

Supporting Information

Accelerated alkaline activation of peroxydisulfate by reduced rubidium tungstate nanorods for enhanced degradation of bisphenol A

Jian Hu, Xiangkang Zeng*, Yichun Yin, Yue Liu, Yang Li, Xiaoyi Hu, Lian Zhang, Xiwang
Zhang

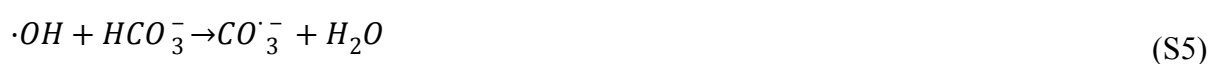
Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia

*Corresponding authors.

E-mail address: xiangkang.zeng@monash.edu (X. Zeng).

Text S1. Effects of HCO_3^- groups.

The BPA degradation efficiency was dramatically decreased from 92.0% to 35.2% when HCO_3^- coexists in the alkaline rRT/PDS system. After further investigation, the HCO_3^- affects the reaction in the following two aspects. Firstly, the pH of the solution decreased to 9.3 after adding 50 mM HCO_3^- groups since HCO_3^- can react with OH^- groups to generate CO_3^{2-} and H_2O (Eq. S1). According to the result in Fig. 3a, lower pH will result in a decrease of BPA degradation. Hence the degradation efficiency of BPA was affected a lot. Secondly, HCO_3^- can quench $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ and generate $\text{CO}_3^{\cdot-}$ and $\text{HCO}_3^{\cdot-}$ radicals (Eqs. S2-S5)². According to the previous study of Hu et al.¹, $\text{CO}_3^{\cdot-}$ and $\text{HCO}_3^{\cdot-}$ radicals can also contribute to BPA degradation. Therefore, it would be hard to investigate the exact reason why the presence of HCO_3^- reduced BPA degradation in this reaction.



