

ChemComm

Accepted Manuscript



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 [Terms & Conditions](#) and the [Ethical guidelines](#) 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.



Journal Name

COMMUNICATION

Extremely Enhanced Contaminants Decomposition Catalyzed by Hemin via the Coupling of Persistent Free Radicals and Ascorbic Acid

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Yuyuan Yao,^a Bin Jiang,^a Yajun Mao,^a Juan Chen,^a Zhenfu Huang,^a Sanqing Huang,^a and Li Zhang^b

www.rsc.org/

Persistent free radicals (PFRs) were mainly reported as negative species. Here we report a positive role of PFRs in enhancing reactive oxygen species (ROS) generation for an extreme rate enhancement in environmental pollutants decomposition.

Persistent free radicals (PFRs) were widely observed in nature, such as combustion-generated matters,^{1,2} airborne PM_{2.5},^{3,4} soils and sediments.^{5,6} The importance of this class of reactive intermediate has been duly noted in environmental, chemical and biological systems due to their persistence and radical reactivity.⁷⁻¹⁰ Generally, the current researches mainly focus on regarding PFRs as deleterious species, which initiated adverse health impacts, such as DNA damage and pulmonary dysfunction.^{11,12} Despite several reports in the discovery of PFRs as oxidants activators to oxidize organic compounds,^{13,14} the positive roles of PFRs were still poorly considered so far.

PFRs are stable in air for a prolonged time and their half-lifetimes are on the order of hours or even days. Such long lifetimes of the radicals are unique, however, they do not preclude radical reactivity. It has been reported that the unpaired electrons in PFRs can be sustainably transferred to electron-acceptors such as higher valent metals.^{7,15} This distinctive property might feature the capability to accelerate some important catalytic redox processes such as iron-mediated cycle involved the intrinsic drawback of slow iron reduction rate to generate reactive oxygen species (ROS) for the degradation of environmental pollutants. Hence, PFRs may be beneficial species in promoting the catalytic efficiency for contaminants decomposition, while comparatively, the knowledge about this role of PFRs is rather limited.

Lately, carbonaceous materials were reported to contain PFRs and gradually received attention in the related

researches.^{13,16} Meanwhile, carbonaceous materials were widely used as catalyst supports, which might endow PFRs potential applications in environmental catalysis.¹⁷⁻²⁰ Among various carbonaceous materials, activated carbon fiber (ACF) has remarkable advantage: it may be formed into felts or fabrics of various shapes, and is therefore amenable to handling in different applications. Moreover, ACF also has the similar characteristics of other carbonaceous materials, such as large specific surface area, unusual chemical and structural stability. Herein, we selected ACF as the representative of PFRs, iron porphyrin (hemin) as the catalyst and H₂O₂ as the oxidant to construct a novel catalytic oxidation system of hemin-ACF/H₂O₂ for contaminants decomposition. However, during the reaction process, continuous electron transfer from PFRs (ACF) to hemin will inevitably cause the loss, or even complete consumption of PFRs, which would decrease the catalytic efficiency. Inspired by the discharging and charging process of battery, a “charging” process (electron donor) is highly desired to supply electron to ACF for the regeneration of PFRs.

Ascorbic acid (AA) is an unsaturated polyhydroxy compound, which enable AA to be an ideal candidate as the electron donor.²¹⁻²² Moreover, compared with other electron donors such as polyphenols,²³ hydroxylamine hydrochloride²⁴ and sodium sulfite,²⁵ AA is nontoxic, relatively cheap, and has extensive sources. Herein, AA was introduced to hypothetically supply electrons for the electron sink, i. e., “charging”. These “discharging” (electron transfer from ACF to hemin) and “charging” (electron transfer from AA to ACF) processes could allow for a higher catalytic efficiency in the production of ROS, resulted in an extreme rate enhancement in contaminants decomposition. This research offers a new insight into the PFRs-enhanced catalytic performance and initiates an inspiring research domain of PFRs in the environmental field.

