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**Porous Carbon Monoliths for Electrochemical Removal of Aqueous Herbicides by
“One-Stop” Catalysis of Oxygen Reduction and H₂O₂ Activation**

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Abstract

The overuse of herbicides has posed a threat to human health and the aquatic environment via DNA mutations and antibiotic gene resistance. Carbon-based cathodic electrochemical advanced oxidation has evolved as a promising technology for herbicide degradation by generating hydroxyl radicals ($\cdot\text{OH}$). However, conventional

electro-Fenton process relies on interaction of multiple species that adds to the system complexity and cost and narrows the working pH range. Herein, a series of porous carbon monoliths (PCMs) were developed as a “one-stop” platform for catalysis of the 2-electron ORR coupled with further catalytic reductive cleavage of H_2O_2 to produce $\cdot\text{OH}$. A PCM prepared using 1,6-hexamethylene diamine (denoted as PCM-HDA) produced H_2O_2 at a level that was 374% higher than that obtained using commercially available carbon black at circum-neutral pH. Meanwhile, the generated H_2O_2 was catalytically decomposed to produce $\cdot\text{OH}$. Based on these results, the PCM-HDA electrode achieved an $80 \pm 2\%$ degradation of napropamide in 60 min over the pH range of 4-10 at a mildly reducing potential, with a $69 \pm 2\%$ TOC reduction at circum-neutral condition in 2 h. This simplified system overcomes the system complexity and pH limitation of the conventional electron-Fenton processes.

Keywords: Water treatment; 2-electron ORR; Advanced oxidation process; Carbon-based catalyst.

1. Introduction

According to the Food and Agriculture Organization of the United Nations (FAO), the annual world pesticide consumption was 2,285,881 tons in 1990 with herbicide accounting for a significant fraction¹. The 1990 consumption was nearly doubled to 4,113,891 tons in 2017, while the annual use is still rapidly increasing¹. The adverse effects of herbicides for animals and human being have been observed by various studies.

For example, glyphosate, one of the most widely used herbicides (Myers, 2016), is a known endocrine disruptor for both humans and animals (Gasnier, 2009; Thongprakaisang, 2013) and it also causes reproductive toxicity in zebrafish (Uren Webster, 2014). Atrazine, another widely used herbicide, was also found to be a possible carcinogen and endocrine disruptor (Pérez, 2006). Worse still, herbicides are usually directly transported by surface runoffs into the surface and groundwater bodies, hence posing a potential threat to aquatic ecosystems and human health (Hunt, 2017).

Various water treatment methods including activated carbon adsorption, ozonation, microbial degradation (Ghatge, 2021), membrane filtration (Plakas, 2012), photochemical and electrochemical processing (Wei, 2011) have been explored for the removal of herbicides from water and soils. Electrochemical advanced oxidation processes (EAOPs) generating hydroxyl radical ($\cdot\text{OH}$) are often used due to its environmental compatibility, energy efficiency, and ease of automation (Martinez-Huitle, 2006; Guinea, 2008). Hydroxyl radical can be produced either via anodic water oxidation (Yang, 2014, 2015) or by cathodic oxygen reduction reaction (ORR) (Liu, 2016; Zhao, 2017; Jiang, 2018a). The anodic production of $\cdot\text{OH}$ often requires electrodes with high oxygen evolution reaction (OER) overpotential such as PbO_2 (Elaissaoui, 2019), boron doped diamond (BDD) (Aquino, 2011) or Ni-Sb co-doped SnO_2 (Yang, 2014, 2015). Use of such electrodes lead to not only increasing total operational costs (Chen, 2004), but also leaching of heavy metals (e.g., Pb, Sn, Ni, Sb) (Sandin, 2020).

On the other hand, cathodic EAOP requires the electrochemical generation of H_2O_2 via 2-electron ORR, which is further converted to $\cdot\text{OH}$ (Jiang, 2018a). Carbon-based materials are good 2-electron ORR catalysts because of their earth abundance, low toxicity, porosity and surface properties (Li, 2016b; Jiang, 2018b), and they have also been successfully coupled with Fe(II)/Fe(III) species to be used in electro-Fenton processes for the removal of a series of pesticides and herbicides. For example, chlortoluron was completely removed by the electro-Fenton process within 20 min (Abdessalem, 2008). In spite of the relatively efficient treatment processes, the electro-Fenton process is pH-limited in that it usually requires a pH below 4 (Sun, 2018). In order to avoid the pH limitations, we have successfully developed an electrospinning-based Fe_3O_4 -loaded carbon fiber cathode (Liu, 2018) and metal-organic-framework-derived multi-phase porous electrocatalysts (Liu, 2019) for the degradation and mineralization of pharmaceuticals and herbicides. However, so far, the catalytic activation of H_2O_2 into $\cdot\text{OH}$ still generally requires interaction of multiple species, such as Fe(II)/ H_2O_2 in Fenton process and $\text{H}_2\text{O}_2/\text{O}_3$ in peroxone process (Bakheet, 2013), which results in increased costs and additional operational complexity (Panizza, 2004). Thus, carbon-based catalysts with “one-stop” catalytic activity for both 2-electron ORR and H_2O_2 activation to produce $\cdot\text{OH}$ over a wide pH range are highly desirable for actual use.