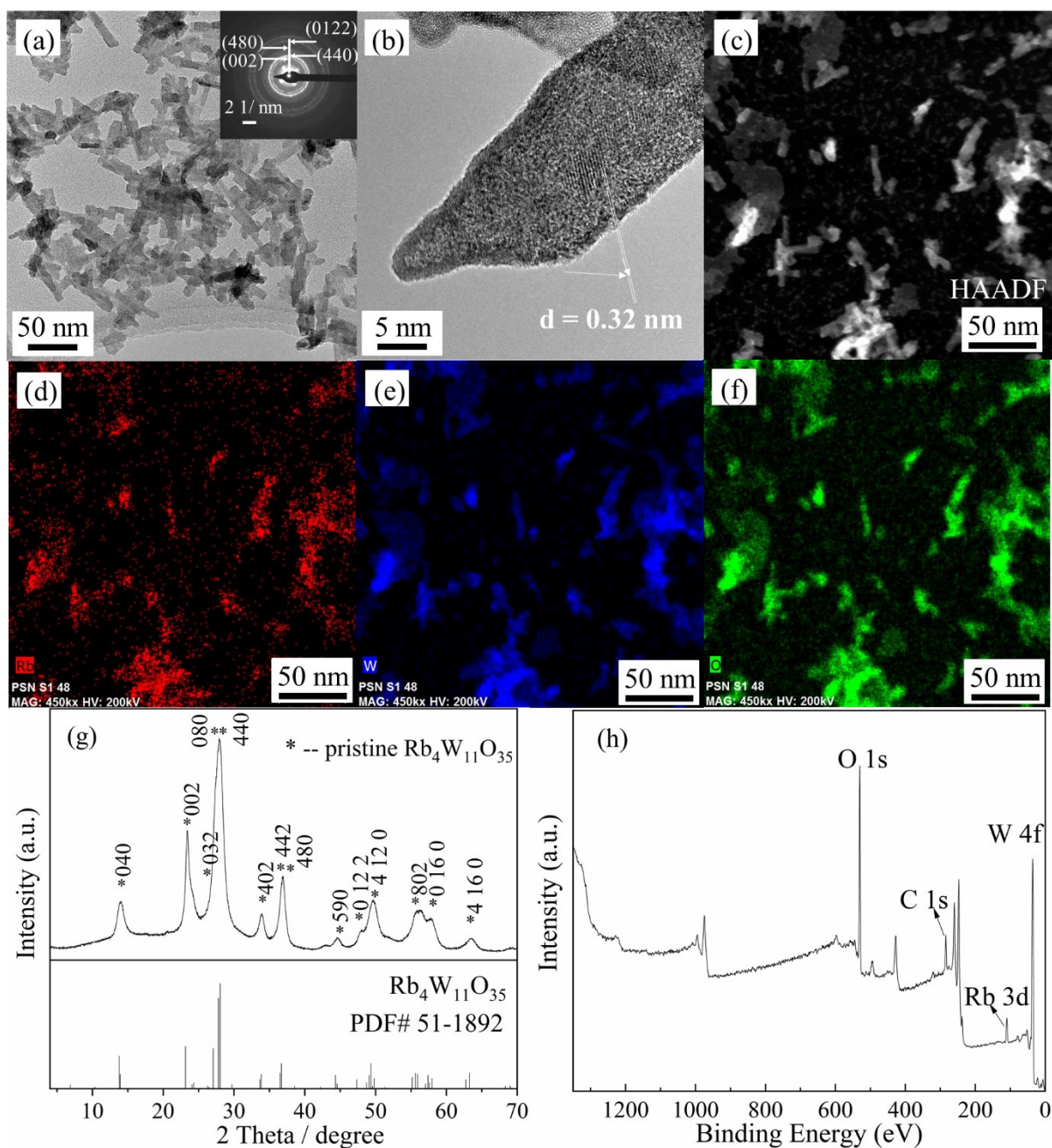


Figure. S1. (a) TEM and (b) HRTEM images of pristine $\text{Rb}_4\text{W}_{11}\text{O}_{35}$ materials. (c) HAADF-STEM image and (d) rubidium, (e) tungsten and (f) oxygen elemental mapping images of pristine $\text{Rb}_4\text{W}_{11}\text{O}_{35}$. (g) XRD pattern and (h) XPS survey spectra of the pristine $\text{Rb}_4\text{W}_{11}\text{O}_{35}$ nanorods.

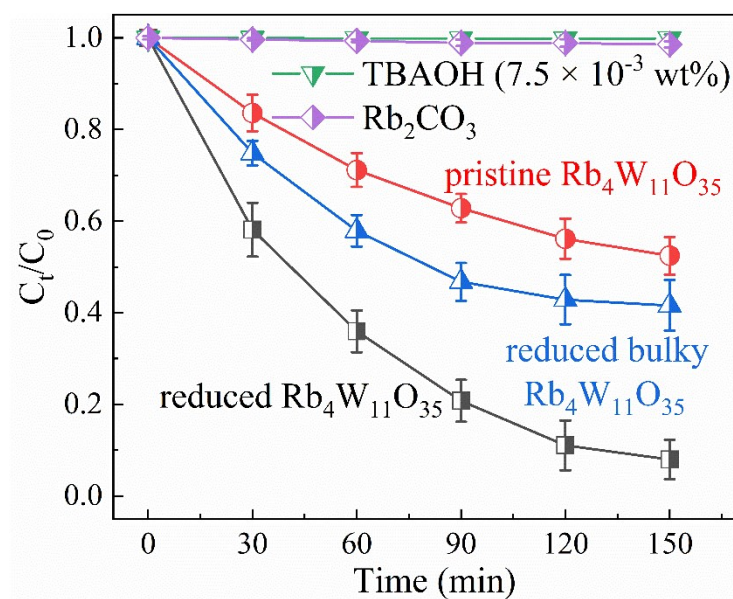


Figure. S2. The BPA removal efficiency by reduced $\text{Rb}_4\text{W}_{11}\text{O}_{35}$ nanorods, reduced bulk $\text{Rb}_4\text{W}_{11}\text{O}_{35}$, pristine $\text{Rb}_4\text{W}_{11}\text{O}_{35}$, Rb_2CO_3 and TBAOH. Reaction conditions: 2 μM catalysts, 20 mM PDS, 5 mg/L BPA, initial pH = 11.0, $T = 293$ K.

Table S1. Comparison of different catalysts for base activation of PDS.