Fig. 1A showed the electron paramagnetic resonance (EPR) spectra of hemin-ACF at room temperature after different reaction time in the hemin-ACF/H₂O₂ system. The narrow singlet signal located at 3513G was attributed to the PFRs in ACF (Fig. S1). After reacting for 60min, the signal intensity of PFRs for hemin-ACF in the hemin-ACF/H₂O₂ system located at

^a National Engineering Lab of Textile Fiber Materials & Processing Technology (Zhejiang), Zhejiang Sci-Tech University, Hangzhou 310018, PR China.

^b The School of Material Science and Chemical Engineering, Ningbo University, Ningbo 325211, PR China.

Email: yyy0571@126.com; Tel: +86 571 86843810; Fax: +86 571 86843255.

†Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

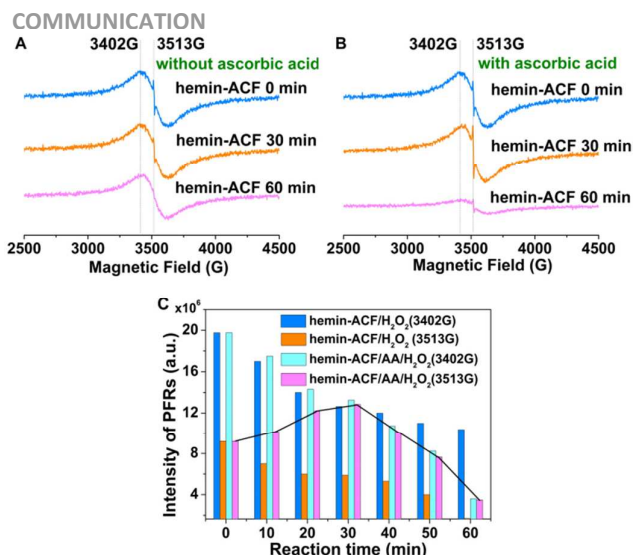


Fig. 1. (A) EPR spectra of hemin-ACF at room temperature after different reaction time in the hemin-ACF/H₂O₂ system. (B) EPR spectra of hemin-ACF at room temperature after different reaction time in the hemin-ACF/H₂O₂/AA system. (C) Intensity of PFRs in hemin-ACF in the hemin-ACF/H₂O₂ and hemin-ACF/AA/H₂O₂ system at different reaction time. Conditions: [hemin-ACF]=10 g/L, [H₂O₂]=50 mM, initial pH 7.3, at 50 °C.

3402G and 3513G decreased 9.38×10^6 and 7.47×10^6 , respectively (Fig. 1A and C), implying the decrease of the PFRs concentration in hemin-ACF, which might be attributed to the electron transfer from ACF to hemin. Meanwhile, the reduction of hemin(Fe^{III}) to hemin(Fe^{II}) in hemin-ACF was evidenced by XPS (Fig. S2), which was in agreement with the literature,²⁷ indicating that ACF could transfer electrons to hemin. In this sense, ACF could serve as an electron sink providing electrons to hemin to accelerate the catalytic cycle of hemin(Fe^{III})/hemin(Fe^{II}).

Moreover, when AA was added into the hemin-ACF/H₂O₂ system (Fig. 1B and C), we interestingly found that the signal intensity of PFRs located at 3513G observed for the hemin-ACF firstly increased 3.66×10^6 in 30 min, suggesting that AA acted as an electron donor to supply electrons to the hemin-ACF, thus increasing the signal intensity of PFRs. Then the intensity decreased 9.36×10^6 from 30 min to 60 min, which was obviously higher than that of 4.21×10^6 in the hemin-ACF/H₂O₂ system (Fig. 1C). These findings suggested that AA coupled with ACF significantly accelerated the electron transfer from ACF to hemin. Furthermore, the effect of AA on the PFRs concentration after cyclic utilizations was investigated. As shown in Fig. S3, the PFRs of hemin-ACF decreased obviously after cyclic utilizations in the hemin-ACF/H₂O₂ system. However, after the introduction of AA, the PFRs of hemin-ACF (at 3513G) conversely increased after cyclic utilizations in the hemin-ACF/AA/H₂O₂ system, demonstrating that hemin-ACF could work like a rechargeable electron sink, which could be repeatedly “charged” by the electron donor AA after “discharging” (i.e. transferring electrons to hemin).

