# Supplementary information

## High-Loaded Single Cu Atoms Decorated On N-doped Graphene for Boosting Fenton-like Catalysis under Neutral pH

Qianyuan Wu[a], Jin Wang[b], Zhiwei Wang[c], Yalan Xu[c], Zhihui Xing[a], Xinyang Zhang[a], Yuntao Guan[a], Guangfu Liao[d]*, Xinzheng Li[a]*

[a]Key Laboratory of Microorganism Application and Risk Control of Shenzhen, Guangdong Provincial Engineering Research Center for Urban Water Recycling and Environmental Safety, Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, China.

[b]College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China.

[c]China Shenzhen Environmental Science and New Energy Technology Engineering Laboratory, Tsinghua-Berkeley Shenzhen Institute, Shenzhen 518055, China.

[d]School of Materials Science and Engineering, Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, Guangdong Laboratory of High-Performance Polymer Composites, Sun Yat-sen University, Guangzhou 510275, China.

* Corresponding author. liaogf@mail2.sysu.edu.cn (Liao G.)

Tel.: (+86-755) 2603-6326. E-mail addresses: lxzq@sz.tsinghua.edu.cn (Li X.)

## *Experimental Section*

**Synthesis of Cu-nanoparticles supported on N-graphene (Cu-NP/NGO-800)**. The synthesis method was the same as that of Cu-SA/NGO-800, except the desired amount of $Na_2CO_3$ and NaOH were added to solution A to adjust pH=10 before adding solution B.

**Synthesis of Arbutus-shape CuO catalyst.** The CuO catalyst was prepared using a one-step hydrothermal technique. In a typical experiment, the desired amount of 20 g/L $Cu(NO_3)_2 \cdot 3H_2O$ as Cu precursor was completely dissolved in 20 mL of distilled water. After stirring for 30 min, a certain amount of 3 mmol/L $Na_2CO_3$ solution was added until the mixed solution reached pH=9 and then 3.8 mmol/L NaOH solution was added until the mixed solution reached pH=10. The mixture stirred for 30 min and then transferred into a Teflon-lined stainless autoclave (100 mL). The autoclave was sealed and maintained at 150 $^oC$ for 12 h. The powders were collected by filtration and alternatively washed with distilled water and ethanol for several times, finally dried at 80 $^oC$ for 4 h. The resulting sample was denoted as CuO. Besides, Cu-HT/NGO was prepared following the same procedure of CuO except adding 50 mg NGO before adjusting pH.

***XAFS measurements.*** The Tungsten LIII-edges XAFS spectra of the standards and samples were collected at the beamline BL1W1B of the Beijing Synchrotron Radiation Facility (BSRF). The typical energy of the storage ring was 1.5 GeV and the electron current was 180 mA in the top-up mode. The white light was monochromatized by a Si (111) double-crystal monochromator and calibrated with a

W foil (LIII edge 10207 eV). Samples were pressed into thin slices, and positioned at 90° to the incident beam in the sample-holder. The XAFS spectra were recorded in transmission mode with two ion chambers.

The XAFS data were analyzed using the software packages Demeter [1]. The spectra were normalized using Athena firstly, and then shell fittings were performed with Artemis. The $\chi$(k) function was Fourier transformed (FT) using $k^3$ weighting, and all fittings were done in R-space. The amplitude reduction factor ($S_0^2$) was estimated to be 0.827 according to the fitting results of the W foil. The coordination parameters of sorption samples were obtained by fitting the experimental peaks with theoretical amplitude.

To further investigate the first-shell backscattering atoms and detect light and heavy scatters, wavelet transform (WT) analysis was employed using the Igor pro script developed by Funke et al. [2]. This qualitative analysis was primarily focused on the nature of the backscattering atoms as well as the bond lengths owing to the fine resolution in both wavenumbers k and radial distribution function R, and complemented the limitation of FT analysis. The Morlet wavelet was chosen as basis mother wavelet and the parameters ($\eta$ = 8, $\sigma$ = 1) were used for a better resolution in the wave vector k.