Herein we report on a series of porous carbon monoliths (PCMs) for the electrochemical degradation and subsequent mineralization of herbicides. The PCMs have a high ORR catalytic activity leading to H_2O_2 production over a wide pH range under a mildly reducing potential of -0.146 V vs. RHE. A PCM prepared using 1,6-hexamethylene diamine (denoted as PCM-HDA) had a H_2O_2 production 374% higher than commercial carbon black (CB). Meanwhile, the generated H_2O_2 was catalytically decomposed to produce $\cdot\text{OH}$, providing a “one-stop” platform for simultaneous catalysis of the 2-electron ORR and further reductive cleavage of H_2O_2 to produce $\cdot\text{OH}$. The exceptional catalytic activity of PCM-HDA was attributed to the mesoporous structure, elevated oxygen content and sp^3 defects in the carbon matrix. Based on these results, the PCMs have been successfully used to degrade and mineralize napropamide, atrazine, and glyphosate over a wide pH range. This simplified system overcomes the pH limitation of the more conventional electron-Fenton processes. In addition to herbicide degradation, PCM-HDA electrode may also be used for the facile treatment an array of relatively recalcitrant aquatic pollutants.

2. Materials and Methods

2.1. Materials

All chemicals were obtained from Sinopharm Chemical Reagent Co. Ltd. except Nafion solution (Alfa Aesar, 5 w/w in water and 1-propanol, $\geq 0.92\text{ meq g}^{-1}$ exchange capacity), and were used without further purification. Solvents were HPLC grade unless

otherwise stated. Herbicides with chemical purity $\geq 97.0\%$ (obtained from Sinopharm Chemical Reagent Co. Ltd.) used in this study are listed in **Table S1**.

2.2. Preparation of Porous Carbon Monoliths

Resorcinol-formaldehyde (RF) precursors were synthesized based on reported methods with some modifications (Hao, 2011). Resorcinol (3.0 g, 27.3 mmol) and Pluronic F127 (1.25 g, 7.6mmol) were dissolved in a mixture of ethanol (11.4 mL) and deionized water (9 mL) at room temperature. Then the specific base used (0.67 mmol) was added into the solution and stirred for 30 min to obtain a transparent solution. Subsequently, 36 wt% formalin (4.42 g) was added into the mixture. The reaction mixture was stirred for 40 min and heated at 90°C for 4 h. The synthesized RF polymer was then dried at 90 °C for 48 h and pyrolyzed at 800°C in nitrogen with a ramping rate of 4 °C min⁻¹, for 2 h to obtain the PCMs. The pyrolysis temperature of 800 °C also allowed for efficient graphitization of the PCM to ensure its good conductivity (Shao, 2018).

Herein, protic organic base 1,6-hexamethylene diamine (HDA), aprotic trimethylamine (TEA) and KOH were used to adjust the rate of RF polymerization, with their pKa's shown in **Table S2**. PCMs as synthesized were denoted in the form PCM-base (for example, PCM synthesized using HDA was denoted as PCM-HDA).

2.3. Material Characterization

The morphology of the RF precursors and the PCMs was examined using a Hitachi SU8010 field-emission scanning electron microscope (FE-SEM). Brunauer–Emmett–

Teller (BET) surface area and pore size distribution were determined through nitrogen adsorption and desorption isotherms taken by a gas adsorption instrument (Micromeritics 3Flex). The X-ray powder diffraction (XRD) patterns were collected using a Bruker D8 A25 Advance diffractometer with Cu-K α radiation ($\lambda=1.5418$ Å). The elemental composition and chemical states of catalysts were characterized by X-ray photoelectron spectroscopy (XPS) using Surface Science Instruments Thermo Scientific ESCALAB 250Xi surface spectrometer with monochromatic Al-K α radiation (1486.6 eV).

2.4. Preparation of Electrodes

For comparison of the electrocatalytic performance, the PCMs were ground and coated onto carbon papers. Specifically, 30 mg of ground PCM powder was suspended in a mixture of 4.47 ml of milli-Q water (resistivity > 18.2 M Ω .cm), 1.5 ml of isopropanol, and 100 μ L of a Nafion solution. The resulting ink was spray-coated onto carbon papers (HCP030P Hesen) with a catalyst loading of 0.75 mg cm⁻². Both sides of the carbon papers (with a total geometric area of 8 cm²) were uniformly coated to avoid exposing the supporting carbon paper substrate to the electrolyte. Carbon papers coated by CB (TIMCAL Super P) were prepared in the same way as control.

2.5. Electrochemical Experiments

Electrochemical experiments were performed in a conventional three-electrode reactor system using a CH CHI660E C17171 potentiostat at room temperature. A platinum (Pt) wire and a saturated calomel electrode (SCE) were used as the counter electrode and the

reference electrode, respectively, while the PCM coated carbon papers were employed as working electrodes. Potentials recorded were converted to the reversible hydrogen electrode (RHE) scale ($\text{RHE} = \text{SCE} + 0.059 \times \text{pH} + 0.241 \text{ V}$). Cyclic voltammetry (CV) was performed in Ar- or O_2 -saturated 0.1 M Na_2SO_4 at a scan rate of 20 mV s^{-1} .

