View Article Online

# Journal of Materials Chemistry A

Materials for energy and sustainability

# Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: X. Duan, W. Li, Z. Ao, J. Kang, W. Tian, H. Zhang, S. Ho, H. Sun and S. Wang, *J. Mater. Chem. A*, 2019, DOI: 10.1039/C9TA04885E.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/materials-a

Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

View Article Online DOI: 10.1039/C9TA04885E

A Manuscript Submitted to Journal of Materials Chemistry A
Origins of boron catalysis in peroxymonosulfate activation and advanced oxidation
Xiaoguang Duan <sup>a,*</sup> , Wenlang, Li <sup>b</sup> , Zhimin Ao <sup>b</sup> , Jian Kang <sup>c</sup> , Wenjie Tian <sup>a</sup> , Huayang Zhang <sup>a</sup> , Shih-Hsin
Ho <sup>d</sup> , Hongqi Sun <sup>e</sup> , Shaobin Wang <sup>a,c,*</sup>
<sup>a</sup> School of Chemical Engineering and Advanced Materials, The University of Adelaide, Adelaide, SA
5005, Australia
<sup>b</sup> School of Environmental Science and Engineering, Institute of Environmental Health and Pollution
Control, Guangdong University of Technology, Guangzhou 510006, China
° Department of Chemical Engineering, Curtin University, Perth, WA 6845, Australia
<sup>d</sup> State Key Laboratory of Urban Water Resource and Environment, School of Environment, Harbin
Institute of Technology, Harbin, China
<sup>e</sup> School of Engineering, Edith Cowan University, Joondalup, WA 6027, Australia
*Corresponding Authors:
xiaoguang.duan@adelaide.edu.au (X.D.)
shaobin.wang@adelaide.edu.au (S.W.)

Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

#### Abstract

Metal-free materials have exhibited great merits to substitute the toxic and scarce metals/oxides in 25 environmental catalysis. In this work, amorphous boron (A-Boron) is exploited as a nonmetal catalyst for 26 peroxides activation. It is discovered that the A-Boron is exclusively reactive for peroxymonosulfate 27 (PMS) activation for degradation of a diversity of organic contaminants including benzenes, phenolics, 28 29 dyes and antibiotics in water. Moreover, comparative tests show that A-Boron stands out among the 30 diverse heterogeneous catalysts such as transition metal oxides, nanocarbons and non-carbonaceous materials (sulfur, phosphorus, boron nitride, and boron carbide). The competitive radical scavenging tests 31 and in situ radical capturing by electron paramagnetic resonance (EPR) unveil that both sulfate (minor 32 33 contribution) and hydroxyl radicals (dominant contribution) are generated and account for the organic oxidation. Advanced characterisation techniques suggest that the boron-based catalysis stems from the 34 short-range ordered grain boundaries and amorphous domains in A-Boron. This is further evidenced by 35 the fact that surface tailored boron samples (A-B-400~1000) after thermal treatment exhibit inferior 36 activities with 10.4-28.3% phenol removal compared with A-Boron (74.3%), due to the formation of 37 surface boric acid/hydroxide that blocks the active boron phases. Theoretical calculations illustrate that 38 the  $(1 \ 0 \ 0)$ ,  $(1 \ 0 \ 1)$  and  $(1 \ 1 \ 0)$  terminations and amorphous regions of elemental boron can directly cleave 39 40 the peroxide O-O bond and decompose PMS to produce the reactive hydroxyl radicals, which is in 41 agreement with the experimental discoveries. This study provides a novel metal-free catalytic system for wastewater treatment and envisages the first mechanistic insights into the origins of boron-based catalysis. 42

43

44

Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

#### 46 Introduction

Metal-free catalysis has renovated the chemical processes to address the inherent demerits of 47 noble/transition metal catalysts of scarcity, expensiveness, poor stability, toxicity and potential secondary 48 contamination. Of particular interest, nanocarbon materials such as graphene and carbon nanotubes 49 become the new favourites in the scientific community attributing to their fascinating features such as 50 high surface areas, superior electronic/thermal conductivity, great acidic/basic resistance, low toxicity, 51 and manoeuvrable dimensional structure and surface chemistry.<sup>1</sup> Functional carbon films and composites 52 are popular adsorbents for removing/accumulating metal ions and organic substances in aqueous 53 solution.<sup>2-4</sup> Additionally, the structure- and/or surface- engineered carbonaceous materials have been 54 55 demonstrated as excellent nonmetal catalysts to drive a diversity of chemical reactions in environmental remediation, chemical synthesis, photocatalysis, energy conversion and storage as well as fuel 56 productions, guaranteeing green and advanced nanotechnologies for a sustainable production.<sup>5-12</sup> 57 58 Notwithstanding the intrinsic complexity of artificial carbocatalysts in structure and chemistry, the catalytic centres vary in different reactions and can be categorized into the sp<sup>2</sup>-conjugated basal plane, 59 edging and tropological defects, oxygen functionalities, heteroatom dopants, and hybrid structures.<sup>13-15</sup> 60 Apart from the mainstream carbons, other nonmetal materials such as boron, sulfate, silicon and 61 phosphorus are also earth-abundant elements and play key roles in the biological system.<sup>16</sup> Among these 62 63 elements, the boron-based catalysis remains mysterious.

Boron is a light and metalloid element which lies between the beryllium (metallic) and carbon (nonmetal) elements in the periodic table. As shown in Figure 1, boron atom possesses five electrons in the groundstate configuration of  $1s^2 2s^2 2p^1$ . The sole electron in p orbital is metallic with a similar radius to the 2s electrons, allowing the excitation of one 2s electron to the p orbital to form electron-sharing and multiplecentred bonds.<sup>17, 18</sup> This feature affords boron superior capability to bind with most of the metal/nonmetal elements. More importantly, the electronic configuration of boron favour the formation of polyhedra (e.g. B<sub>12</sub> icosahedra) in the bulk structure which helps fulfil the imperfections of the electron-deficient boron atoms.<sup>18</sup> To date, over sixteen polymorphs have been discovered in the bulk boron featured by the interlinked polyhedra, whereas most of their crystal structures have not been fully unveiled yet. Moreover, the commercial boron powders with multiple polymorphs are always recognized to be amorphous due to the long-range randomness.