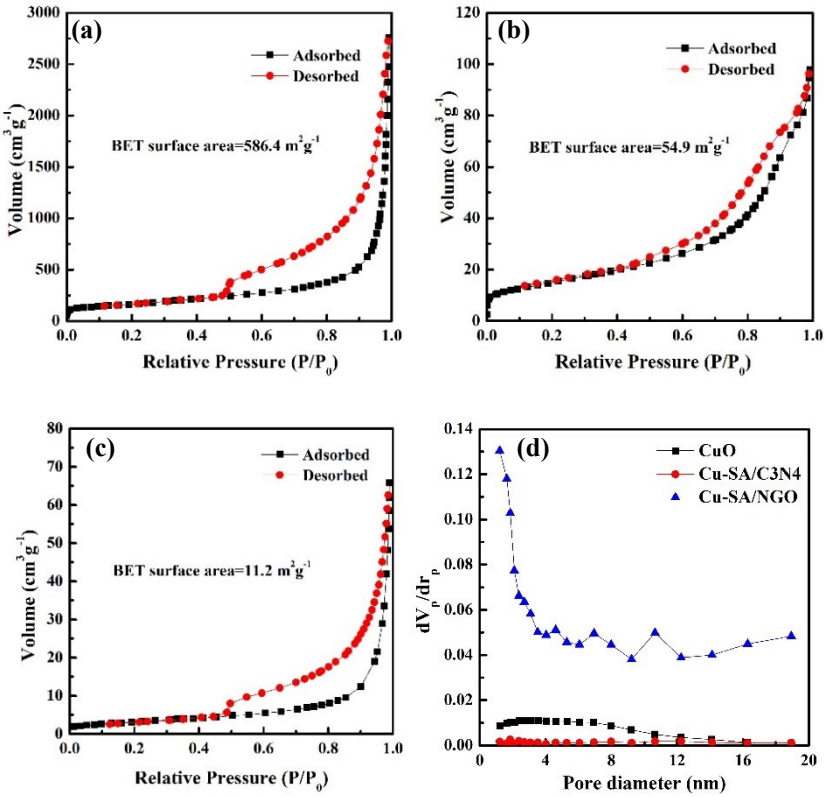


**Fig. S1** $N_2$ adsorption-desorption isotherms of (a) Cu-SA/NGO, (b) Cu-SA/$C_3N_4$, (c) CuO and pore diameter distribution of Cu-SA/NGO, Cu-SA/$C_3N_4$ and CuO.