For determination of the production rates of H_2O_2 , $\cdot\text{OH}$, and herbicide degradation rates, experiments were conducted under constant potential conditions and 30 mL 0.1 M Na_2SO_4 was used as electrolyte. For measurement of $\cdot\text{OH}$ production rate, 10 mg L^{-1} terephthalic acid (TA) was used as a chemical probe. The initial concentration of herbicides was 10 mg L^{-1} for all herbicide degradation experiments. For above experiments, electrolyte pH was adjusted by 1 M H_2SO_4 and 1 M NaOH solutions, and maintained by 0.1 M phosphate buffer solution (Sigma-Aldrich). The buffer concentration was kept 50 mM in the electrolyte.

To explore the performance in practice, herbicide degradation experiments were also performed on PCM pellets of $0.5 \text{ cm} \times 1 \text{ cm} \times 2 \text{ cm}$. Specifically, the PCM was held by a platinum clip as the Ohmic contact. The test was conducted in 30 mL circum-neutral Na_2SO_4 electrolyte with 10 mg L^{-1} napropamide.

2.6. Analytical Methods

The electrolyte solutions were sampled at predetermined time intervals during the electrochemical tests to measure the H_2O_2 and $\cdot\text{OH}$ produced as well as herbicide degradation rates. Specifically, the concentration of H_2O_2 was quantified by the

spectrophotometric method using titanium oxalate (Sellers, 1980) and the absorbance of the sample aliquot was measured using a JASCO V-750 spectrophotometer at 400 nm. Hydroxyl radical was quantified using TA, which forms the 2-hydroxyterephthalic acid (TAOH) adduct in the presence of $\cdot\text{OH}$. The concentration of TAOH was quantified using a fluorescence spectroscopy (Hitachi F7000) with an excitation wavelength of 350 nm and a monitored emission wavelength of 430 nm.

The concentrations of herbicides were analyzed using a high-performance liquid chromatography (Waters Acquity UPLC) system coupled with an e2998 photodiode array detector and an e2695 separation module. A Sunfire C18 column (4.6 mm * 50 mm; 5 μm particles) was used along with 0.1% phosphoric acid and methanol as the mobile phase at a flow rate of 0.8 mL min⁻¹. The transformation products (TP) of napropamide were analyzed by liquid chromatography–mass spectrometry (LC-MS) using an Agilent 6460 LC-MS instrument equipped with a triple quadrupole mass spectrometer (Agilent, Santa Rosa, CA). 0.1% formic acid and methanol were used as the mobile phase in LC. The chemical oxygen demand (COD) of the napropamide solution was quantified by a Hach DR-3900 spectrophotometer using 431 COD ULR program after dichromate digestion (DRB-200, Hach), and the total organic carbon (TOC) was determined using an Analytik Jena MultiN/C3100 TOC analyzer.

3. Results and Discussion

3.1. Material synthesis

SEM, XRD and XPS were employed in this study to characterize the morphology, structures and chemical states of the PCMs. As shown by SEM images (**Figure S1**), all three PCMs had an interconnected porous morphology. The porosity of PCMs were further characterized by N₂ adsorption-desorption experiments (**Figure 1a**), with the pore distribution shown in **Figure 1b**. PCM-HDA had abundant mesopores concentrated at ~6.4 nm, while the PCM-TEA and PCM-KOH possessed smaller porosity concentrated at ~2.8 nm and ~1.9 nm, respectively. This was consistent with the report by Hao et al. (Hao, 2011) that use of protic amines in the synthesis led to larger porosity in the resulting carbon monoliths compared to aprotic counterparts. However, the measured porosity of PCM-HDA and PCM-TEA was larger than their report, which could be ascribed to the different temperatures employed to dry the RF polymers before pyrolysis. Specifically, as opposed to 50 °C employed by Hao et al., the as-synthesized RF polymers were dried at 90 °C for 48 h, which led to faster evaporation of the residue formaldehyde and solvents, and therefore larger porosity. Given the high specific surface area of the PCMs, larger porosity is beneficial to diffusion and overall electrocatalytic performance. PCM-HDA had the highest specific surface area of 610.04 m² g⁻¹ (**Table S3**), 9% higher than PCM-TEA (560.23 m² g⁻¹) and 30% higher than PCM-KOH (470.72 m² g⁻¹), consistent with Hao et al. (Hao, 2011).

Figure 1. (a) N₂ adsorption-desorption isotherms and (b) pore size distribution of PCMs.