75

76

Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

Figure 1. Illustration of the electronic configuration and atomic structure of boron.

Different from the recent overwhelming popularity in engaging carbonaceous materials to drive a diversity of heterogeneous reactions as aforementioned, nonmetal boron-based catalytic systems have been less explored. Taking a few samples, boron has been used as a dopant to transferring graphene and diamonds into n-type semiconductors with improved conductivity and activity in electrochemistry.<sup>19-21</sup> Due to the lower electronegativity ( $\chi_B = 2.04 vs \chi_C = 2.55$ ) and electron-deficient nature, co-doping boron into Ndoped graphene in different B-C-N configurations can effectively tailor the electron distribution and spin culture of the surrounding carbon atoms, herein regulating the carbocatalysis in oxygen reduction

85

86

87

88

89

90

91

92

93

94

95

96

97

98

Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

reactions.<sup>22, 23</sup> Additionally, boron phosphide (BP) is a semiconducting material with tetrahedrally

coordinated covalent B-P bonds into a crystal structure.<sup>16</sup> BP has been demonstrated as a robust and effective photocatalyst with a band gap of 2.0 eV for continuous hydrogen evolution under visible-light radiation ( $\lambda > 400$  nm) in formaldehyde solution.<sup>24</sup> Moreover, cubic boron nitride is constructed as a graphene-like honeycomb and can be fabricated into two-dimensional sheets (h-BN) as well as 1dimensional nanotubes (BNNT). Hermans and co-workers first reported that h-BN and BNNT can be exploited as nonmetal catalysts for oxidative dehydrogenation (ODH) of propane to propene.<sup>25, 26</sup> In the ODH reaction, the oxygen molecule is prone to be first activated at the edging sites of h-BN and BNNT to form a B-O-O-N unit, which subsequently attacks the β-hydrogen in propane. Such a catalytic process results in an ultrahigh propane conversion rate and selectivity which outperformed most of the reported metal/metal-free catalysts to date. More recently, elemental boron is applied as a photothermal catalyst with a satisfactory response to a broad light-absorption spectrum for photocatalytic reduction of carbon dioxide, taking advantage of the *in situ* produced hydrogen from boron hydrolysis as the proton and electron source.<sup>27</sup> Nevertheless, the exploitation of boron-based materials in environmental catalysis is still in infancy.

In this study, amorphous boron is applied as a metal-free catalyst for peroxide activation and degradation 99 of micropollutants in water. To our delight, the amorphous boron demonstrated a superior activity to 100 101 activate peroxymonosulfate (PMS) in catalytic oxidation, which outperforms most of transition metal oxides, carbonaceous and non-carbon materials. The generated reactive oxygen species (ROS) in the 102 amorphous boron (A-Boron)/PMS system were identified by both selective radical screening and in situ 103 104 radical capture techniques. The hydroxyl radicals were identified as the dominant ROS that could 105 effectively degrade a diversity of organics. This is different from the carbocatalytic persulfate activation via a nonradical pathway, which is selective to the electronic features of the organics due to the mild 106

107 oxidising capacity of the transition state of the activated PMS@carbon complex.<sup>28</sup> For the first time, the
108 active sites and origins of boron-driven catalysis were unveiled by integration of advanced
109 characterisations, deliberate material design and density functional theory (DFT) calculations. Therefore,
110 this study will dedicate to the development of novel advanced oxidation processes (AOP) systems for
111 water remediation and envisages new insights into boron catalysis in heterogeneous reactions.

#### 112 Experimental

#### 113 Chemicals

Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

Chemicals including potassium peroxymonosulfate (PMS), potassium peroxydisulfate (PDS), melamine, 114 phenol, nitrobenzene (NB), benzoic acid (BA), p-hydroxybenzoic acid (PHBA), 4-chlorophenol (4-CP), 115 116 methyl orange (MO), methylene blue (MB), rhodamine B (RhB), ibuprofen (IBP), sulfachloropyridazine (SCP), 5,5-dimethyl-1-pyrroline N-oxide (DMPO), and boric acid were purchased from Sigma-Aldrich, 117 118 Australia. Some catalyst materials such as boron amorphous powder (A-Boron, >95%) crystalline boron 119 (C-Boron, 99.7% trance metals basis, 1cm), sulfur (99.998% trace metals basis), red phosphorus (99.99% trace metals basis), boron nanopowder (< 150 nm, 99.99% trace metals basis), boron carbide (< 10  $\mu$ m, 120 98%), and titanium oxide (TiO<sub>2</sub>, anatase) were also purchased from Sigma-Aldrich. Nanomaterials such 121 as fullerene, black phosphorus nanosheets, boron nitride nanotubes, and multi-walled carbon nanotubes 122 123 were purchased from XFNANO materials Tech., Co Ltd, China. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), methanol 124 (MeOH, anhydrous) and tert-butyl alcohol (TBA, analytical grade) were purchased from Chem Supply, 125 Australia. Nanodiamond was purchased from Ray Techniques Ltd., Israel. An activated carbon was obtained from BDH Chemicals. 126

127 Synthesis of catalysts

The amorphous boron was modified to tailor the surface chemistry and crystal structure by annealing ABoron under an inert atmosphere. Specifically, A-Boron was put in a quartz boat in a tube furnace and

heated to 400, 700 and 1000 °C at a ramping rate of 5 °C/min and annealed for 1 h under N<sub>2</sub> atmosphere. 130 The derived products were denoted as A-B-400, -700 and -1000, respectively. A biochar was derived by 131 fast-pyrolysis of straw stalk at 450 °C for 2 h in the tube furnace under N<sub>2</sub> ambience. Graphitic carbon 132 nitride  $(g-C_3N_4)$  was derived by direct pyrolysis of melamine in a crucible at 550 °C for 4 h in a muffle 133 furnace. The detailed synthesis procedures of manganese oxides (MnO<sub>2</sub> and Mn<sub>3</sub>O<sub>4</sub>), cobalt oxide (Co<sub>3</sub>O<sub>4</sub>), 134 and magnetite (Fe<sub>3</sub>O<sub>4</sub>) could be found in Text S1 (Electronic Supplementary Information, ESI<sup>+</sup>).<sup>29-32</sup> Other 135 metal oxides such as nickel oxide (NiO), gallium oxide ( $Ga_2O_3$ ) and cerium oxide ( $CeO_2$ ) were derived 136 via direct thermal decomposition of their corresponding metal nitrate salts in a muffle furnace at 450 °C 137 138 for 1 h. Boron oxide was derived by annealing boric acid at 400 °C for 1 h in a muffle furnace.

