@AA and OA, defective levels notably decreased from 1.06 to 0.98 ~ 0.70 due to the accommodation of AA and OA, suggesting AA and OA mainly deployed on carbon peripheries and consumed partial structural defects. With respect to Fe/CBC@HQ, the incorporation of HQ with an aromatic ring obviously affected the peak intensities and its I_D/I_G slightly decreased to 0.97. Comparatively, Fe/CBC@TA maintained a similar defective level to Fe/CBC (I_D/I_G values both at 1.06). Besides, the characteristic peak at 2700 cm^{-1} assigned to G^2 band is another Raman footprint of sp^2-carbons associated with G band [55]. The remained G^2 peak of Fe/CBC@TA indicated the sp^2-carbon framework with high density of π-electrons could be preserved to promise faster electron transfer in redox reactions. Thus, Fe/CBC@TA still maintained both a higher defective level and an intact sp^2-carbon framework, suggesting a great potential for good catalytic performance.

Changes of surface functionalities of Fe/CBC during electron shuttles accommodation are presented in **Fig. 2d** using FTIR. Raw Fe/CBC possessed several characteristic peaks at 2680, 2352, 2100, 1588, 1084, and 470 cm^{-1} assigned to -OH (hydrogen bonding), C≡N, C≡C, C=O and C=N, -OH and C-O, and Fe-O, respectively [6]. The appearance of Fe-O peak confirmed the conclusion in XRD and TEM that Fe was successfully housed within carbon domain. Only a small fraction of redox-active moieties (RAMs) remined on Fe/CBC, which was attributed to the high carbonization level and coincided with Raman analysis. After electron shuttles accommodation, obvious decrease of -OH and C-O peak intensity was observed and it might indicate the chemical adsorption participated in this process. Besides, Fe-O peak intensity dramatically declined, indicating the cover of metal core by organics.

As shown in **Table 2**, the approximate elemental analysis by SEM-mapping and the ultimate analysis by EA were summarized to differentiate the surface compositions before and after electron shuttles accommodation. Amongst, Fe/CBCs accommodated with electron shuttles exhibited greater oxygen levels compared with raw Fe/CBC (9.89, 8.66, 12.82, and 9.47 wt. % compared with 4.36 wt. %) and Fe/CBC@TA showed a highest ratio, corroborating that more RAMs were introduced onto carbon surface.

To carefully investigate the surface properties after electron shuttle incorporation, XPS spectra of Fe/CBC and Fe/CBC@TA were compared. All Fe/CBCs spectra mainly incorporated three elements, *i.e.*, C 1s, O 1s, and N 1s. The absence of Fe 2p signal peak corresponded to the hierarchical structure (carbon layer > 10 nm) observed in **Fig. 3**, because X-ray could only penetrate a layer with width less than 10 nm. As illustrated in C 1s spectra (**Fig. 4a**), overall raw spectra intensity could be deconvoluted into five constituents at 284. 6, 284.9, 285.7, 287.1, and 289.5 eV, assigned to C=C and C-C, C-O, C=O, OH-C=O and C-N, and π-π shake-up satellites, respectively. Raw Fe/CBC possessed a large fraction of sp^2- and sp^3-hybridized bonds as well as π-π shake-up satellites, which was correlated to its highly graphitization degree. Its deficiency in oxygen level would lead to the weak affinity towards peroxides and pollutants to initiate the redox reactions. Amongst all the oxygen-containing functionalities, C-O and C=O were reported to be most reactive in peroxides activation and adopted as index parameter herein [29, 34, 45]. Low C-O/C=O level of Fe/CBC (11.45 %) was found to be remarkably elevated to 47.22 % after TA accommodation, and most of the increased oxygen content was correlated to electron-rich C-O (28.1 %). O 1s spectra (**Fig. 4b**) was also divided into four characteristic peaks at 532.5, 533.8, 535.7, and 537.2 eV, assigned to C=O and O-C=O, C-O-H and C-O-C, C-O-C=O, and absorbed water, respectively. TA was considered to interact with the active sites previously holding water, and inert ester groups (C-O-C=O) were markedly diluted to smaller fraction on surface. The significant increase of peak intensity ratio at 532.9 eV (from 24.58 to 39.49 %) might be ascribed to the introduction of α-OH in TA. Similarly, pH and $\mathrm{pH_{pzc}}$ values were also reduced from 8.82 to 7.61 and 5.40 to 4.82 due to the acidity of TA surface functionalities (**Table 1**). Nitrogenous level was also investigated with N 1s spectra, deconvoluted into 398.6, 400.1, and 402.6 eV correlated to pyridinic N in six-membered heteroring, pyrrolic N in five-membered heteroring, and oxynitride ($\mathrm{-NO_x}$), respectively. Typical edge-functionalized nitrogenous dopants were found to account for most doped nitrogen contents, suggesting ammonia gas post-treatment mainly promoted interfacial nitrogen level. The introduction of TA reduced pyrrolic level from 42.85 to 33.08 % and this might be due to the vacant orbital in five-membered heteroring to bond with electron-rich TA. Intriguingly, the measured N level increased from 2.84 % for Fe/CBC to 3.51 % (**Table 1**), which might indicate the stability of these edge-functionalized nitrogenous dopants [56].