The XRD patterns showed that PCM-HDA, PCM-TEA and CB were mainly composed of graphitic carbon (**Figure S2**). The influence of pyrolysis on elemental composition and chemical states was studied by XPS (**Figure S3**). During preparation of PCM-HDA, the pyrolysis reduced the O content from 29.74 at% in RF-HDA to 23.66 at% in PCM-HDA, while N (2.63 at% in RF-HDA) was completely removed. Prolonged pyrolysis of 4 h led to further decrease of oxygen content to 9.05 at% (**Table 1**). On the other hand, the high-resolution C1s and O1s spectra of PCM-HDA, PCM-TEA and CB were shown in **Figure 2**. The O1s spectra could be deconvoluted to C-O (533.0 eV) and C=O (531.8 eV), while the C1s spectra could be deconvoluted to graphitic C=C (284.5 eV), sp³ C-C (285.4 eV), C-O (286.5 eV) and O-C=O (288.9 eV) (Díez, 2015; Dong, 2018; Lu, 2018). Notably, apart from the higher O content, PCM-HDA also had a substantially higher C-C/C=C peak area ratio (0.51) compared to PCM-TEA (0.26) and CB (0.11) (**Table 1**). As pointed out by Liu et al. (Liu, 2015) and Lu et al. (Lu, 2018), C-C XPS peak is

intimately related to the formation of sp³ defects in the graphite basal plane or at the edge. In the meantime, the Raman spectra (**Figure 3**) of PCM-HDA, PCM-TEA and CB showed two peaks at 1320 cm⁻¹ (D band) and 1585 cm⁻¹ (G band), with the D band associated with the introduction of sp³ defects. The intensity ratio of D band to G band (I_D/I_G) was 1.77 for PCM-HDA, substantially higher than that for PCM-TEA (1.06) and CB (0.60) (**Table 1**). This confirmed the higher content of sp³ defects in PCM-HDA. However, 4 h pyrolysis time led to further graphitization of the carbon lattice, as shown by the small C-C/C=C peak area ratio of 0.067 and I_D/I_G ratio of 0.48 in **Table 1**. Comparing the XPS results of RF-HDA, PCM-HDA and PCM-HDA-4h, it could be concluded that 2h pyrolysis of RF-HDA led to PCM-HDA rich in remaining oxygen and sp³ defects, while prolonged pyrolysis caused extensive graphitization, as characterized by sharp decrease in oxygen content and sp³ defects in PCM-HDA-4h.

Table 1. Elemental composition, C-C/C=C XPS peak area ratios and I_D/I_G Raman peak intensity ratios of CB, PCM-TEA, PCM-HDA, PCM-HDA-4h and RF-HDA.

Materials	Elemental Composition (at%)			C-C/C=C	I_D/I_G
	C	N	O	peak area ratio	Ratio
CB	88.69	-	11.31	0.11	0.60
PCM-TEA	80.73	-	19.27	0.26	1.06
PCM-HDA	76.34	-	23.66	0.51	1.77
PCM-HDA-4h	90.95	-	9.05	0.067	0.48
RF-HDA	67.63	2.63	29.74	0.36	-

Figure 2. High-resolution C1s, O1s and N1s XPS spectra of (a)-(c) CB, (d)-(f) PCM-TEA and (g)-(i) PCM-HDA.

Figure 3. Raman spectra of PCM-HDA, PCM-TEA, CB and PCM-HDA-4h.

3.2. Electrochemical generation of H_2O_2 and $\cdot OH$

The electrocatalytic activity of the PCM electrodes was examined by CV in O_2 saturated, circum-neutral 0.1 M Na_2SO_4 electrolyte (**Figure 4**). Irreversible reduction peaks near 0.3 V vs. RHE were observed for all three PCMs that were assigned to ORR as these peaks were absent in the control experiments using an Ar-saturated electrolyte. Furthermore, ORR peaks were also determined for PCM-HDA at pH 1, 4, 10 and 13 as shown by the CV data (**Figure S4**). The onset potentials increased monotonically from 0.137 V at pH 1 to 1.008 V at pH 13, which also agrees with the thermodynamics of ORR that a lower proton activity leads to higher Nernstian potential, for both 2-electron (**Equation 1**) and 4-electron (**Equation 2**) processes. It's worth noting that a ~ 0.3 V positive peak shift was achieved by PCM-HDA under similar conditions compared to previous reported mechanically interlocked anthraquinone on SWCNTs (AQ-MINT) electrode (Wielend, 2020). This result confirms the catalytic activity of the PCM-HDA electrode under a mildly reducing potential.

Figure 4. CV voltammograms of (a) PCM-HDA, (b) PCM-TEA and (c) PCM-KOH in O_2 (red) and Ar (black) saturated circum-neutral 0.1 M Na_2SO_4 electrolyte with a scan rate of 20 mV s^{-1} .

The H_2O_2 production of the PCMs was compared under constant potential condition in circum-neutral Na_2SO_4 electrolyte (**Figure 5**). CB was used as the benchmark since it has been used extensively in 2-electron ORR catalysis for H_2O_2 production and water treatment (Luo, 2015; Li, 2016a). Specifically, the potential was set to -0.146 V vs. RHE for all electrodes to ensure effective ORR at various pH. Pure carbon paper showed little H_2O_2 production, demonstrating it as a good substrate for electrochemical tests. PCM-HDA electrode had the best H_2O_2 production rate of $1004 \pm 40 \mu\text{mol L}^{-1} \text{ cm}^{-2} \text{ h}^{-1}$ (**Figure 5a**), 69% higher than PCM-TEA ($594 \pm 16 \mu\text{mol L}^{-1} \text{ cm}^{-2} \text{ h}^{-1}$) and 374% higher than CB electrode ($212 \pm 24 \mu\text{mol L}^{-1} \text{ cm}^{-2} \text{ h}^{-1}$). However, PCM-KOH only had a H_2O_2 production rate of $139 \pm 23 \mu\text{mol L}^{-1} \text{ cm}^{-2} \text{ h}^{-1}$. The difference in H_2O_2 production rates of the PCMs reflected their different ORR catalytic activity as well as the selectivity of 2-electron ORR (**Equation 1**) over 4-electron ORR (**Equation 2**) and hydrogen evolution reaction (HER, **Equation 3**).