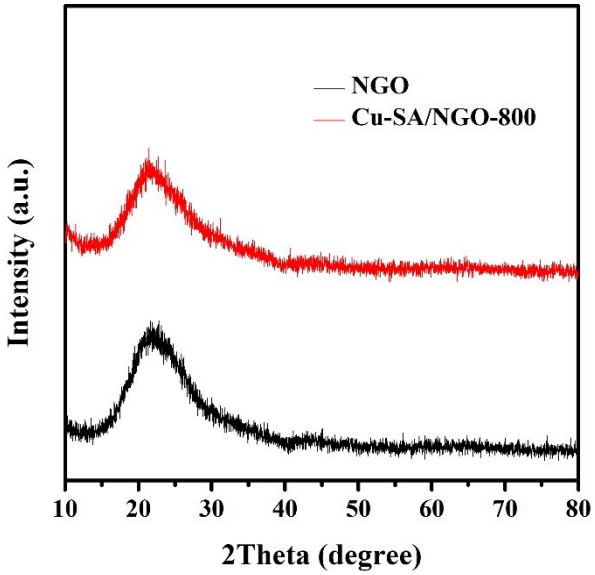


**Fig. S2** XRD patterns of Cu-SA/NGO-800 and NGO.

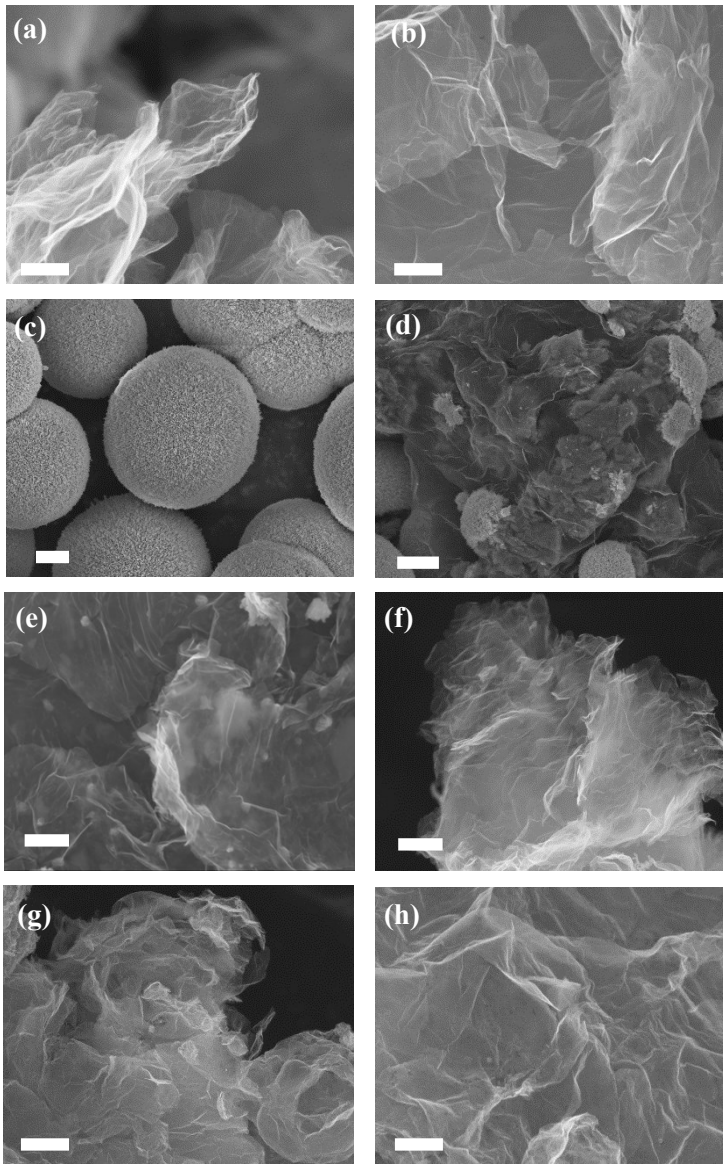


**Fig. S3** Scanning electron microscope (SEM) images GO (a), NGO (b), CuO (c), Cu-HT/NGO (d), Cu-NP/NGO (e), Cu-SA/NGO-800 (f), Cu-SA/NGO-850 (g), Cu-SA/NGO-900 (h). Scale bars: (a) 200 nm, (b) 200 nm, (c) 500 nm, (d) 1 μm, (e) 200 nm, (f) 500 nm, (g) 1 μm, (h) 200 nm.

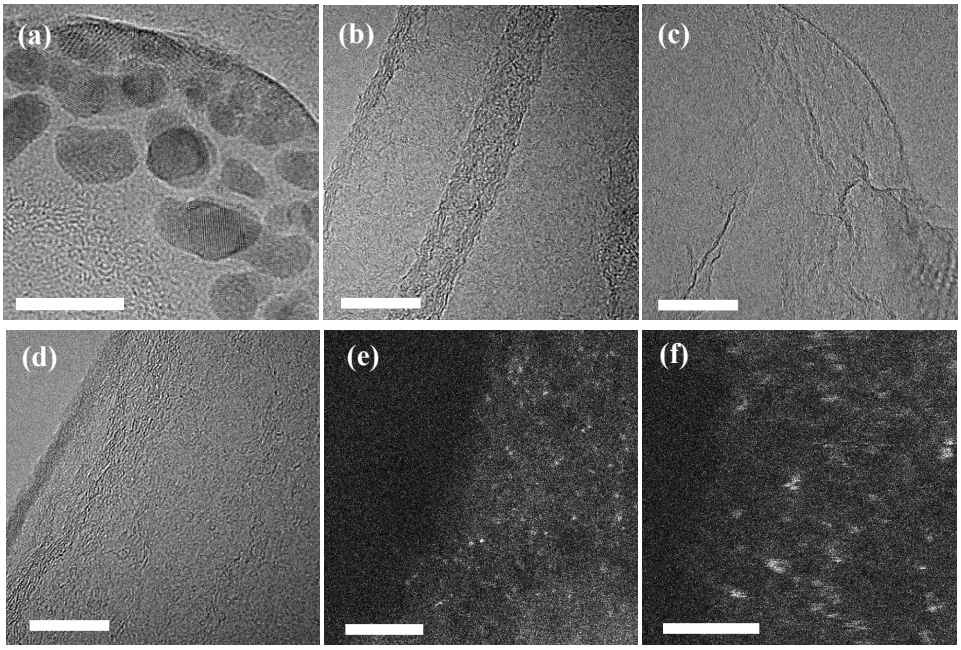


**Fig. S4** HRTEM images of Cu-NP/NGO (a), Cu-SA/NGO-800 (b), Cu-SA/NGO-850 (c), Cu-SA/NGO-900 (d) and HAADF-HRTEM images of Cu-SA/NGO-850 (e), Cu-SA/ NGO-900 (f). Scale bars: (a) 10 nm, (b) 10 nm, (c) 10 nm, (d) 10 nm, (e) 2 nm, (f) 1 nm.