3.3. Catalytic performance of Fe/CBCs

To evaluate the electrocatalysis of Fe/CBCs, a ubiquitous PMS-based activation system was exploited as the representative strategy for green and environmental remediation. Oxone is a crystalline powder which can promptly dissolve in aqueous solution to release PMS molecules ($\mathrm{HO\text{-}OSO_3^-}$). Under the presence of proper catalysts, reactive oxygen species (ROSs) including robust sulfate radicals ($\cdot\mathrm{SO_4^-}$, E˚= 2.5-3.1) and hydroxyl radicals (·OH, E˚= 1.9-2.7) could be readily generated after the homolytic cleavage of peroxide bond in PMS. These radicals impressively outperform their parent precursor (Oxone, E˚= 2.07) and potentially reach the rapid degradation or mineralization of concomitant organic pollutants. BPA was selected as the model organic pollutant because it is widespread in industrial wastewater and poses highly environmental concern to human health as a toxic endocrine disruptor [57].

The addition of sole Oxone powder led to sluggish degradation of BPA with ~ 20 % removal in 60 min (**Fig. S5**), suggesting that PMS alone could not efficiently degrade BPA in the absence of catalysts. As demonstrated in **Fig. 5a**, the presence of raw Fe/CBC dramatically elevated the removal rate to 81.6 %, reaching a desirable catalytic performance for Fe-incorporated biochar. Parallel adsorption capacities of Fe/CBCs were also investigated, and results implied adsorption behaviour played a vital role in electrocatalysis. Previously, many relevant researches have also implied the same scenario that adsorption of pollutant is exclusively verified to be the rate-limiting step and determines the occurrence of electron transfer on carbon surface [25, 34, 52]. The extraordinary adsorption capacity (75.6 %) might reciprocally account for its excellent catalytic performance.

Preliminarily, overdosed 100 mg L^{-1} electron shuttles were added and they all demonstrated similar catalytic performance (**Fig. S5**, ~ 50 % BPA removal) in the homogeneous system, indicating the selected four representative organics possessed similar catalysis to evolve ROSs. Comparatively, the catalytic performance of Fe/CBCs@AA, OA, TA, and HQ were also investigated. The accommodation of AA, OA, and HQ resulted in both decreased adsorption capacities (34.1 ~ 56.2 %) and removal rates (57.8 ~ 74.1 %) independent of their accommodation efficiency (58.1 ~ 100.0 %), suggesting that the quantity of incorporated organics showed poor correlation with catalytic performance. Interestingly, Fe/CBC@TA demonstrated highest degradation rate at 95.1 %, while its adsorptive performance slightly dropped to 67.1 % due to the decreased S_{BET}. This phenomenon might indicate a distinct mechanism of Fe/CBC@TA from the other electron shuttles. Recently, Xu et al. found the adsorbed TA on biochar prepared at 700 ℃ (BC700) could increase its surface C-O content and thus enhance the electron mediation for Cr(VI) reduction [45]. Given similar phenomenon was also found in C 1s and O 1s spectra as well as FTIR curve of Fe/CBC@TA, C-O was considered as the key oxygen-containing moiety in the catalytic performance. Therefore, Fe/CBC@TA with the highest reactivity was chosen as the representative catalyst in the following sections.