# 139 *Characterisations*

Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

The crystal structures of the boron samples were examined by X-ray diffraction (XRD, Bruker D8A) using 140 a Cu K $\alpha$  X-ray at  $\lambda = 1.542$  Å. The elemental information of the samples was obtained from X-ray 141 photoelectron spectroscopy (XPS) in a Kratos AXIS Ultra DLD system under ultrahigh vacuum condition. 142 143 All XPS surveys were calibrated by setting primary C 1s at 284.5 eV and Shirley background was applied in the peak fitting for the high-resolution spectra. High-resolution transmission electron microscopy 144 145 (HRTEM, FEI Titan G2 80-200) was operated to get the crustal and morphology information of the boron catalysts at 80 kV and energy-dispersive X-ray spectroscopy (EDX) elemental mapping was also 146 performed on the same instrument. The Brunauer-Emmett-Teller (BET) surface area and pore distribution 147 were measured on a TriStar apparatus at -196 °C in liquid nitrogen. The particle size distribution was 148 measured on a Malvern Mastersizer 2000 instrument. Electron paramagnetic resonance (EPR, Bruker) 149 was applied at the X-band with a mid-range frequency (8-12 GHz) to detect the electronic states of the 150 solid boron catalysts and reactive radical species in the boron-based AOPs system. The solid sample was 151 tested on the EPR with the settings of centre field of 3515.0 G, microwave frequency of 9.86 mW, receiver 152

gain of 20 dB, the scan time of 60 s, and scan number of 2. The liquid samples were analysed with the

settings of centre field = 3515.0 G, microwave frequency = 18.57 mW, receiver gain = 30 dB, scan time

= 30 s, and scan number = 2. A radical trapping agent of 5, 5-dimethyl-1-pyrroline n-oxide (DMPO) was used to capture the free radicals in the solution identified by their hyperfine splitting constants of  $\alpha_{N}$ =14.9G,  $\alpha_{H}$ =14.9 G for DMPO-OH, and  $\alpha_{N}$ =13.2 G,  $\alpha_{H}$ =9.6 G,  $\alpha_{H}$ =1.48G,  $\alpha_{H}$ =0.78 G for DMPO-SO<sub>4</sub>. Catalytic performance evaluation The catalytic activities of the boron samples were evaluated for activation of peroxides for degradation of organic contaminants in aqueous solution. The reaction was performed in a batch reactor immersed in a water bath to maintain the reaction temperature (25 °C) under constant stirring by an overhead stirrer with a polytetrafluoroethylene (PTFE) blade at 400 rpm. An organic solution (0.1 mM) was prepared by dilution of its stock solution with a high concentration. The catalyst and peroxide were added into the organic solution to initiate the oxidation. An optimal PMS dosage (3.3 mM) was applied for complete mineralisation of the target organic (phenol). At set time intervals, the reaction solution was withdrawn and filtered to remove the solid catalyst. Then the filtrate was instantly mixed with methanol solution in a 2 mL vial at a volume ratio of 2:1 to terminate the oxidation. Phenol, NB, BA, PHBA, PBA, 4-CP were analysed on a Thermal Fisher HPLC using an Acdaim OA column ( $150 \times 4$  mm, 5 µm). IBP and SCP were analysed by an Acdaim 120 C18 ( $100 \times 2.1 \text{ mm}$ ,  $2.2 \mu \text{m}$ ). Organic dyes such as MB, RhB, MO were

171 respectively.

153

154

155

156

157

158

159

160

161

162

163

164

165

166

167

168

169

170

Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

172 *Theoretical methodology* 

The theoretical computations were carried out using the DMol3 module.<sup>33</sup> The exchange-correlation energy was processed by generalised gradient approximation (GGA) using modified Perdew–Burke– Ernzerhof (PBE) function<sup>34</sup>. The DFT-D correction was applied to take into account of the van der Waals

analysed on a Jasco V-570 UV-vis spectrometer under the wavelengths of 664, 554 and 454 nm,

interactions. DFT semi-core pseudopotential (DSPP) was used for the core treatment.<sup>35</sup> Spin-polarisation was applied and the double- $\xi$  numerical polarisation (DNP) was used in the expansion of molecular orbitals. The criteria for energy, maximum force and displacement were converged to 10<sup>-5</sup> Ha, 0.002 Ha/Å and 0.005Å, respectively.

180 The adsorption energies  $(E_{ads})$  of PMS onto different boron slabs were calculated by the below 181 equation.

$$E_{ads} = E_{substrate+PMS} - E_{PMS} - E_{substrate}$$

Where  $E_{\text{substrate+PMS}}$  is the total energy of adsorbed composites;  $E_{\text{PMS}}$  is the energy of a free PMS

184 molecule;  $E_{\text{substrate}}$  is the total energy of optimised boron slab.

Ì



Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

182

Figure 2. (a) Catalytic performances of A-Boron for activating different peroxides. Comparisons of the catalytic activity of A-Boron with (b) nanocarbons, (c) non-carbon metal-free materials, and (d) transition metal-oxides. (Experimental conditions: phenol = 0.1 mM, catalyst= 0.2 g/L, PMS = 3.3 mM (= PDS = $H_2O_2$  in Figure 1a), temperature = 25 °C.)