Figure 5. (a) The H₂O₂ and (b) hydroxyl radical production of PCM and CB electrodes in circum-neutral 0.1 M Na₂SO₄ electrolyte under -0.146 V (except for the control group PCM-HDA+H₂O₂ in (b) where 400 mg L⁻¹ H₂O₂ was used in place of -0.146 V to study the activation of H₂O₂ by PCM-HDA in the absence of applied potential). 10 mg L⁻¹ TA was used as a ·OH probe to quantify the hydroxyl radical production in (b).

The influence of pH and potential on H₂O₂ production was explored for the PCM-HDA. **(Figure 6)** The H₂O₂ production rate at pH 4 was $1031 \pm 19 \mu\text{mol L}^{-1} \text{cm}^{-2} \text{h}^{-1}$, slightly higher than that of pH 7 ($1004 \pm 40 \mu\text{mol L}^{-1} \text{cm}^{-2} \text{h}^{-1}$) and pH 10 ($945 \pm 51 \mu\text{mol L}^{-1} \text{cm}^{-2} \text{h}^{-1}$), agreeing to the CV results that the PCM-HDA electrode efficiently catalyzed 2-electron ORR over a wide pH range for electrochemical H₂O₂ generation. On the other hand, raising the applied potential significantly lowered the H₂O₂ production rate. For example, raising the potential from -0.146 V to 0.054 V vs. RHE at pH ~7 decreased the H₂O₂ production rate to $796 \pm 43 \mu\text{mol L}^{-1} \text{cm}^{-2} \text{h}^{-1}$. This suggests that -0.146 V is an appropriate working potential for the PCM-HDA at circum-neutral pH.

The higher specific surface area and the mesoporous structure may partially account for the enhanced electrocatalytic activity of PCM-HDA compared to PCM-TEA and PCM-KOH. Due to the smaller porosity, the effective catalytic sites of PCM-TEA and PCM-KOH surfaces may be limited by pore diffusion (Hao, 2011; Ferrero, 2016). On the other hand, the ORR activity of PCM-HDA could also be attributed to the elevated oxygen content and sp³ structural defects, as indicated by the studies by Lu et al. (Lu, 2018) and Liu et al. (Liu, 2015). Various characterizations, together with DFT calculations, were employed by Lu et al. (Lu, 2018) to reveal the apparent enhancing effects of C-O and C=O groups for the 2-electron ORR catalysis and H₂O₂ production, while Liu et al. (Liu, 2015) determined that sp³ defects are crucial for the exceptional H₂O₂ production performance of the hierarchically porous carbon.

Figure 6. The H_2O_2 production of PCM-HDA electrode in 0.1 M Na_2SO_4 electrolyte at (a) pH 4, (b) pH 7 and (c) pH 10.

Besides H_2O_2 production, PCM-HDA and PCM-TEA were also capable of *in situ* activating H_2O_2 into $\cdot\text{OH}$ in circum-neutral 0.1 M Na_2SO_4 electrolyte under -0.146 V, as shown by fluorescent probe experiments (**Figure 5b**). Specifically, $\cdot\text{OH}$ was produced over PCM-HDA, PCM-TEA and CB electrodes at a nearly constant rate within an hour, with the relative production rates in the order of PCM-HDA > PCM-TEA > CB, which is similar to the results of H_2O_2 production. It's highly worth noting that PCM-HDA and PCM-TEA have been demonstrated as “one-stop” catalysts to simultaneously catalyze 2-electron ORR and H_2O_2 activation to directly produce $\cdot\text{OH}$ without the needs for Fe(II)/Fe(III) or O_3 , which has been rarely reported for pure carbon-based systems. However, PCM-HDA was unable to activate H_2O_2 in the absence of the applied potential, indicating that the activation of H_2O_2 over PCM-HDA surface was an electrocatalytic process. Due to the absence of redox active metal species, it is unlikely for PCM-HDA to catalyze H_2O_2 cleavage through Fenton-like mechanism. Instead, PCM-HDA may

activate H_2O_2 through reductive cleavage processes, as shown in Equation (4) and (5) (Milazzo and Carioli, 1978; Sheng, 2014).