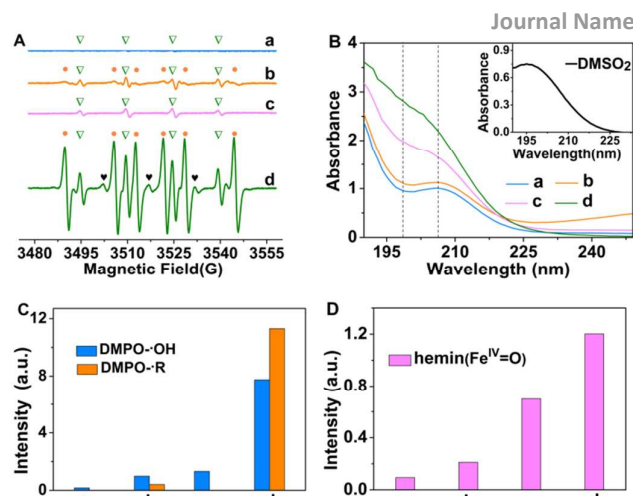


Fig. 2. (A) DMPO-trapped EPR spectra. ∇ : hydroxyl radicals; \bullet : carbon-based radicals; \heartsuit : oxidized DMPO nitroxide metabolite ($\alpha_N=15.0$ G). (B) UV/Vis spectroscopy of oxidation products of DMSO. The inset shows the absorption spectrum of 1 mM DMSO₂ aqueous solution. (C) \bullet OH and \bullet R amounts calculated according to EPR signal intensity of DMPO- \bullet OH and DMPO- \bullet R adducts. (D) hemin(Fe^{IV}=O) amounts calculated according to DMSO method. Conditions: (a) hemin/H₂O₂, (b) hemin/AA/H₂O₂, (c) hemin-ACF/H₂O₂ and (d) hemin-ACF/AA/H₂O₂. Other detailed conditions and methods were demonstrated in the Supplementary Information.

To further testify the role of PFRs in enhancing the generation of ROS, spin-trap experiments were carried out. First, the types of ROS in the systems were identified as shown in Fig. 2A, the hemin/H₂O₂ system exhibited 1:2:2:1 quartet of lines in the electron paramagnetic resonance (EPR) spectrum with the hyperfine coupling parameters ($\alpha_N=\alpha_H=14.9$ G), which is attributed to DMPO- \bullet OH adduct (curve a). When ACF was introduced to the hemin/H₂O₂ system, there was no formation of new ROS in the system (curve c), while the addition of AA brought the unexpected occurrence of a new sextet signal with hyperfine coupling parameters ($\alpha_H=22.8$ G, $\alpha_N=15.8$ G) (curves b and d). This signal was assigned to the DMPO adducts of carbon-based radicals (\bullet R) derived from the decomposition of AA, which could be hydroxyalkyl fragments \bullet C(OH)₂CH(OH)CH₂OH and \bullet C(OH)₂CH₂OH ($\alpha_H=22.8$ G, $\alpha_N=15.8$ G)²⁸ produced from the possible types of ascorbate cleavage products (Fig. S4). It has been reported that the formation of hemin(Fe^{IV}=O) was accompanied by the generation of \bullet OH in the catalytic cycle of hemin,²⁹ we therefore detected the hemin(Fe^{IV}=O) (for details, see Supplementary Information, Detection of hemin(Fe^{IV}=O)) and the results showed that hemin(Fe^{IV}=O) was formed in the hemin-involved systems (Fig. 2B).