#### 190 Results and discussion

Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

The catalytic activity of A-Boron was evaluated in activating different typical peroxides for phenol 191 192 oxidation. Figure 2a depicts that the A-Boron manifests a particular selectivity toward the peroxides. Specifically, A-Boron can effectively activate PMS for catalytic oxidation of phenol (74.3%) in 120 min. 193 In contrast, neither PDS nor  $H_2O_2$  (pH = 3) can be activated by A-Boron with less than 5% organic 194 195 removal. Compared with the compact peroxide bonds and symmetric structures of PDS (-3OS-O-O-SO3-) 196 and  $H_2O_2$  (HO-OH), the asymmetry molecular structure of PMS (H-O-O-SO<sub>3</sub><sup>-</sup>) is more vulnerable to be 197 cleaved in a catalytic reaction to cause an imbalanced electron distribution via a redox process. The similar 198 scenario was also discovered in the carbon-driven AOPs system where the carbon nanotubes (CNT) are more active to PMS than H<sub>2</sub>O<sub>2</sub> or PDS.<sup>36</sup> A further increase of catalyst loading can yield a greater phenol 199 oxidation because more catalytic sites are introduced for PMS activation to generate massive ROS. (Figure 200 S1†) 201

The catalytic performance of A-Boron was compared with other metal and metal-free materials. As illustrated in Figure 2b and S2<sup>†</sup>, the reactivity of A-Boron is comparable to the pristine multi-walled carbon nanotubes (MWCNT) with 76.1% phenol oxidation and surpasses reduced graphene oxide (rGO) with 38.5% phenol removal. Both MWCNT and rGO have been intensively reported as effective carbocatalysts for persulfates activation.<sup>37-40</sup> Additionally, A-Boron is more active than other carbonaceous materials with lower phenol removals such as fullerene (C<sub>60</sub>, 4.7%), nanodiamond (ND, 10.3%), graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>, 8.7%), activated carbon (AC, 5.5%), and biochar (BC, 8.7%).

210

211

212

213

214

215

216

217

218

A wide range of other metal-free and non-carbon materials are also evaluated in Figure 2c and S3<sup>+</sup>. Apart

Chemistry A Accepted Manuscrip

Journal of Materials

from the phosphorene (also known as black phosphorus, P-black) and red phosphorus (P-red) with mediocre activities of 24.4% and 11.6% phenol degradation accordingly, other materials such as sulfur (S, 7.2%), boron carbide (BC, 6.5%), silicon oxide (SiO<sub>2</sub>, 4.0%), hexagonal boron nitride nanosheet (h-BN-NS, 3.5%) and nanotubes (h-BN-NT, 1.6%) manifested poor catalytic activities for PMS activation. To our delight, A-Boron also outperforms the benchmark metal catalysts of  $Co_3O_4$  (19.2%) as well as manganese oxides of  $MnO_2$  (59.3%) and  $Mn_3O_4$  (48.2%) in Figure 2d and S4<sup>†</sup>. Besides, A-Boron exhibits a much higher activity than other transition metal oxides of NiO (59.3%), Fe<sub>3</sub>O<sub>4</sub> (15.2%), TiO<sub>2</sub> (4.8%), Ga<sub>2</sub>O<sub>3</sub> (4.1%) and CeO<sub>2</sub>(3.1%). The metal-free amorphous boron stands out among the heterogeneous catalysts as a high-performance PMS activator for catalytic degradation.



Figure 2. (a) Catalytic activity of boron samples (Experimental conditions: phenol = 0.1 mM, catalyst= 0.2 g/L, PMS = 3.3 mM, temperature = 25 °C); (b) specific surface areas and pore volumes of the corresponding boron samples.

For the investigation of the origins of boron catalysis, a series of boron samples were synthesised and evaluated in their performances (Figure 2a and S5<sup>†</sup>). A-Boron was thermally treated at different

Journal of Materials Chemistry A Accepted Manuscrip

temperatures to regulate the crystallinity and surface chemistry of the amorphous phase. As a result, the 225 phenol oxidation efficiency gradually declines with elevated pyrolysis temperature from 400 to 1000 °C. 226 In contrast to A-Boron with 74.3% phenol degradation, A-B-400, 700, and 1000 yield only 28.3%, 22.4%, 227 and 10.4% phenol removals, respectively. A bulky boron crystallite (C-boron) also gives a lower phenol 228 removal of 10.3%. Nitrogen sorption analysis in Figure 2b and S6<sup>+</sup> depicts that the specific surface areas 229 230 (SSA) of boron samples increase from 10.3  $m^2/g$  (A-Boron) to 18.5  $m^2/g$  (A-B-400), and then the SSAs slightly decline to 17.9 m<sup>2</sup>/g for A-B-700 and sharply drop to 8.3 m<sup>2</sup>/g for A-B-1000. The corresponding 231 pore volumes of the samples follow the same trends. The increases in SSA and pore volume of the 232 233 annealed borons (A-B-400 and 700) are possibly due to the thermal expansion of the aggregated particles, while the decrease in the SSA of A-B-1000 can be ascribed to sintering of the boron species into larger 234 particles (Figure S7<sup>†</sup>). More importantly, the differences in SSA and reactivity of these samples suggest 235 that the catalytic performances of the boron-based materials are independent of the SSA and the activity 236 may predominantly lie in the intrinsic structure and surface chemistry. 237







ournal of Materials Chemistry A Accepted Manuscrip

The surface compositions and chemical states of the boron samples were analysed by the X-ray 240 photoelectron spectroscopy. As illustrated in Figure S8<sup>+</sup>, the high-resolution B 1s profile can be fitted into 241 three peaks locating at 186.8, 188.6, and 191.8 eV, representing for the B-B, boride, and B-O/B-OH bonds, 242 respectively. The boride is attributed to the presence of surface metal impurities (K, Na, Ca, Mg, Figure 243 S9<sup>†</sup>). Acid washing of A-Boron in Figure S10<sup>†</sup> impressively boosts the oxidation rate with complete 244 245 phenol removal in 90 min, suggesting that the surface metal borides/oxides are catalytically inactive and elemental boron provides the intrinsic catalytic sites. Interestingly, the peak intensities of B-O/B-OH 246 increase significantly after the thermal annealing (A-B-1000), implying the formation of new boron 247 248 species. For identification of the altered surface atomic arrangement of the boron samples, the crystalline structures of A-Boron, A-B-1000, and C-Boron were analysed by XRD. As illustrated in Figure 3a, crystal 249 250 C-boron displayed many peaks, most of which can be assigned to the boron facets according to the JCPDS card (No. 01-089-2777, Figure S11<sup>+</sup>). In contrast, A-Boron only manifests two major peaks at 10.1° and 251 11.3° and several minor peaks between 17.4° to 21.6°, accounting for boron facets (Figure S12<sup>+</sup>). The 252 relatively low intensities of A-Boron compared to C-boron may be due to the existence of amorphous 253 phase with low crystallinity and fewer exposed facets. The amplified spectra in Figure 3b indicate that the 254 intensities of the boron peaks slightly decrease due to the thermal pyrolysis. Moreover, several new peaks 255 256 appear, which are identified to be H<sub>3</sub>BO<sub>3</sub> (JCPDS, No. 01-073-2158) in Figure S13<sup>+</sup>. Herein, the XRD spectra are in good agreement with the XPS analysis that impurities such as H<sub>3</sub>BO<sub>3</sub> or B(OH)<sub>3</sub> are 257 258 generated on the surface of amorphous boron during the thermal treatment, which are possibly stemmed 259 from the surface hydrolysis and oxidation.