Due to its high oxidation potential and non-selective reactivity, $\cdot\text{OH}$ has been widely applied in removal of numerous chemical contaminants from water. However, H_2O_2 activation has been achieved primarily with O_3 , UV or the Fe(II)/Fe(III) redox couple (Sun, 2018), which adds to the total cost (CAPEX and OPEX) and system complexity. In fact, multiple carbon materials including activated carbon (Veksha, 2015), carbon nanotubes and biochar (Fang, 2014; Huang, 2016) have been shown to catalytically convert H_2O_2 into hydroxyl radical. The H_2O_2 decomposition mechanism over activated carbon and carbon nanotubes has been studied by Khalil et al. (Khalil, 2001) and Voitko et al. (Voitko, 2015), both of whom highlighted the electron donor capability of carbon materials for H_2O_2 decomposition. Specifically, Khalil et al. attributed the H_2O_2 decomposition activity of activated carbon mainly to its surface basicity, while Voitko et al. noted that the decomposition of H_2O_2 was promoted by the electron-donating N-containing groups in carbon nanotubes. On the other hand, biochar was also successfully applied in removal of 2-chlorobiphenyl through H_2O_2 activation, where electron paramagnetic resonance (EPR) spectra revealed the persistent free radicals (PFRs) within biochar, which were identified to be the likely sites for H_2O_2 activation (Fang, 2014). As for the H_2O_2 activation by PCMs, it is inferred that the H_2O_2 activation was related mainly to structural defects, as they are shown to raise the local electron

density (Qiu, 2020). Future studies are required to confirm the activation mechanism of H_2O_2 over PCMs.

3.3. Electrochemical Degradation of Napropamide

With remarkable activity to catalyze 2-electron ORR and the *in situ* activation of H_2O_2 for $\cdot\text{OH}$ production, PCM-HDA and PCM-TEA electrodes achieved effective degradation of napropamide (**Figure 7**). Degradation was quantified in terms of pseudo first-order kinetic (**Figure S5**) with $R^2 > 0.98$ (**Table S4**). Under an applied potential of -0.146 V vs. RHE, the PCM-HDA electrode obtained $80 \pm 2\%$ reduction in the napropamide concentration within 60 min, whereas the degradation by PCM-TEA ($64 \pm 2\%$) and CB electrodes ($48 \pm 3\%$) were clearly less effective (**Figure 7a**). In order to distinguish the contribution of chemical degradation from that of adsorption, two-step experiments were performed in addition. Specifically, the PCM electrodes were immersed in the electrolyte for 120 min to allow for the adsorption saturation, after which -0.146 V was applied for electrochemical degradation of napropamide. The electrolyte was purged with O_2 over the entire process. As shown by **Figure 7b**, $\sim 36\%$ (3.6 mg L^{-1}) napropamide was removed through adsorption by PCM-HDA, PCM-TEA and CB in 120 min. After -0.146 V was applied, PCM-HDA electrode reduced the napropamide concentration to 0.7 mg L^{-1} in 90 min, while PCM-TEA and CB electrodes reduced the napropamide to 1.5 and 2.7 mg L^{-1} , respectively, while PCM-TEA and CB electrodes reduced the napropamide to 1.5 and 2.7 mg L^{-1} , respectively. This indicated that PCMs

may remove napropamide by initial adsorptive uptake and subsequent electrochemical degradation. The results also confirmed the better performance of PCM-HDA electrode than PCM-TEA and CB in electrochemical degradation of napropamide.

In order to further study the electrochemical transformation of napropamide over PCM-HDA electrode at pH 7 under -0.146 V, the electrolyte was sampled at different electrolysis time and analyzed by LC-MS, and the obtained chromatograms were shown in **Figure S6**. With increasing reaction time, one can easily notice the shrinkage of the peak eluting at 17.9 min, as well as the growth of the peaks eluting at 6.8 min and 20.0 min, respectively. The peak at 17.9 min was assigned to napropamide and its sodium adduct (**Figure S7**). On the other hand, the peaks at 6.8 and 20.0 min should correspond to the TPs. We didn't try to identify the other peaks since their area didn't change significantly with reaction time and they were assumed to be irrelevant to napropamide degradation.

The structures of the TPs were proposed based on their MS spectra (**Figure S7**). The peak eluting at 6.8 min corresponded to two main peaks in MS spectrum. TP (1) was assumed to originate from the breaking of the ether bonds in napropamide caused by hydroxyl radical attacking, which agreed with previous study on phototransformation of napropamide (Aguer, 1998), and TP (2) stemmed from further fragmentation of TP (1). On the other hand, the peak eluting at 20.0 min corresponded to only one peak in MS spectrum. TP (3) was assumed to have formed by dimerization of the 1-naphthol that was

generated along with TP (1) from breaking of the ether bonds in napropamide. This is consistent with previous reports that hydroxyl radical oxidation could lead to dimerization and oligomerization of organic pollutants (Tan, 2012; Olmez-Hanci, 2013). Besides high-efficient napropamide degradation, the PCM-HDA electrode also achieved a 74% COD reduction (**Figure 7c**) and a $69 \pm 2\%$ TOC reduction (**Figure 7d**) over 2 h under -0.146 V at circum-neutral pH in the 0.1 M Na_2SO_4 electrolyte, rendering itself a powerful electrode for electrochemical water remediation.

Figure 7. (a) Degradation of 10 mg L⁻¹ napropamide by PCM-HDA, PCM-TEA and CB electrodes at pH 7 under -0.146 V vs. RHE; (b) electrochemical degradation of napropamide by PCM-HDA electrode after reaching adsorption equilibrium; (c) COD and (d) TOC removal by PCM-HDA electrode under -0.146 V in circum-neutral 0.1 M Na_2SO_4 electrolyte.