Second, the amounts of \bullet OH, \bullet R and hemin(Fe^{IV}=O) in the systems were further investigated. The relative amounts of \bullet OH and \bullet R were calculated according to EPR signal intensity of DMPO- \bullet OH and DMPO- \bullet R adducts in various catalytic systems. It was found that the introduction of ACF and AA resulted in the promoted formation of \bullet OH with the order of

hemin<hemin/AA<hemin-ACF<hemin-ACF/AA, while the participation of AA caused the generation of $\bullet R$ with the order of hemin/AA<hemin-ACF/AA (Fig. 2C). Especially, the coupling of ACF and AA brought much greater enhancing effect on the $\bullet OH$ generation than the sum of that of ACF plus AA, implying that ACF coupled with AA showed a synergistic effect in the production of $\bullet OH$. Moreover, the promoted formation of hemin($Fe^{IV}=O$) caused by the introduction of ACF and AA was also in the order of hemin<hemin/AA<hemin-ACF<hemin-ACF/AA (Fig. 2D), indicating both ACF and AA enhanced the hemin($Fe^{IV}=O$) formation. It is of note that the hemin/AA/ H_2O_2 system generated higher intensity of $\bullet OH$ and hemin($Fe^{IV}=O$) than that of the sole hemin/ H_2O_2 (Fig. 2), indicating that AA could transfer electron to hemin, enhancing hemin-catalyzed generation of ROS. However, the ROS generated in the hemin/AA/ H_2O_2 system was obviously much less than that of the hemin-ACF/AA/ H_2O_2 system (Fig. 2), implying that the direct electron transfer from AA to hemin was not mainly responsible for the dramatically enhanced generation of ROS, while the electron transfer from AA to ACF might be the dominant reason for the ROS enhancement in the hemin-ACF/AA/ H_2O_2 system.

Based on these findings mentioned above, we envisioned that PFRs could be applied in catalytic decomposition of organic pollutants due to the generation of ROS.³⁰⁻³³ Reactive Red M-3BE (RR M-3BE) was employed as the target contaminant to test the performance of our system, as shown in Fig. 3A. Hemin/ H_2O_2 could not efficiently remove RR M-3BE (curve a), while the introduction of sole AA or ACF accelerated the dye decomposition with over 80% removal rate in 60 min (curves b and c). Amazingly, when AA and ACF were co-introduced, we found that 100% of RR M-3BE was rapidly eliminated in 1 min (curve d). All of the RR M-3BE decomposition curves obeyed pseudo-first-order kinetics (Fig. 3B). The RR M-3BE decomposition rate constant was calculated to be 3.9039 min^{-1} in the hemin-ACF/AA/ H_2O_2 system, which was about 2169 times that (0.0018 min^{-1}) in the hemin/ H_2O_2 system, 114 times that (0.0342 min^{-1}) in the hemin/ H_2O_2 /AA system and even 48 times that (0.0815 min^{-1})

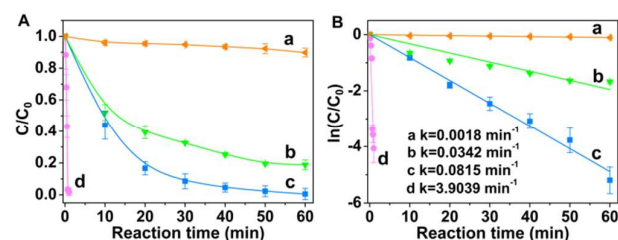
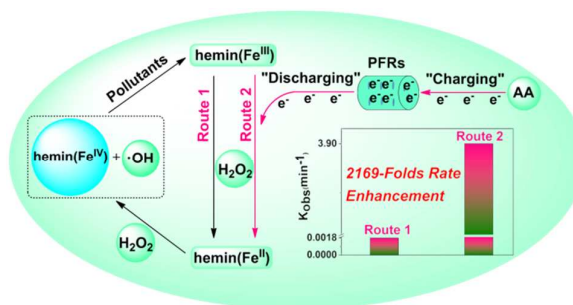


Fig. 3. (A) Time profiles of RR M-3BE decomposition in different systems: (a) hemin/ H_2O_2 ; (b) hemin/AA/ H_2O_2 ; (c) hemin-ACF/ H_2O_2 ; (d) hemin-ACF/AA/ H_2O_2 . (B) Plots of $\ln(C/C_0)$ versus time for the RR M-3BE decomposition in different systems. Conditions: [RR M-3BE]=50 μM , [H_2O_2]=50 mM, [AA]=3 mM, [hemin]=169 μM , [hemin-ACF]=10 g/L (containing 169 μM hemin), initial pH 7.3, T=50 $^\circ C$.