Journal of Materials Chemistry A Accepted Manuscrip



Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM. 0 00

261

Figure 4. HRTEM images of (a, b) for A-Boron and (c, d) for A-B-1000.

The HRTEM images in Figure 4a and b clearly illustrate that A-Boron presents some crystalline domains 262 with different lattice spacings. Moreover, small regions with disorder-packed borons are also spotted 263 between these grain boundaries. Figure 4c and d show that new layers are generated and cover the crystal 264 boron surface after the thermal treatment, which are assigned to the oxidised boron species. This can be 265 266 evidenced by the electron paramagnetic resonance (EPR) spectra, which can respond to unpaired electrons in materials with a magnetic property. Thus, for the elements in different valence states, electron density 267 and/or local binding configurations can manifest great differences in peaking shapes and positions. 268 269 Different from the crystal boron (C-boron) with a sharp peak in Figure 5a, A-Boron and A-B-1000 display 270 shifted and broader peaks, suggesting the different electronic states of the amorphous phase. The amplified spectra in Figure 5b show that the content of amorphous boron slightly declines for A-B-1000 and a shoulder peak emerges attributed to the new surface species, which well supports the XPS, XRD and TEM results as aforementioned. Therefore, the declined reactivity of amorphous boron after the thermal annealing can be ascribed to the formation of boron impurities, which cover the surface of amorphous boron and prevent the reaction with PMS. Figure S14<sup>+</sup> shows that boron in the high valence states (such as  $H_3BO_3$  and  $B_2O_3$ ) cannot catalyse PMS and present many inferior reactivities for organic oxidation than A-Boron.



Figure 5. (a) Electron paramagnetic resonance spectra of the boron samples and (b) magnified spectra of
A-Boron and A-B-1000.

281

278

Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

For identifying the intrinsic reactive oxygen species accounting for phenol oxidation in the A-Boron/PMS system, in situ radical screening and capturing tests are performed. Methanol (MeOH) and tert-butyl alcohol (TBA) are utilised to selectively scavenge hydroxyl radicals ( $k_{MeOH} = 9.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{TBA} =$ (3.8-7.6) × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>) or/and sulfate radicals ( $k_{MeOH} = 3.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{TBA} =$  (4.0 - 9.1) × 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>).<sup>41</sup> Based on the distinct reaction rate constants of the radical quenching agents toward the two free radicals,

Chemistry A Accepted Manuscrip

Journal of Materials

TBA is typically used to selectively quench 'OH, whilst MeOH can effectively terminate the oxidation by 287 both 'OH and SO<sub>4</sub>'-. As depicted in Figure 6a, the addition of TBA significantly retards the phenol removal 288 efficiency from 74.3% to 40.2% in 120 min, suggesting that 'OH is generated and contribute to the phenol 289 oxidation. Moreover, the addition of MeOH further prohibits the oxidation with only 13.9% of phenol 290 removal. Therefore, both sulfate and hydroxy radicals play crucial roles in the A-Boron/PMS system, 291 292 which is different from the carbon/PMS systems relying on nonradical pathways by an electron-transfer regime or singlet oxygenation.<sup>42-44</sup> Moreover, the generated ROS are *in situ* captured by 5,5-dimethyl-1-293 pyrroline N-oxide (DMPO) as the spin trapping agent in the EPR analysis. The spectrum in Figure 6b 294 295 confirms that 'OH and  $SO_4$ ' are generated. The large amounts of hydroxyl radicals possibly stem from the catalytic activation of PMS by amorphous boron as well as the interconversion from sulfate radicals 296 by water oxidation.45-47 297



Figure 6. (a) Selective radical quenching tests by addition of methanol and tert-butyl alcohol. (b) The
EPR spectrum of in situ radical capturing by DMPO. (Experimental conditions: phenol = 0.1 mM,
catalyst= 0.2 g/L, PMS = 3.3 mM, temperature = 25 °C, DMPO = 50 mM)

302

Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

Moreover, the A-Boron/PMS system was also applied for degradation of a diversity of organic 303 contaminants to evaluate the oxidation capacity. Figure 7 and S15<sup>+</sup> display that the amorphous boron can 304 effectively decompose the phenolics (phenol, PHBA, PBA, and 4-CP), dyes (MO, MB and RhB), 305 antibiotics (IBP and SCP) and other aromatic organics such as NB and BA. Of particular interest, NB is a 306 chemical probe for hydroxyl radicals with a reaction constant of  $3.9 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, which cannot be 307 degraded by sulfate radicals with a relatively low reaction rate constant of  $< 1.0 \times 1.0 \times 1.0^{6} \text{ M}^{-1} \text{ s}^{-1}$ .<sup>48-50</sup> The 308 high efficacy of NB and BA removals were achieved, suggesting that a myriad of hydroxyl radicals and 309 some sulfate radicals are produced in the A-Boron/PMS system and account for the organic oxidation. 310 311 These results are in agreement with the radical quenching experiments. In contrast, previous studies reported that carbon-based AOPs systems are not relying on free radicals but a nonradical pathway.<sup>28</sup> 312 Those carbon/persulfate systems typically manifest a mild redox potential with specific selectivity toward 313 314 the organic substrates.<sup>28</sup> Persulfates (PMS/PDS) tend to be activated by carbons to form a metastable and surface-confined complex that attacks the organics via an electron-shuttle mechanism and such a 315 nonradical pathway cannot oxidise the organics with a higher redox potential (over 9.0 eV) or a poor 316 adsorptive capacity.<sup>51-53</sup> Herein, the boron-based oxidation is similar to the metal-catalysed AOPs systems 317 and the surface boron atoms may chemically interact with the PMS molecule to activate the peroxide O-318 O bond and deliver electrons via B-O bond(s) to produce highly reactive free radicals ('OH and SO<sub>4</sub>-). 319 These free radicals are capable of decomposing various organic contaminants via a series of chemical 320 321 reactions such as addition, H-abstraction or electron transfer to realise a great adaptability and high 322 mineralisation efficiency in aqueous oxidation.