3.4. Catalytic mechanism of Fe/CBC@TA

To differentiate the ROSs participating in the catalytic reaction, several scavenging agents were selected to in situ quench respective target ROSs, *i.e.*, EtOH towards both $\cdot SO_4^-$ and $\cdot OH$ ($k_{\cdot OH}$ = (1.2–1.8) × 10^9 M^{-1} s^{-1}, $k_{SO_4^{\cdot -}}$ = (1.6–7.7) × 10^9 M^{-1} s^{-1}) , TBA towards $\cdot OH$ ($k_{\cdot OH}$ = (3.2–7.6) × 10^8 M^{-1} s^{-1}, $k_{SO_4^{\cdot -}}$ = (4.0–9.5) × 10^5 M^{-1} s^{-1}), and NaN_3 towards singlet oxygen $^1O_2$ ($k_{^1O_2}$ = 1.0 × 10^9 M^{-1} s^{-1}). All kinetic experimental data were fitted a pseudo-first-order kinetics model. As illustrated in **Fig. 5b**, the addition of EtOH significantly reduced the reaction constant rate from 0.175 min^{-1} for Fe/CBC@TA to 0.061 min^{-1}, indicating the coexistence of $\cdot SO_4^-$ and $\cdot OH$. Then, TBA that could merely react with $\cdot OH$ was added to differentiate the respective contributions of $\cdot SO_4^-$ and $\cdot OH$. The results showed that $\cdot OH$ accounted for a large fraction of involved reactive species with a margin at 0.081 min^{-1} greater than that of EtOH-scavenged group. NaN_3 was also added to verify the evolvement of $^1O_2$, and reaction rate constant indicated a nonnegligible decline to 0.109 min^{-1}. Noteworthily, NaN_3 cannot exclusively confirm the participation of $^1O_2$, as it could consume $\cdot OH$ and PMS molecules simultaneously. Thus, EPR technique was employed to further determine the generated ROSs. Two different spin-trapping agents, namely DMPO towards $\cdot SO_4^-$ and $\cdot OH$, and TEMP towards $^1O_2$, were adopted to in situ capture the generated ROSs in catalytic reactions. Fe/CBC was also set as a control group to verify the critical role of TA. As illustrated in **Fig. 5c**, the captured species were identical for both Fe/CBC and Fe/CBC@TA when using DMPO agent. The appearance of DMPO-OH (hyperfine splitting: $\alpha_H = \alpha_N$ = 14.9 G) and DMPO-SO_4 (hyperfine splitting: α_N = 13.2 G, α_H = 9.6 G, α_H = 14.8, and α_H = 0.78 G) adducts coincided with the conclusion in scavenging experiments. Comparatively, the evolvement of radicals for

Fe/CBC@TA procrastinated to 5 min (peak intensity: 1724.6 a.u. at 5 min) in contrast to the rapid generation of ROSs for Fe/CBC (peak intensity: 2451.6 a.u. at 1 min). According to the nature of radical-involved AOPs, ROSs will be generated as long as the catalyst and PMS simultaneously coexist. This might imply the participation of another mechanism after TA accommodation. Parallel EPR tests were performed with TEMP as the spin-trapping agent, and results showed a distinct two-phase mechanistic route compared with one-phase mechanism of Fe/CBC. Characteristic peaks of TEMPO adduct appeared (hyperfine splitting: $\alpha_N = 16.9$ G) in Fe/CBC@TA curve and maintained an increasing trend with intensity value from 660.7 to 937.2 a.u. in 5 min. These results confirmed the ROSs generated in Fe/CBC@TA and PMS system were generally two-phase mechanism, whereby $^1O_2$ governed in the starting phase and then $\cdot SO_4^-$ and $\cdot OH$ radicals took over in the following phase. This distinct two-phase mechanism might be responsible for the smaller leaching amount for Fe/CBC@TA, because $^1O_2$ is an interfacial ROSs generated on carbon surface and in great association with electron transfer regime. Besides, greater RSE value of Fe/CBC@TA (**Table1**, 276.6 ± 13.7) compared with that of Fe/CBC at 262.8 ± 9.5 also indicated a higher efficiency of PMS utilization.

Previously, Duan claimed the evolvement of $^1O_2$ was highly associated with electron transfer regime on carbon surface. The PMS molecules would interact with electron-rich functionalities to form a metastable complex, and accept electrons transferred along the carbon substrate with intact *sp*^{2}-hybridized carbon π-network. This process usually accompanied with the oxidation of water molecules to generate $\cdot OH$ [29]. With the well-developed hierarchical structure, the free-flowing electrons in inner Fe core could transport *via* the highly graphitized carbon domain. Therefore, the formation of redox cycling of Fe and ROSs could be achieved directly in the solid phase without the dissolution of Fe into Fe^{2+}/Fe^{3+} and thus reduced leaching amount. Accordingly, the plausible catalytic mechanistic pathway could be illustrated in **Fig. 6**.