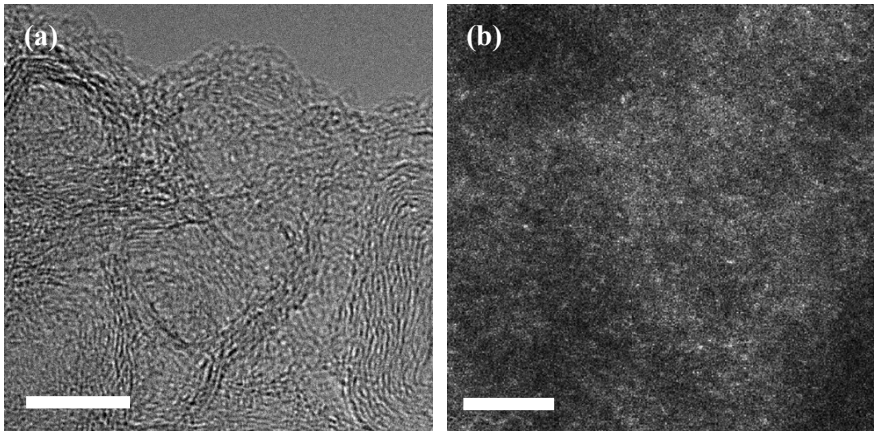


**Fig. S5** HRTEM and HAADF-HRTEM images of Cu-SA/$C_3N_4$. Scale bars: (a) 10 nm, (b) 1 nm.

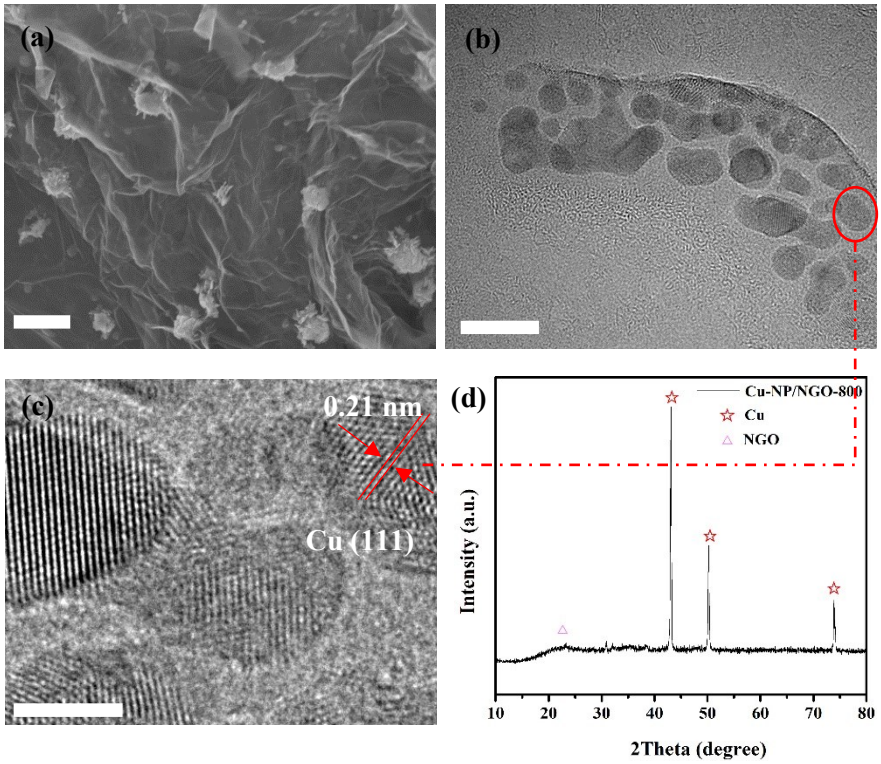


**Fig. S6** SEM (a), HRTEM (b), enlarged HRTEM images of Cu-NP/NGO-800 (c), and XRD pattern of Cu-NP/NGO-800 (d). Scale bars: (a) 200 nm, (b) 10 nm, (c) 2 nm.