Journal of Materials Chemistry A Accepted Manuscript



 Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

 252
 952

 955
 952

 956
 956

**Figure 7.** Catalytic degradation of various organic contaminants by A-Boron/PMS system. (Experimental conditions: organics = 0.1 mM, catalyst= 0.2 g/L, PMS = 3.3 mM, temperature = 25 °C)

Based on the XRD, EPR and HRTEM images as discussed above, it can be referred that the atoms in amorphous boron are not completely randomly distributed and some are compacted into small crystal domains/clusters with distinct exposed facets. Thus, A-Boron is proposed to be long-range disordered, however, possesses some crystalline grain boundaries in the local domains.<sup>54</sup> The reactivity of A-boron may be dependent on the properties of these short-range ordered facets to drive the metal-free catalysis. 330 The role of these crystal terminations in PMS activation was investigated by density functional theory 331 332 (DFT) calculations in terms of the PMS adsorption onto different boron facets. As depicted in Figure 8ac, a PMS molecule is prone to intimately react with boron atoms via B-O bonds and can be directly 333 dissociated into two parts (OH and SO<sub>4</sub>) over the boron slabs of the (100), (101) and (111) terminations. 334 335 The efficient cleavage of the peroxide O-O bond in PMS (HO-OSO<sub>3</sub><sup>-</sup>) implies the generation of sulfate or hydroxyl radicals on boron. The computation also monitors the electron migration from boron slab to PMS 336 molecule. It can be observed that 0.824, 0.988 and 0.718 e were transferred to PMS from boron (1 0 0), 337 338 (1 0 1) and (1 1 0) facets, respectively. The electron migration and PMS reduction further drive the radical generation. Moreover, Table S1<sup>+</sup> displays the distribution of the migrated electrons and adsorption 339

Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

energies. The majority of the charge is delivered to  $SO_4$  and only a minor proportion of the electron is transported to OH. This implies the generation of sulfate ion ( $SO_4^{2-}$ ) and hydroxyl radical (OH), which agrees with the radical capturing (EPR) tests.

In contrast, over the (001) (Figure 8d) and (111) (Figure 8e) facets, one oxygen atom would be detached 343 from the PMS molecule and bind with two boron atoms to form a B-O-B bond, leaving a protonated 344 sulfate ion/radical into the water solution. Therefore, these two terminations may be less reactive than the 345 346 other three facets for radical production, especially for hydroxyl radicals. Since the detached oxygen may cause boron oxidation, boron in a high valence state of boron oxide (B<sub>2</sub>O<sub>3</sub>) was also investigated for PMS 347 adsorption. As shown in Figure S16<sup>+</sup>, PMS only weakly interacts with the (0 0 1) termination of boron 348 349 oxide via van der Waals attractions with a low adsorption energy of -0.14 eV, limited electron transfer of 0.003 e and slightly prolonged O-O bond from 1.332 Å (free PMS molecule) to 1.333 Å. Therefore, PMS 350 351 cannot be activated on  $B_2O_3$  and the boron catalysis favours a reductive state for binding with the peroxide 352 bonds and subsequent electron transfer to produce reactive radicals. Particularly, the reaction between the  $(0\ 0\ 1)/(1\ 1\ 1)$  boron facets with PMS will cause direct oxidation of surface boron, giving rise to inferior 353 reducibility for electron migration, the formation of non-reactive boron oxides and poor stability (Figure 354  $S17^{\dagger}$ ) in multiple runs. Therefore, it can be inferred by the theoretical calculation that the (1 0 0), (1 0 1), 355 356 and (1 1 0) terminations provide the intrinsic catalytic sites for PMS decomposition to evolve hydroxyl 357 and sulfate radicals for catalytic oxidation. Since A-Boron may contain some amorphous regions with 358 randomly distributed boron atoms, a fully relaxed disordered boron cluster (B75) is also applied to mimic the amorphous boron to react with PMS. As depicted in Figure S18<sup>†</sup>, the PMS molecule can be directly 359 360 cleaved into hydroxyl and sulfate groups, suggesting that amorphous boron can also serve as a PMS 361 activator for metal-free oxidation. The adsorption energy is a significant indicator in catalytic reactions.<sup>55</sup>

- Boron (1 0 1) and B75 yielded the lowest adsorption energies with -10.6 eV and -9.58 eV, respectively,
- implying the intimately coupling with PMS for activation.

Top view

Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

364



Figure 8. Illustrations of PMS adsorption and dissociation onto different boron facets of (a) (1 0 0), (b)
(1 0 1), (c) (1 1 0), (d) (0 0 1) and (e) (1 1 1).

In summary, amorphous boron is long-ranged disordered, yet some short-range ordered and amorphous 367 boron domains co-existed in the boron samples. The electron-deficient nature of boron atoms facilitates 368 369 the self-assembling into multiple interlinked polyhedra, building up to both small crystals and amorphous regions in the large boron particles. As a result, A-Boron can be used as a metal-free catalyst for PMS 370 activation to evolve free radicals for organic oxidation. The DFT calculations indicate that both amorphous 371 372 cluster and some short-range ordered terminations of the  $(1 \ 0 \ 0), (1 \ 0 \ 1)$  and  $(1 \ 1 \ 0)$  can effectively cleave PMS molecules with simultaneous electron transfer for production of hydroxyl and sulfate radicals, which 373 is confirmed the by radical quenching tests and EPR capture technology. By masking the reactive boron 374 surfaces to form oxidised boron impurities, the borons gradually lose the activity suggesting the reductive 375

boron surfaces are more favourable for PMS activation. Interestingly, the boron manifests a metallic behaviour in AOPs catalysis to produce free radicals rather than the nonradical pathway in metal-free carbocatalysis. Despite that both boron and carbon are reductive materials which can sacrifice electrons to peroxides, boron is an insulating material in nature, which is intrinsically different from the highlyconjugated sp<sup>2</sup> carbon network with superior electron conductivity for an electron-mediated nonradical pathway. Therefore, the boron-based system can produce highly oxidising free radicals to decompose a wide spectrum of microcontaminants with outstanding mineralisation efficiency.