Catalyst	Pollutants (mM)	PDS dosage (mM)	Catalyst dosage (g/L)	pH values	Time used for removal	Pseudo first-order rate constant (<i>k</i>)	R ² values	References
NaHCO ₃	Acetaminophen, 0.01	10	2.1	8.3	7 h, 70%	0.17 h ⁻¹	-	3
Glucose	Nitrobenzene, 1	200	0.9	12.5	8h, 98%	-	-	4
Mn _{0.6} Zn _{0.4} -Fe ₂ O ₄	BPA, 0.1	5	0.5	9.0	60min, 78%	-	-	5
Magnetite/Cu ²⁺	Anisole, 0.1	1.1	Magnetite- 0.5 Cu ²⁺ -6.4×10 ⁻³	11.0	22h,58%	-	-	6
Carbon nanotubes	Phenol, 0.1	1.0	0.1	11.0	60min, 90%	0.0146 min ⁻¹	0.935	7
rGO-Ag ₀ /Fe ₃ O ₄	BPA, 0.01	1.0	0.1	10.0	3h, 20%	-	-	8
reduced Rb ₄ W ₁₁ O ₃₅	BPA, 0.02 (5 mg/L)	20	5.8×10 ⁻³ g/L (2 μM)	11.0	150 min, 92 %	0.0173 min ⁻¹	0.9957	This work

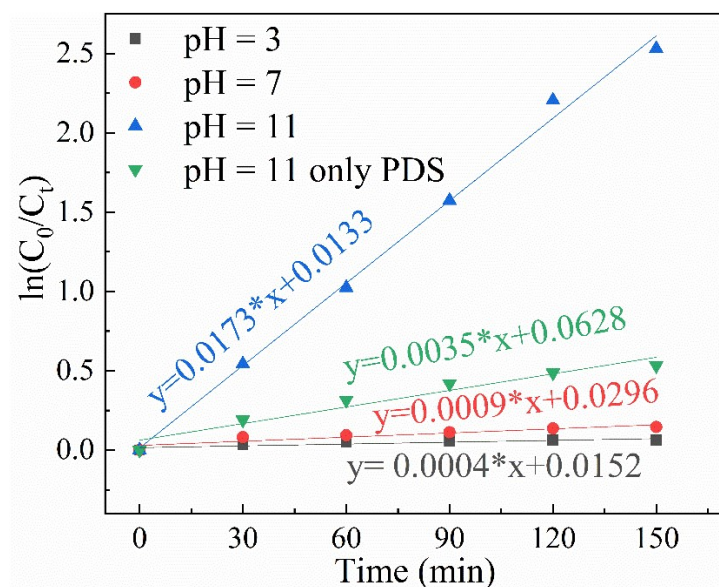


Figure. S3. Pseudo first-order kinetic curves of BPA removal under different initial pH values and conditions. Reaction conditions: 2 μM reduced $\text{Rb}_4\text{W}_{11}\text{O}_{35}$ nanorods, 20 mM PDS, 5 mg/L BPA, $T = 293\text{ K}$.

Table S2. Comparison of pseudo first-order rate constants under different initial pH values and conditions.

pH	Pseudo first-order rate constant (k_{obs} , min^{-1})	R^2 values
3	0.0004	0.8025
7	0.0009	0.8628
11	0.0173	0.9957
11 (only PDS)	0.0035	0.9458

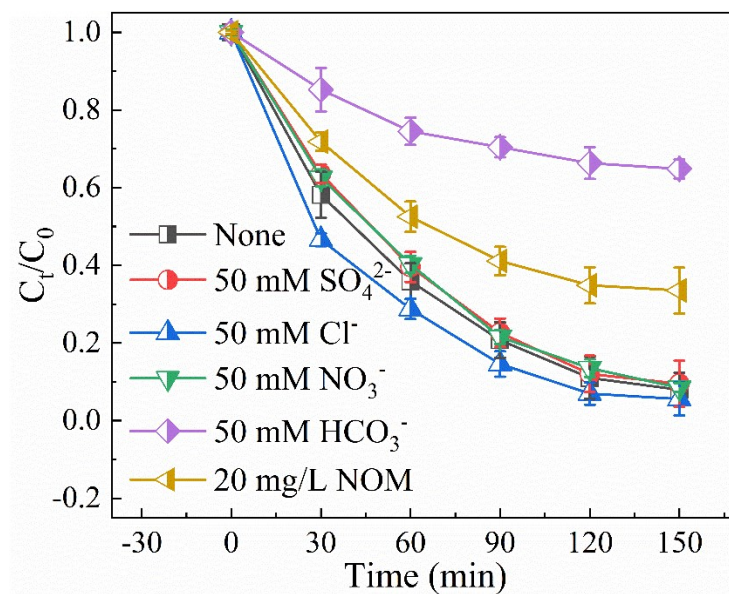


Figure. S4. Effects of inorganic anions SO_4^{2-} , Cl^- , NO_3^- , HCO_3^- and NOM on the degradation of BPA in the alkaline rRT/PDS system. Reaction conditions: 2 μM reduced $\text{Rb}_4\text{W}_{11}\text{O}_{35}$ nanorods, 20 mM PDS, 5 mg/L BPA, initial pH = 11.0, $T = 293$ K.