Scheme 1. The proposed catalytic cycle of hemin with or without the introduction of AA and ACF.

in the hemin-ACF/ H_2O_2 system. When RR M-3BE was replaced by several other aromatic compounds including Acid Red 1 (AR1), Acid Orange 7 (AO7), Reactive Red X-3B (RRX-3B), Methyl Blue (MB), 8-Hydroxyquinoline (8-HQ) and 4-Nitrophenol (4-NP), similar extreme rate enhancement of contaminants oxidative decomposition was found in the hemin-ACF/AA/ H_2O_2 system (Table S1). To further testify the validity of our envisagement, designed experiments were performed to exclude the interference of the pH, adsorption and decomposition products of AA (Fig. S6-S13, Table S2). Moreover, the $\bullet R$ were proved not able to effectively decompose the contaminants, while the $\bullet OH$ and hemin($Fe^{IV}=O$) were mainly responsible for the enhanced decomposition (Fig. S14).

These findings mentioned above suggested that PFRs (ACF) played a key role of electron sink, continuously transferring electrons to hemin (i.e. "discharging"). When the PFRs were gradually consumed during the process of electron transfer, AA could serve as an electron donor to supply electrons to the electron sink (i.e. "charging"), thus maintaining the amounts of PFRs in ACF. Therefore, PFRs coupled with AA sustainably provided electrons for the rate-determining conversion of hemin(Fe^{III}) to hemin(Fe^{IV}), thus accelerating the catalytic cycle of hemin, resulting in strongly enhanced production of $\bullet OH$ and hemin($Fe^{IV}=O$) (Route 2), further promoting the oxidative decomposition of RR M-3BE by 2169-folds compared with that of the sole hemin/ H_2O_2 system (Route 1) (Scheme 1). In addition, from the perspective of structure change of hemin-ACF and electrochemistry, the mechanism for extremely enhanced decomposition was also investigated (Fig. S21, Schemes S1 and S2).

The current work provides a new insight into the role of PFRs in extremely enhancing the generation of ROS for the contaminants decomposition. In the hemin-ACF/ H_2O_2 /AA system, $\bullet OH$ and hemin($Fe^{IV}=O$) were the main ROS for the extremely enhanced decomposition of organic pollutants, while the novel radicals $\bullet R$ derived from the decomposition of AA with a strong signal intensity were proved not able to effectively destroy the pollutants, but might find promising applications in other fields. The findings of this study provide a new insight into the PFRs-enhanced catalytic performance for environmental pollutants decomposition, which might bring an inspiring research domain of PFRs in the environmental field.

This work was supported by the State Key Program of National Natural Science of China (No. 51133006), the National Natural Science Foundation of China (No. 51103133, 51302246), the Natural Science Foundation of Ningbo (No. 2015A610047) and Zhejiang Provincial Natural Science Foundation of China (No. LY14E030015, LQ15E030005).

- 30 X. Duan, Z. Ao, H. Sun, L. Zhou, G. Wang, S. Wang, *Chem. Commun.*, 2015, DOI: 10.1039/C5CC05101K.
 31 X. Duan, H. Sun, J. Kang, Y. Wang, S. Indrawirawan S. Wang, *ACS Catal.*, 2015, **5**, 4629.
 32 X. Duan, K. O'Donnell, H. Sun, Y. Wang, S. Wang, *Small*, 2015, **11**, 3036.
 33 H. Sun, Y. Wang, S. Liu, L. Ge, L. Wang, Z. Zhu, S. Wang, *Chem. Commun.*, 2013, **49**, 9914.