## 383 Conclusions

Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

In this study, borons were investigated as metal-free catalysts for heterogeneous activation of 384 peroxymonosulfate for advanced oxidation. It is unveiled that the amorphous boron can effectively 385 386 decompose PMS molecules to generate reactive oxygen species for organic degradation in water. The 387 catalytic performance of A-Boron outperforms most of the transition metals, non-carbon materials and 388 nanocarbons, and can compete with the benchmark nonradical activator of carbon nanotubes. The radical 389 quenching test and EPR technique unveil that both sulfate and hydroxyl radicals are generated, and 390 hydroxyl radicals dominantly account for the pollutant oxidation. As a result, the A-Boron/PMS system 391 can degrade a diversity of organic contaminants. The characterisation techniques suggested that A-Boron 392 samples are long-range disordered whilst possessing some crystal terminations in local domains together with amorphous phase between the grain boundaries. Both the short-range ordered boron grain boundaries 393 and amorphous regions may contribute to the PMS activation. However, thermal treatment of A-boron 394 395 can introduce inactive boron oxide or boron acid on the surface, which will cover the active boron terminations and deteriorate the catalytic performance. The theoretical calculations further consolidated 396 that both the amorphous boron clusters and crystal facets of (1 0 0), (1 0 1), (1 1 0) can directly dissociate 397 PMS molecules to produce sulfate and hydroxyl radicals. The study not only envisages the insights into 398

boron catalysis in heterogenous reaction but also provides a novel and green AOPs system. The boron/PMS system with powerful hydroxy radicals is highly efficient for catalytic decomposition of various aqueous microcontaminants, which can provide new solutions for wastewater purification or soil decontamination by state-of-the-art metal-free catalysis without concerning about the secondary contamination by metal catalysis.

404

Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM.

#### 405 **Conflicts of interest**

406 The authors declare no conflicts of interest.

## 407 Acknowledgements

408 The authors appreciate the financial support from the Australian Research Council (DP190103548) and

409 Open Research Projects from State Key Laboratory (SKL-ChE-16C05 and QAK201808). We also

410 acknowledge the financial support from the National Science Foundation of China (NSFC, No. 21777033)

and Science and Technology Program of Guangdong Province (2017B020216003).

#### 412 Notes and references

- Y. W. Zhu, S. Murali, W. W. Cai, X. S. Li, J. W. Suk, J. R. Potts and R. S. Ruoff, *Adv. Mater.*, 2010, 22, 3906-3924.
- 415 2. M. Jabli, T. A. Saleh, N. Sebeia, N. Tka and R. Khiari, *Sci. Rep.*, 2017, 7, 14448.
- 416 3. T. A. Saleh, J. Clean Prod., 2018, **172**, 2123-2132.
- 417 4. T. A. Saleh, J. Water Supply Res. Technol., 2015, 64, 892-903.
- 418 5. D. S. Su, G. D. Wen, S. C. Wu, F. Peng and R. Schlogl, *Angew. Chem. Int. Ed.*, 2017, 56, 936-964.
- 419 6. S. Navalon, A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *Chem. Rev.*, 2014, **114**, 6179-6212.
- 420 7. D. W. Wang and D. S. Su, *Energ. Environ. Sci.*, 2014, 7, 576-591.
- 421 8. Q. J. Xiang, J. G. Yu and M. Jaroniec, *Chem. Soc. Rev.*, 2012, **41**, 782-796.
- 422 9. X. G. Duan, H. Q. Sun and S. B. Wang, *Accounts Chem. Res.*, 2018, **51**, 678-687.
- 423
   10.
   T. A. Saleh, K. O. Sulaiman and S. A. Al-Hammadi, Appl. Catal. B, 2019, DOI: 424
   doi.org/10.1016/j.apcatb.2019.1004.1062.
- 425 11. T. A. Saleh, Environ. Sci. Pollut. Res., 2015, 22, 16721-16731.
- 426 12. T. A. Saleh, *Desalin. Water Treat.*, 2016, **57**, 10730-10744.
- 427 13. X. B. Fan, G. L. Zhang and F. B. Zhang, *Chem. Soc. Rev.*, 2015, 44, 3023-3035.
- 428 14. S. Navalon, A. Dhakshinamoorthy, M. Alvaro, M. Antonietti and H. Garcia, *Chem. Soc. Rev.*, 2017, 46, 4501-4529.