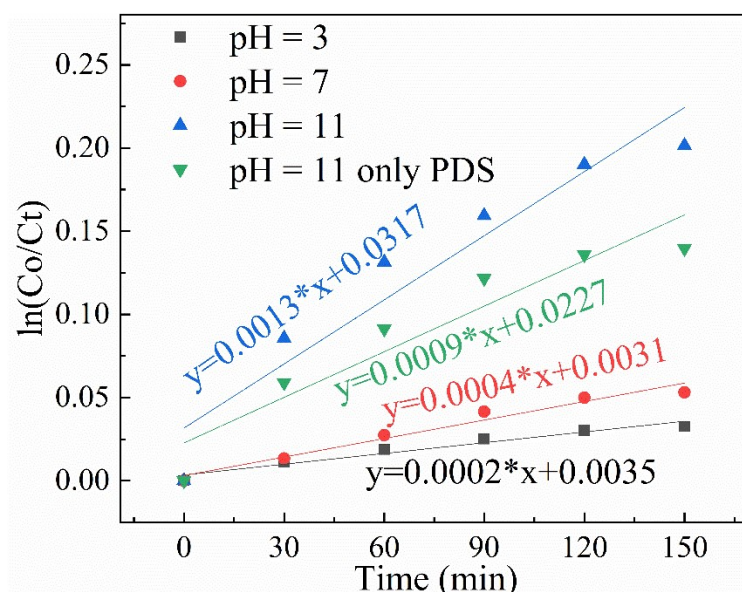


Figure. S5. Pseudo first-order kinetic curves of PDS decomposition under different initial pH values and conditions. Reaction conditions: 2 μM reduced $\text{Rb}_4\text{W}_{11}\text{O}_{35}$ nanorods, 20 mM PDS, 5 mg/L BPA, $T = 293 \text{ K}$.

Table S3. Comparison of pseudo first-order rate constants of PDS decomposition under different initial pH values and conditions.

pH	Pseudo first-order rate constant ($k_{\text{obs}}, \text{min}^{-1}$)	R^2 values
3	0.0002	0.9532
7	0.0004	0.9653
11	0.0013	0.914
11 (only PDS)	0.0009	0.8989

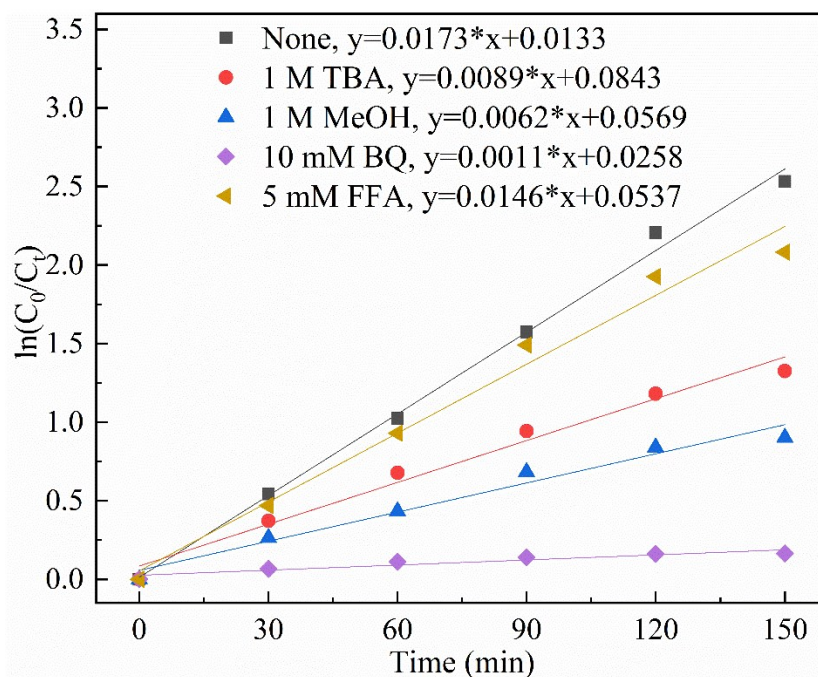


Figure. S6. Pseudo first-order kinetic curves of each quenching test. Reaction conditions: 2 μ M reduced $\text{Rb}_4\text{W}_{11}\text{O}_{35}$ nanorods, 20 mM PDS, 5 mg/L BPA, initial pH = 11.0, $T = 293$ K.