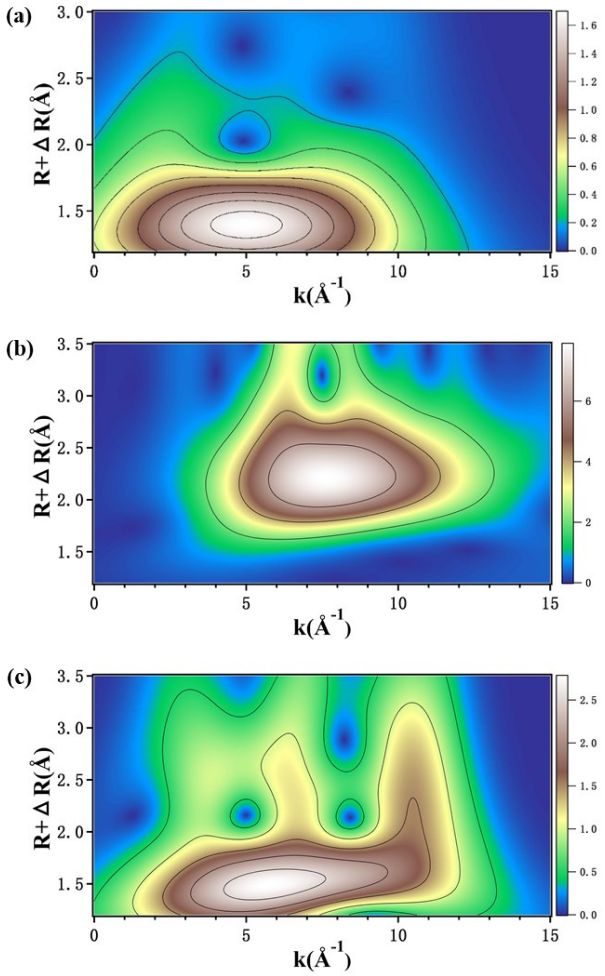


**Fig. S7** The Wavelet transform-EXAFS of Cu-SA/NGO (a), Cu foil (b) and CuO (c).

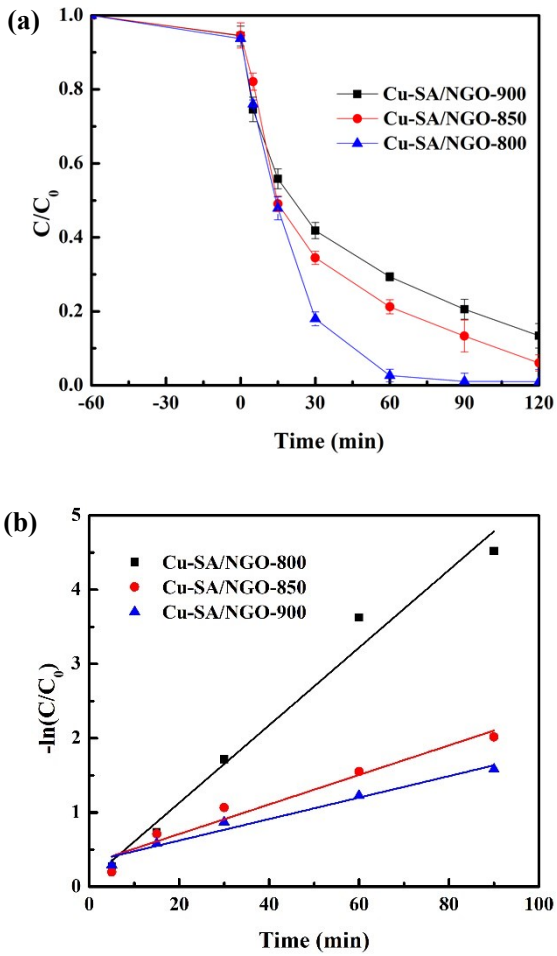


**Fig. S8** Fenton-like degradation of APAP over Cu-SA/NGO-800, Cu-SA/NGO- 850 and Cu-SA/NGO-900 catalysts (a) and its pseudo-first-order kinetic model fitting curves (b). Reaction conditions: 20 mg/L paracetamol, pH=7, 20 mM $H_2O_2$, 0.05 g/L catalyst, 303 K.