- 430 15. C. Tang and Q. Zhang, *Adv. Mater.*, 2017, **29**, 1604103.
- 431 16. Y. X. Fang and X. C. Wang, *Angew. Chem. Int. Ed.*, 2017, **56**, 15506-15518.
- 432 17. H. F. Schaefer and F. E. Harris, *Phys. Rev.*, 1968, 167, 67.
- 433 18. Z. H. Zhang, E. S. Penev and B. I. Yakobson, *Chem. Soc. Rev.*, 2017, 46, 6746-6763.
- 434 19. N. J. Yang, S. Y. Yu, J. V. Macpherson, Y. Einaga, H. Y. Zhao, G. H. Zhao, G. M. Swain and X. Jiang,
  435 *Chem. Soc. Rev.*, 2019, 48, 157-204.
- 436 20. H. T. Liu, Y. Q. Liu and D. B. Zhu, J. Mater. Chem., 2011, 21, 3335-3345.
- 437 21. L. J. Yang, S. J. Jiang, Y. Zhao, L. Zhu, S. Chen, X. Z. Wang, Q. Wu, J. Ma, Y. W. Ma and Z. Hu, *Angew.*438 *Chem. Int. Ed.*, 2011, **50**, 7132-7135.
- 439 22. Y. Zhao, L. J. Yang, S. Chen, X. Z. Wang, Y. W. Ma, Q. Wu, Y. F. Jiang, W. J. Qian and Z. Hu, J. Am.
  440 Chem. Soc., 2013, 135, 1201-1204.
- 441 23. Y. Zheng, Y. Jiao, L. Ge, M. Jaroniec and S. Z. Qiao, Angew. Chem. Int. Ed., 2013, 52, 3110-3116.
- 442 24. L. Shi, P. Li, W. Zhou, T. Wang, K. Chang, H. B. Zhang, T. Kako, G. G. Liu and J. H. Ye, *Nano Energ.*, 2016, 28, 158-163.
- J. T. Grant, C. A. Carrero, F. Goeltl, J. Venegas, P. Mueller, S. P. Burt, S. E. Specht, W. P. McDermott, A. Chieregato and I. Hermans, *Science*, 2016, **354**, 1570-1573.
- A. M. Love, B. Thomas, S. E. Specht, M. P. Hanrahan, J. M. Venegas, S. P. Burt, J. T. Grant, M. C.
  Cendejas, W. P. McDermott, A. J. Rossini and I. Hermans, *J. Am. Chem. Soc.*, 2019, 141, 182-190.
- 448 27. G. G. Liu, X. G. Meng, H. B. Zhang, G. X. Zhao, H. Pang, T. Wang, P. Li, T. Kako and J. H. Ye, *Angew. Chem. Int. Ed.*, 2017, 56, 5570-5574.
  - 28. X. G. Duan, H. Q. Sun, Z. P. Shao and S. B. Wang, *Appl. Catal. B*, 2018, **224**, 973-982.
- 451 29. X. Wang and Y. D. Li, *Chem.-Eur. J.*, 2003, 9, 300-306.
- 452 30. E. Saputra, S. Muhammad, H. Q. Sun, H. M. Ang, M. O. Tade and S. B. Wang, *Appl. Catal. B*, 2013, 142, 729-735.
- 454 31. Y. J. Yao, Z. H. Yang, H. Q. Sun and S. B. Wang, *Ind. Eng. Chem. Res.*, 2012, **51**, 14958-14965.
- 455 32. Y. X. Wang, H. Q. Sun, H. M. Ang, M. O. Tade and S. B. Wang, Chem. Eng. J., 2014, 245, 1-9.
- 456 33. B. Delley, J. Chem. Phys., 2000, 113, 7756-7764.
- 457 34. B. Hammer, L. B. Hansen and J. K. Norskov, *Phys. Rev. B.*, 1999, **59**, 7413-7421.
- 458 35. B. Delley, *Phys. Rev. B*, 2002, **66**, 155125.
- 459 36. X. G. Duan, Z. M. Ao, H. Q. Sun, L. Zhou, G. X. Wang and S. B. Wang, *Chem. Commun.*, 2015, **51**, 15249460 15252.
- 461 37. H. Q. Sun, C. Kwan, A. Suvorova, H. M. Ang, M. O. Tade and S. B. Wang, *Appl. Catal. B*, 2014, 154, 134462 141.
- 463 38. C. T. Guan, J. Jiang, C. W. Luo, S. Y. Pang, Y. Yang, Z. Wang, J. Ma, J. Yu and X. Zhao, *Chem. Eng. J.*,
  464 2018, 337, 40-50.
- 465 39. H. Q. Sun, S. Z. Liu, G. L. Zhou, H. M. Ang, M. O. Tade and S. B. Wang, ACS Appl. Mater. Interfaces, 2012, 4, 5466-5471.
- 467 40. X. G. Duan, H. Q. Sun, Z. M. Ao, L. Zhou, G. X. Wang and S. B. Wang, *Carbon*, 2016, **107**, 371-378.
- 468 41. C. J. Liang and H. W. Su, Ind. Eng. Chem. Res., 2009, 48, 5558-5562.
- 469 42. D. G. Li, X. G. Duan, H. Q. Sun, J. Kang, H. Y. Zhang, M. O. Tade and S. B. Wang, *Carbon*, 2017, 115, 649-658.
- 471 43. X. Cheng, H. Guo, Y. Zhang, G. V. Korshin and B. Yang, *Water Res.*, 2019, 157, 406-414.
- 472 44. X. Chen, X. Duan, W.-D. Oh, P.-H. Zhang, C.-T. Guan, Y.-A. Zhu and T.-T. Lim, *Appl. Catal. B*, 2019, 253, 419-432.
- 474 45. X. G. Duan, S. Indrawirawan, J. Kang, W. J. Tian, H. Y. Zhang, H. Q. Sun and S. B. Wang, *Sustain. Mater.* 475 *Technol.*, 2018, 18, e00082.
- 476 46. J. Cai, T. Niu, P. Shi and G. Zhao, 2019, *Small*, 1900153, doi.org/10.1002/smll.201900153.
- 477 47. X. Chen, W. D. Oh, Z. T. Hu, Y. M. Sun, R. D. Webster, S. Z. Li and T. T. Lim, *Appl. Catal. B*, 2018, 225, 243-257.
- 479 48. P. Neta, V. Madhavan, H. Zemel and R. W. Fessenden, J. Am. Chem. Soc., 1977, 99, 163-164.

- 480 49. G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, 17, 513481 886.
- 482 50. Y. Yang, J. Jiang, X. L. Lu, J. Ma and Y. Z. Liu, *Environ. Sci. Technol.*, 2015, **49**, 7330-7339.
- 483 51. P. D. Hu, H. R. Su, Z. Y. Chen, C. Y. Yu, Q. L. Li, B. X. Zhou, P. J. J. Alvarez and M. C. Long, *Environ.*484 *Sci. Technol.*, 2017, **51**, 11288-11296.
- 485 52. S. S. Zhu, X. C. Huang, F. Ma, L. Wang, X. G. Duan and S. B. Wang, *Environ. Sci. Technol.*, 2018, 52, 8649-8658.
- 487 53. E. T. Yun, J. H. Lee, J. Kim, H. D. Park and J. Lee, *Environ. Sci. Technol.*, 2018, **52**, 7032-7042.
- 488 54. Z. Jia, X. G. Duan, P. Qin, W. C. Zhang, W. M. Wang, C. Yang, H. Q. Sun, S. B. Wang and L. C. Zhang,
   489 *Adv. Funct. Mater.*, 2017, 27, 1702258
- 490 55. C. Liu, H. Dong, Y. Ji, N. Rujisamphan and Y. Li, J. Colloid Interface. Sci., 2019, **551**, 130-137.

#### **Table of Contents Entry**



Published on 21 June 2019. Downloaded on 6/22/2019 4:34:30 AM. 494 495 496

Journal of Materials Chemistry A Accepted Manuscript Amorphous boron is employed as a novel and high-performance metal-free catalyst for activation of peroxymonosulfate for degrading various organic contaminants in water.