Table S4. Comparison of pseudo first-order rate constants under different quenching tests.

Radicals Scavengers	Pseudo first-order rate constant (k_{obs} , min^{-1})	R^2 values
none	0.0173	0.9957
1 M TBA	0.0089	0.9809
1 M MeOH	0.0062	0.9724
10 mM BQ	0.0011	0.9025
5 mM FFA	0.0146	0.9826

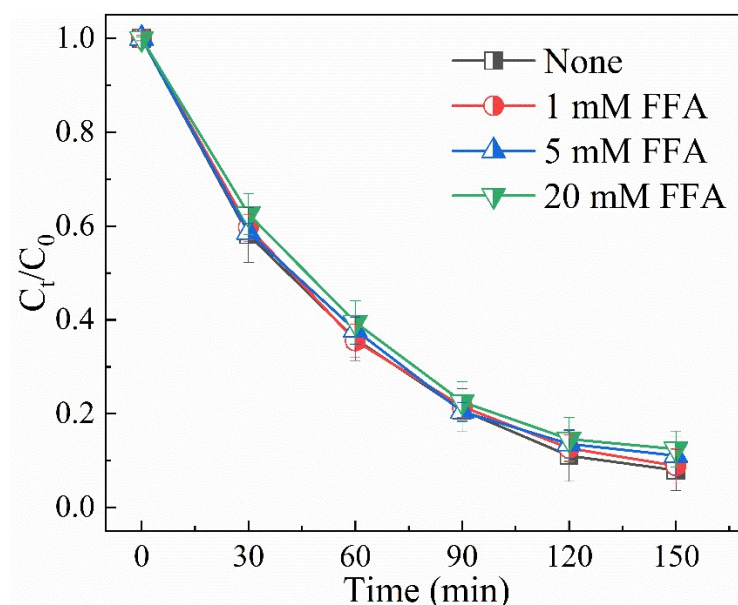


Figure. S7. Effect of FFA with different concentrations: 1, 5 and 20 mM on the degradation of BPA. Reaction conditions: 2 μ M reduced $\text{Rb}_4\text{W}_{11}\text{O}_{35}$ nanorods, 20 mM PDS, 5 mg/L BPA, initial pH = 11.0, $T = 293$ K.

References:

1. L. Hu, G. Zhang, M. Liu, Q. Wang and P. Wang, Enhanced degradation of Bisphenol A (BPA) by peroxymonosulfate with $\text{Co}_3\text{O}_4\text{-Bi}_2\text{O}_3$ catalyst activation: effects of pH, inorganic anions, and water matrix, *Chemical Engineering Journal*, 2018, **338**, 300-310.
2. A. Ghauch and A. M. Tuqan, Oxidation of bisoprolol in heated persulfate/ H_2O systems: kinetics and products, *Chemical Engineering Journal*, 2012, **183**, 162-171.
3. M. Jiang, J. Lu, Y. Ji and D. Kong, Bicarbonate-activated persulfate oxidation of acetaminophen, *Water research*, 2017, **116**, 324-331.
4. R. J. Watts, M. Ahmad, A. K. Hohner and A. L. Teel, Persulfate activation by glucose for in situ chemical oxidation, *Water research*, 2018, **133**, 247-254.
5. B. Deng, Y. Li, W. Tan, Z. Wang, Z. Yu, S. Xing, H. Lin and H. Zhang, Degradation of bisphenol A by electro-enhanced heterogeneous activation of peroxydisulfate using Mn-Zn ferrite from spent alkaline Zn-Mn batteries, *Chemosphere*, 2018, **204**, 178-185.
6. J. Chen, X. Zhou, Y. Zhu, Y. Zhang and C.-H. Huang, Synergistic Activation of Peroxydisulfate with Magnetite and Copper Ion at Neutral Condition, *Water Research*, 2020, 116371.
7. W. Ren, L. Xiong, X. Yuan, Z. Yu, H. Zhang, X. Duan and S. Wang, Activation of peroxydisulfate on carbon nanotubes: Electron-transfer mechanism, *Environmental science & technology*, 2019, **53**, 14595-14603.
8. C. M. Park, J. Heo, D. Wang, C. Su and Y. Yoon, Heterogeneous activation of persulfate by reduced graphene oxide–elemental silver/magnetite nanohybrids for the oxidative degradation of pharmaceuticals and endocrine disrupting compounds in water, *Applied Catalysis B: Environmental*, 2018, **225**, 91-99.