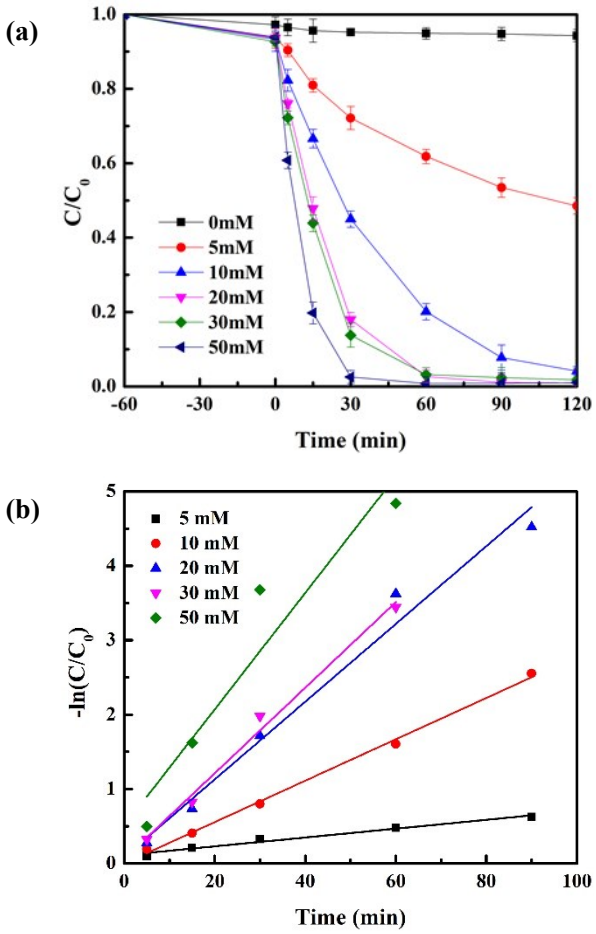


**Fig. S9** The effects of $H_2O_2$ concentration over Cu-SA/NGO-800 catalyst on paracetamol degradation. Reaction conditions: 20 mg/L APAP, pH=7, 0.05 g/L catalyst, 303 K.

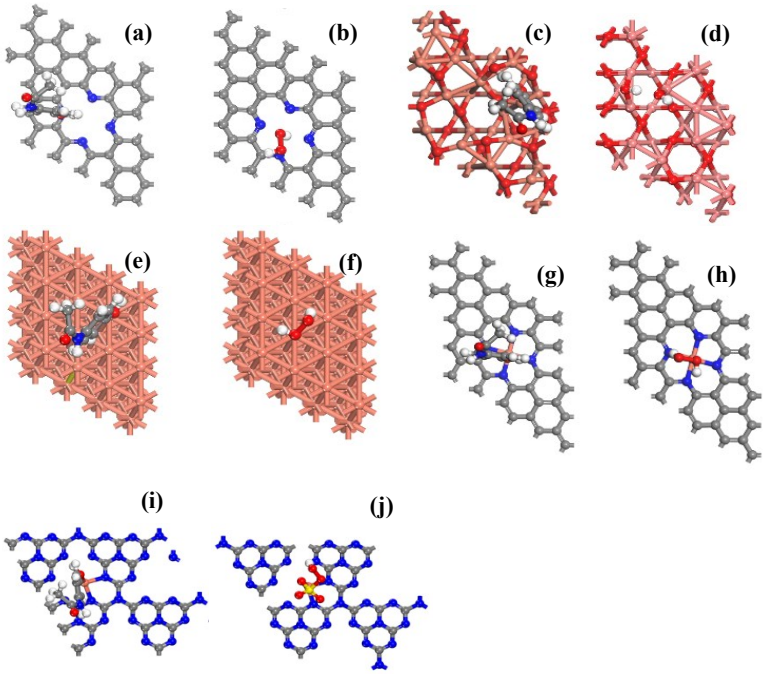


**Fig. S10** Local adsorption configurations of APAP on (a) NGO, (b) Cu, (c) CuO, (d) Cu-SA/NGO and (i) Cu-SA/$C_3N_4$; adsorption configurations of $H_2O_2$ adsorbed on (e) NGO, (f) Cu, (g) CuO, (h) Cu-SA/NGO and (j) Cu-SA/$C_3N_4$. Cu (orange), C (gray), N (blue), hydrogen (white), oxygen (red).

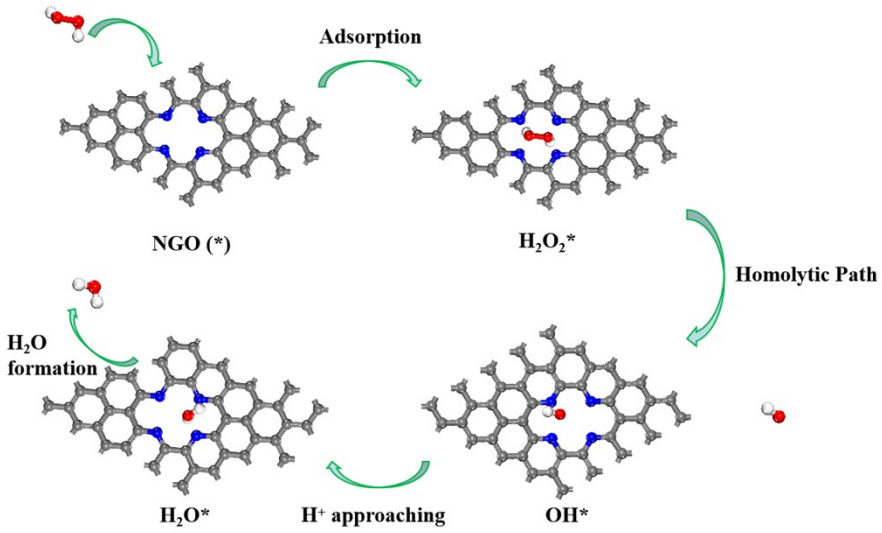


**Fig. S11** First principle calculations on the proposed reaction mechanism schematics of NGO in Fenton reaction toward generating •OH under acidic (protonated) catalytic milieu.