It is also indispensable to elucidate the physicochemical properties after catalytic reaction to explore the underlying catalytic mechanism. Oh et al. claimed that carbonaceous materials like CNTs, graphene, biochar, *etc.* would undergo irreversible oxidative erosion by the generated radicals in AOPs [39]. As shown in **Fig. S3f** and **Fig. S6**, no obvious morphological and crystalline change could be found on spent Fe/CBC@TA after catalytic reaction. This might be ascribed to the protective role of surface electron shuttle. Control group of Fe/CBC associated with 100 mg L^{-1} TA was also performed on SEM, and its image (**Figs. S3h**) showed the pore structure was almost blocked by the organic substances, indicating the necessity of conducting accommodation procedure. More pore volume was released after the consumption of electron shuttles (**Figs. S3d-g**), and the freed S_{BET}, S_{ext}, and V_{total} (**Table 1**, 905.58 m^2 g^{-1}, 508.04 m^2 g^{-1}, and 0.65 cm^3 g^{-1}, respectively) suggest the release of active sites and potential reusing capability. Furthermore, spent Fe/CBC still maintained partial defective level (**Fig. S7**, $I_D/I_G = 0.95$) to further accommodate TA. For all Fe/CBCs in **Fig. 3d**, their FTIR curves were nearly identical with an obvious up-shift of C-O bond peak, a down-shift of C-N bond peak, and the evolvement of C=C bond peak. The shifting C-O and C-N bonds confirmed their crucial role in carbocatalysis, and the appearance of C=C bond might correspond to the consumption of introduced oxygen-moieties on carbon surface.

3.5. Activation energy and recyclability of Fe/CBC@TA

To further investigate the catalytic mechanism of Fe/CBC@TA, activation energy as a representative indicator in carbocatalysis was chosen to explore the thermodynamics. As shown in **Fig. 7a**, the activation energy for raw Fe/CBC was calculated to be 10.01 kJ mol^{-1} with a high coefficient of determination ($R^2 = 0.996$), falling into the energy range of diffusion-controlled reactions (10-13 kJ mol^{-1}). This value coincided with the high adsorption capacity of Fe/CBC (**Fig. 5a**) and indicated the mass transfer process should predominantly determine its reaction rate constant. Comparatively, Fe/CBC@TA demonstrated a higher activation energy (E_a = 15.11 kJ mol^{-1}, $R^2 = 0.998$), exceeding the energy threshold for diffusion-controlled reactions. This phenomenon confirmed the two-phase mechanism illustrated in the previous section, where interfacial chemical reactions happened on carbon surface to evolve distinct ROSs owing to the TA accommodation.

Additionally, recyclability of Fe/CBC and Fe/CBC@TA was examined to verify the depletion of catalytic sites. All catalytic runs for Fe/CBC@TA outperformed those of raw Fe/CBC (**Fig. 7b**), especially in the second run with final removal rate of 73.0 % versus 47.6 % in 60 min. These results also suggested the metal leaching and passivation could be significantly alleviated due to the introduction of TA. After three-time recycling, the removal rates of Fe/CBC and Fe/CBC@TA both declined to less than 50 %. With thermal annealing regeneration (**Text S2.**, supporting information), the catalytic performance of Fe/CBC@TA could be elevated to 67.9 % (1.30 times of 3rd run) compared with the inferior regenerated efficiency of Fe/CBC of 42.9 % (1.08 times of 3rd run) due to the well-preserved metal content. The regeneration process also covered its graphitization feature with lower I_D/I_G ratio (0.87) and distinctive G^2 band compared with Fe/CBC@TA (**Fig. S7**).

4. Conclusion

In summary, a novel hierarchical Fe incorporated biochar could be fabricated *via* a facile hydrothermal carbonisation coupled with microwave irradiation process. After accommodating TA on the as-prepared Fe/CBC, a protective functional layer was formed on Fe/CBC which dramatically reduced the metal leaching amount from 2.436 to 0.578 mg L^{-1} at pH value of 6. With the exhaustive material characterizations by XRD, Raman, FTIR, XPS, *etc.*, a large amount of C-O bond was found to be readily introduced and its well-developed core-shell structure could be successfully preserved. Its catalytic performance was evaluated with a ubiquitous PMS activation system for the removal of BPA, Fe/CBC@TA exhibited a highest removal rate of 95.1 % compared with 81.6 % for Fe/CBC. With the help of scavenging experiments and EPR technique, the catalytic mechanism intriguingly conversed from one-phase mechanism (mainly radicals) for Fe/CBC to two-phase mechanism (hybrid ROSs with the emergence of mild $^1O_2$) for Fe/CBC@TA. Besides, the activation energy calculated from thermodynamics (15.11 kJ mol^{-1} versus 10.01 kJ mol^{-1}) and recyclability experiment results also showed the superiority of Fe/CBC@TA. Overall, the Fe/CBC@TA showed superior environmental sustainability owing to its mitigated metal leaching, elevated recyclability, and newly evolved two-phase catalytic mechanism.

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