Degradation of napropamide was studied under different conditions in order to understand the mechanism of electrochemical degradation induced by the PCM-HDA electrode (**Figure 8a**). There was no appreciable degradation of napropamide in 60 min by 400 mg L⁻¹ H₂O₂, showing that catalysis of 2-electron ORR alone was unable to degrade napropamide. Then napropamide degradation tests were performed in Ar- and O₂-purged electrolyte, respectively. In Ar-purged solution, the dissolved oxygen (DO) was determined by a Mettler Toledo dissolved oxygen meter to be 0.82 mg L⁻¹. Meanwhile, a 35 ± 1% removal of napropamide was achieved under -0.146 V by PCM-HDA electrode over 60 min. Considering the low DO level, the degradation was attributed to electrosorption. On the contrary, in O₂-purged solution, the DO was determined to be 38.15 mg L⁻¹, reaching the saturation value of 36.63 mg L⁻¹ calculated according to previous study (Tromans, 2000). Under this condition, an 80 ± 2% removal was obtained by PCM-HDA electrode over 60 min. Notably, when isopropanol (IPA) was added to the O₂-saturated electrolyte as a ·OH scavenger, 38 ± 2% napropamide removal was achieved in 60 min by PCM-HDA electrode, which was similar to that in Ar-purged electrolyte. This indicated that ·OH was primarily responsible for the degradation of napropamide. On the other hand, since Pt anode was also reported to catalyze oxidation of water and H₂O₂ to generate a series of reactive oxygen species (Guinea, 2008) that may contribute to napropamide degradation, the degradation tests

were also performed in an H-type reactor, with a cation exchange membrane separating the anodic and cathodic chambers. Similar to the membrane-less setup, a $76 \pm 2\%$ removal of napropamide in the cathodic chamber was achieved in the cathodic chamber over 60 min, indicating that the anodic contribution to napropamide degradation was negligible, and that PCM-HDA cathode was primarily responsible for the $\cdot\text{OH}$ production. We note that the performance of the PCM-HDA electrode was better than similar materials reported previously (Liu, 2019). This improved activity could be attributed to the higher oxygen content and the higher level of sp^3 defects induced by the shorter pyrolysis time in this study. The reaction process is illustrated in **Scheme 1**: $\cdot\text{OH}$ was produced over PCM-HDA through sequential 2-electron ORR and H_2O_2 catalytic decomposition, which then reacted with herbicide molecules to fully oxidize them into CO_2 and H_2O . The excellent activity of PCM-HDA could be attributed to the elevated oxygen content and sp^3 defects, as well as large specific surface area and mesoporous structure. This again confirmed that PCM-HDA can function as a “one-stop” catalyst for both 2-electron ORR and following H_2O_2 activation to generate $\cdot\text{OH}$.

Figure 8. Degradation of napropamide by PCM-HDA electrode (a) under different conditions, (b) at different pH, (c) at different applied potentials at pH 7, and (d) degradation of various herbicides at pH 7 under the applied potential of -0.146 V.

~80% napropamide removal by PCM-HDA electrode was maintained over the pH range of 4-10 (**Figure 8b**), indicating that the PCM-HDA electrode is relatively efficient in a broad pH range. This facilitates its application in water treatment. In comparison, the conventional Fenton reaction requires pH to be ≤ 4 . Despite that a number of heterogeneous catalysts have been developed to catalyst Fenton reaction at circum-neutral pH (Liu, 2018; Sun, 2018; Liu, 2019), this work has provided an all-carbon solution for cathodic H_2O_2 and $\cdot OH$ generation, avoiding the possible Fe leaching problem. On the other hand, the applied potential has a pronounced effect on the degradation of napropamide (**Figure 8c**), consistent with the H_2O_2 production (**Figure 6**).

At pH 7, PCM-HDA electrode only achieved $48 \pm 1\%$ napropamide degradation under 0.254 V in 60 min, while $80 \pm 2\%$ and $86 \pm 1\%$ degradation was obtained under -0.146 and -0.346 V, respectively. However, more negative applied potentials also led to higher current density and energy consumption. To fully examine the effect of the applied potential, the energy efficiency (in terms of quantity of napropamide removed with respect to energy consumption) was calculated and shown in **Figure S8**. The energy consumption was calculated assuming SCE as the counter electrode. A current of 24 mA was obtained for -0.146 V vs. RHE, which led to the maximum energy efficiency of $247.2 \text{ mmol kWh}^{-1}$. On the other hand, the current was 26 mA for -0.346 V vs. RHE, resulting in an energy efficiency of $232.0 \text{ mmol kWh}^{-1}$. The lowered energy efficiency might be due to the lower selectivity of 2-electron ORR and H_2O_2 reductive cleavage. This showed that -0.146 V vs. RHE was the optimal potential for PCM-HDA electrode.

Beyond napropamide, $63 \pm 2\%$ and $54 \pm 3\%$ degradation were also achieved for glyphosate and atrazine by PCM-HDA under -0.146 V at pH 7 (**Figure 8d**). The degradation of the herbicides by PCM-HDA electrode was well-fitted by pseudo first-order kinetic model (**Figure S9 – S11**), with $R^2 > 0.98$ (**Table S4 and S5**).