**Table S1.** Summary of metal loading of single-atom-embedded graphene

| Catalyst | Metal element | metal loading (wt.%) | Ref. |
|---|---|---|---|
| Cu-SA/NGO | Cu | 5.8 | This work |
| Cu/G | Cu | 5.4 | [3] |
| Cu-$N_4$-C | Cu | 4.9 | [4] |
| FeCo-NC | Co | 3.4 | [5] |
| Co-NG | Co | 2.31 | [6] |
| Pt/GO | Pt | 2.67 | [7] |
| Ni-NG | Ni | 2.07 | [8] |
| $Co_1$-G | Co | 1.2 | [9] |
| Ru-N/G-750 | Ru | 1.7 | [10] |
| SANi-NG | Ni | 2.26 | [11] |

**Table S2.** The catalytic performance comparison of recently reported Fenton-like catalysts for $H_2O_2$ activation.

| Catalyst (loading, g/L) | $H_2O_2$ (mmol/L) | Pollutant (mg/L) | pH | Removal effeciency | Ref |
|---|---|---|---|---|---|
| CQDs/Cu-MIO (0.25) | 48.5 | OFX (12) | 6.4 | 100% (40 min) | [12] |
| d-g-$C_3N_4$–Cu (2.0) | 10 | BPA (25) | 7 | 90% (10 min) | [13] |
| Cu-MSMs (0.058) | 10 | PHT (10) | 7 | 96% (60 min) | [14] |
| BiCu9/$Bi^0$ (1.4) | 20 | 2-CP (10) | 6 | 100% (120 min) | [15] |
| CuVOx (1.0) | 50 | FLC (20) | 5 | 100% (90 min) | [16] |
| $LaAl_{0.95}Cu_{0.05}O_3$ (1.0) | 10 | 2-CP (10) | 7 | 100% (120 min) | [17] |
| CuCN-500 (1.0) | 300 | BPA (10) | 7 | 96% (60 min) | [18] |
| CuCN-500 (0.2) | 300 | TC (10) | 7 | 100% (30 min) | [18] |
| 2.5wt%Cu/TUD-1 (0.1) | 90 | BPA (100) | 3.5 | 95% (180 min) | [19] |
| 7.5CuY (1.0) | 52.2 | Congo red (99.62) | 7 | 93.6% (150 min) | [20] |
| $LaTi_{0.4}Cu_{0.6}O_3$ | 20 | RhB (8) | 6.8 | 94% (120 min) | [20] |
| γ-Cu-$Al_2O_3$-$Bi_{12}O_{15}C_{l6}$ (1.0) | 8 | BPA (20) | 7 | | [21] |
| MSACM (1.0) | 48.9 | Phenol (80) | 4 | 64% (120 min) | [22] |
| 5Cu/$Al_2O_3$-750 (1.0) | 1000 | RhB (10) | 5.14 | 95% (30 min) | [23] |
| Cu-$Al_2O_3$-4.5wt%g-$C_3N_4$ (0.5) | 12.5 | RhB (10) | 7 | 45% (10 min) | [24] |
| 5Fe2.5Cu-$Al_2O_3$（1.0） | 29.9 | NB (100) | 3 | 94% (30 min) | [25] |
| 2.5wt%Cu/TUD-1（0.1） | 90 | BPA (100) | 3.5 | 95% (180 min) | [26] |
| Cu-SA/NGO (0.05) | 20 | APAP | 7 | 97% (60 min) | This work |

**Reference**

[1] H. Funke, A.C. Scheinost and M. Chukalina, *Phys. Rev. B.,* 2005, 71, 094110.

[2] B. Ravel and M. Newville, *J. Synchrotron. Radiat.,* 2005, 12, 537-541.

[3] G.K. Han, Y. Zheng, X. Zhang, Z.Q. Wang, Y. Gong, C.Y. Du, M.N. Banis, Y.M. Yiu,T.K. Sham, L. Gu, Y.R. Sun, Y.J. Wang, J.P. Wang, Y.Z. Gao, G.P. Yin and X.L. Sun, *Nano Energy,* 2019, **66**, 104088.

[4] W. Li, C.G. Min, F. Tan, Z.P. Li, B.S. Zhang, R. Si, M.L. Xu, W.P. Liu, L.X. Zhou, Q.M. Wei, Y.Z. Zhang and X.K. Yang, *ACS Nano,* 2019, 13, 3177-3187.