Notes and references

- E. Vejerano, S. M. Lomnicki, B. Dellinger, *Environ. Sci. Technol.*, 2012, **46**, 9406.
- S. Lomnicki, H. Truong, E. Vejerano, B. Dellinger, *Environ. Sci. Technol.*, 2008, **42**, 4982.
- W. Gehling, B. Dellinger, *Environ. Sci. Technol.*, 2013, **47**, 8172.
- J. Saravia, G. I. Lee, S. Lomnicki, B. Dellinger, S. A. Cormier, *J. Biochem. Mol. Toxicol.*, 2013, **27**, 56.
- A. L. N. dela Cruz, W. Gehling, S. Lomnicki, R. L. Cook, B. Dellinger, *Environ. Sci. Technol.*, 2011, **45**, 6356.
- A. L. N. dela Cruz, R. L. Cook, S. M. Lomnicki, B. Dellinger, *Environ. Sci. Technol.*, 2012, **46**, 5971.
- L. Khachatryan, E. Vejerano, S. Lomnicki, B. Dellinger, *Environ. Sci. Technol.*, 2011, **45**, 8559.
- S. Balakrishna, S. Lomnicki, K. M. McAvey, R. B. Cole, B. Dellinger, S. A. Cormier, *Part. Fibre Toxicol.*, 2009, **6**, 11.
- T. M. Lachocki, D. F. Church, W. A. Pryor, *Environ. Res.*, 1988, **45**, 127.
- N. Lubick, *Environ. Sci. Technol.*, 2008, **42**, 8178.
- B. Dellinger, W. A. Pryor, R. Cueto, G. L. Squadrito, V. Hegde, W. A. Deutsch, *Chem. Res. Toxicol.*, 2001, **14**, 1371.
- S. A. Cormier, S. Lomnicki, W. Backes, B. Dellinger, *Environ. Health Perspect.*, 2006, **114**, 810.
- G. Fang, J. Gao, C. Liu, D. D. Dionysiou, Y. Wang, D. Zhou, *Environ. Sci. Technol.*, 2014, **48**, 1902.
- G. Fang, C. Liu, J. Gao, D. D. Dionysiou, D. Zhou, *Environ. Sci. Technol.*, 2015, **49**, 5645.
- L. Khachatryan, B. Dellinger, *Environ. Sci. Technol.*, 2011, **45**, 9232.
- A. Valavanidis, N. Iliopoulos, G. Gotsis, K. Fiotakis, *J. Hazard. Mater.*, 2008, **156**, 277.
- T. Xue, S. Jiang, Y. Qu, Q. Su, R. Cheng, S. Dubin, C. Chiu, R. Kaner, Y. Huang, X. Duan, *Angew. Chem. Int. Ed.*, 2012, **51**, 3822.
- S. Ikeda, S. Ishino, T. Harada, N. Okamoto, T. Sakata, H. Mori, S. Kuwabata, T. Torimoto, M. Matsumura, *Angew. Chem. Int. Ed.*, 2006, **45**, 7063.
- B. Wu, D. Hu, Y. Kuang, B. Liu, X. Zhang, J. Chen, *Angew. Chem. Int. Ed.*, 2009, **48**, 4751.
- J. Wei, Q. Yue, Z. Sun, Y. Deng, D. Zhao, *Angew. Chem. Int. Ed.*, 2012, **51**, 6149.
- W. Zhao, Z. Ma, D. Yan, J. Xu, H. Chen, *Anal. Chem.*, 2012, **84**, 10518.
- H. Görner, *J. Photoch. Photobio. B.*, 2007, **87**, 73.
- H. Wu, X. Huang, M. Gao, X. Liao, B. Shi, *Green Chem.*, 2011, **13**, 651.
- L. Chen, J. Ma, X. Li, J. Zhang, J. Fang, Y. Guan, P. Xie, *Environ. Sci. Technol.*, 2011, **45**, 3925.
- L. Yi, H. Zhao, S. Chen, L. Jin, D. Zheng, Z. Wu, *Talanta*, 2003, **61**, 403.
- Y. Yao, Y. Mao, Q. Huang, L. Wang, Z. Huang, W. Lu, W. Chen, *J. Hazard. Mater.*, 2014, **264**, 323.
- X. Yang, X. Xu, J. Xu, Y. Han, *J. Am. Chem. Soc.*, 2013, **135**, 16058.
- P. J. Thornalley, A. Stern, *Carbohydr. Res.*, 1984, **134**, 191.
- Y. Huang, W. Ma, J. Li, M. Cheng, J. Zhao, *J. Phys. Chem. B*, 2003, **107**, 9409.