Scheme 1. Illustration of the working mechanism of PCM-HDA electrode. Specifically, 2-electron ORR was catalyzed over the PCM-HDA surface to produce H_2O_2 , which was then activated to produce $\cdot\text{OH}$ for herbicide degradation. The exceptional performance of PCM-HDA could be ascribed to the mesoporosity, elevated oxygen content and sp^3 defects. Oxygen-containing functional groups were marked with color patches.

3.4. Stability and Reusability

Herein in this study, the stability and reusability of PCM-HDA electrode was characterized by subjecting it to six continuous cycles of napropamide degradation tests (**Figure 9**) at an applied potential of -0.146 V at circum-neutral condition. The napropamide removal by PCM-HDA in 60 min maintained $\sim 80\%$ over the six cycles without noticeable performance deterioration, confirming the durability of PCM materials.

Figure 9. Napropamide (10 mg L^{-1}) degradation in six continuous cycles by PCM-HDA electrode.

Despite the number of previous reports on the use of carbon-based materials for the electrocatalysis of the ORR, the industrial application of these materials is hindered by their powdery form, and hence binding agents are often used to attach them to conductive surfaces (Luo, 2015). However, the use of binders significantly compromises the catalytic performance by reducing the conductivity and porosity of carbon-based materials (Wang, 2014). A binder-free monolithic approach with tunable porosity, on the other hand, can provide enhanced activity and stability and has been successfully implemented in several studies for ORR catalysis (Chen, 2015; Zhou, 2016). Herein, we have prepared crack-free porous carbon monoliths by the pyrolysis of RF aerogel precursors. As shown in **Figure S12**, the pyrolyzed PCMs still retained the macroscopic shape (e.g. cylindrical in **Figure S12**) of the RF monolith precursors, implying that the shape of PCM monoliths can be easily controlled by the shape of RF precursors.

In order to understand the performance of PCM for herbicide degradation in practice, a pellet of PCM-HDA (0.5 cm *1 cm*2 cm) was subjected to a napropamide degradation test under -0.146 V in circum-neutral 0.1 M Na₂SO₄ electrolyte. 88 ± 1% napropamide degradation was observed over 60 min with no appreciable peeling off of carbon materials (**Figure 10**), confirming the feasibility of PCM-HDA for practical applications.

Figure 10. Degradation of napropamide by monolithic PCM-HDA (0.5 cm *1 cm*2 cm) in circum-neutral 0.1 M Na₂SO₄ electrolyte under -0.146 V.

4. Conclusion

Herein, a series of PCMs were developed as a “one-stop” platform for catalysis of the 2-electron ORR coupled with further reductive cleavage of H₂O₂ to produce ·OH. Oxygen was electrochemically reduced to H₂O₂ over the various PCMs at circum-neutral pH, and the PCM-HDA produced H₂O₂ at a level that was 374% higher than that obtained using CB. The H₂O₂ production rates maintained in the pH range of 4-10. Meanwhile, the generated H₂O₂ was catalytically decomposed to produce ·OH. The exceptional catalytic activity of the PCM-HDA was attributed to its large specific surface

area, mesoporous structure and elevated content of oxygen and sp³ defects. Based on these results, the PCM-HDA electrode obtained an $80 \pm 2\%$ degradation of napropamide in 60 min over the pH range of 4-10 at an applied potential of -0.146 V vs. RHE, and a $69 \pm 2\%$ TOC reduction was obtained at circum-neutral pH in 2 h. Besides napropamide, $63 \pm 2\%$ and $54 \pm 3\%$ degradation were also obtained for glyphosate and atrazine by the PCM-HDA within 60 min at an applied potential of -0.146 V at pH ~7. The stability of the PCM-HDA electrode was demonstrated by the maintained ~80% napropamide degradation in six consecutive runs. Compared to conventional Fenton systems, the PCMs provide a simplified “one-stop” platform that overcomes the system complexity and pH limitation. In addition to herbicide degradation, the PCM-HDA electrode may also be used for the facile treatment of an array of relatively recalcitrant aquatic pollutants.

CRedit author statement

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Notes

The authors declare no competing financial interest.

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Graphical Abstract

CRedit author statement

Menglin Yu: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Writing – review & editing. **Heng Dong:** Investigation, Formal analysis, Writing – Original drafting and validation. **Kai Liu:** Conceptualization, Methodology. **Yingdie Zheng:** Investigation. **Michael R. Hoffmann:** Writing – review & editing. **Weiping Liu:** Funding acquisition, Resources, Project administration, Supervision. Writing – review & editing.

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Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Highlights

- PCM-HDA had a 310% higher H_2O_2 production at circum-neutral condition than CB.
- The generated H_2O_2 was catalytically decomposed over PCM-HDA to produce $\cdot\text{OH}$.
- More O content and sp^3 defects along with mesoporosity enhanced PCM-HDA activity.
- The PCM-HDA electrode obtained an ~80% degradation of napropamide in 60 min.
- Efficient removal of napropamide was achieved by PCM-HDA in the pH range of 4-10.