[5] X.N .Li, X. Huang, S.B. Xi, S. Miao, J. Ding, W.Z. Cai, S. Liu, X.L. Yang, H.B. Yang, J.J. Gao, J.H. Wang, Y.Q. Huang, T. Zhang and B. Liu, *J. Am. Chem. Soc.,* 2018, **140**, 12469-12475.

[6] C. Gao, S. Chen, Y. Wang, J. Wang, X. Zheng, J. Zhu, L. Song, W. Zhang and Y. Xiong, *Adv. Mater.,* 2018, **30**, 1704624.

[7] S.H. Sun, G.X. Zhang, N. Gauquelin, N. Chen, J.G. Zhou, S.L. Yang, W.F. Chen,X.B. Meng, D.S. Gen, M.N. Banis, R.Y. Li, S.Y. Ye, S. Knights, G.A. Botton, T.K. Sham and X.L. Sun, *Sci. Rep.,* 2013, **3**, 1775-1784.

[8] Jiang, K. S. Siahrostami, T. Zheng, Y. Hu, S. Hwang, E. Stavitski, Y. Peng, J. Dynes, M.Gangisetty, D. Su, K. Attenkofer and H. Wang, *Energy Environ. Sci.,* 2018, **11**, 893-903.

[9] C. Gao, S. Chen, Y. Wang, J. Wang, X. Zheng, J. Zhu, L. Song, W. Zhang and Y. Xiong, *Adv. Mater.,* 2018, **30**, 1704624.

[10] C. Zhang, J. Sha, H. Fei, M. Liu, S. Yazdi, J. Zhang, Q. Zhong, X. Zou, N. Zhao,

H. Yu, Z. Jiang, E. Ringe, B.I. Yakobson, J. Dong, D. Chen and J.M. Tour, *ACS Nano,* 2017, **11**, 6930-6941.

[11] P. Zhai, T. Wang, W. Yang, S. Cui, P. Zhang, A. Nie, Q. Zhang and Y. Gong, *Adv. Energy Mater.,* 2019, 9, 1804019.

[12] X.K. Tian, H. Jin, Y.L. Nie, Z.X. Zhou, C. Yang, Y. Li and Y.X. Wang, *Chem. Eng. J.,* 2017, 328, 397-405.

[13] N. Jiang, L. Lyu, G.F. Yu, L.L. Zhang and C. Hu, *J. Mater. Chem. A.,* 2018, 6, 17819-17828.

[14] L. Lyu, L.L. Zhang and C. Hu, *Chem. Eng. J.,* 2015, **274**, 298-306.

[15] L.L. Zhang, L. Lyu, Y.L. Nie and C. Hu, *Sep. Purif. Technol.,* 2016, **157**, 203-208.

[16] N.Q. Zhang, C.J. Xue, K. Wang and Z.Q. Fang, *Chem. Eng. J.,* 2020, **380**, 122516.

[17] H.H. Wang, L.L. Zhang, C. Hu, X.K. Wang, L. Lyu and G.D. Sheng, *Chem. Eng. J.,* 2018, **332**, 572-581.

[18] J.N. Zhu , X.Q. Zhu , F.F. Cheng, P. Li, F. Wang, Y.W. Xiao and W.W. Xiong, *Appl. Catal. B,* 2019, **256**, 117830.

[19] M.P. Pachamuthu, S. Karthikeyan, R. Maheswari and A.F. Lee , A. *Appl. Surf. Sci.,* 2017, **393**, 67-73.

[20] L. Singh, P. Rekha and S. Chand, *Sep. Purif. Technol.,* 2016, **170**, 321-336.

[21] L.L. Zhang, Y.L. Nie, C. Hu and J.H. Qu, *Appl. Catal. B,* 2012, **125**, 418-424

[22] Z.Q. Xie , J.J. Zhou, J.N. Wang, C.P. François-Xavier, T. Wintgens, *Appl. Catal.*

*B,* 2019, **253**, 28-40.

[23] Y.H. Ling, M.C. Long, P.D. Hu, Y. Chen and J.W. *J. Hazard. Mater.,* 2014, **264**, 195-202.

[24] Y.Y. Sheng, Y. Sun, J. Xu, J. Zhang and Y.F. Han, *AICHE J.,* 2017, **64**, 538-549

[25] S.Q. Xu, H.X. Zhu, W.R. Cao, Z.B. Wen and J.N. Wang, C.P. *Appl. Catal. B,* 2018, **234**, 223-233.

[26] Y. Sun, Z.X. Yang, P.F. Tian, Y.Y. Sheng, J. Xu and Y.F. Han, *Appl. Catal. B,* 2019, **244**, 1-10.