Electronic Supplementary Information For

Interfacial peroxidase-like catalytic activity of surface-immobilized cobalt phthalocyanine on multiwall carbon nanotubes

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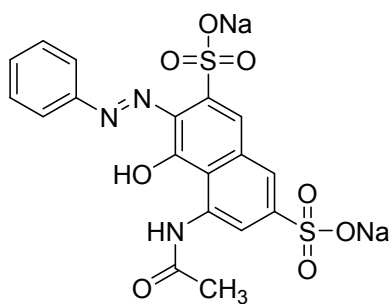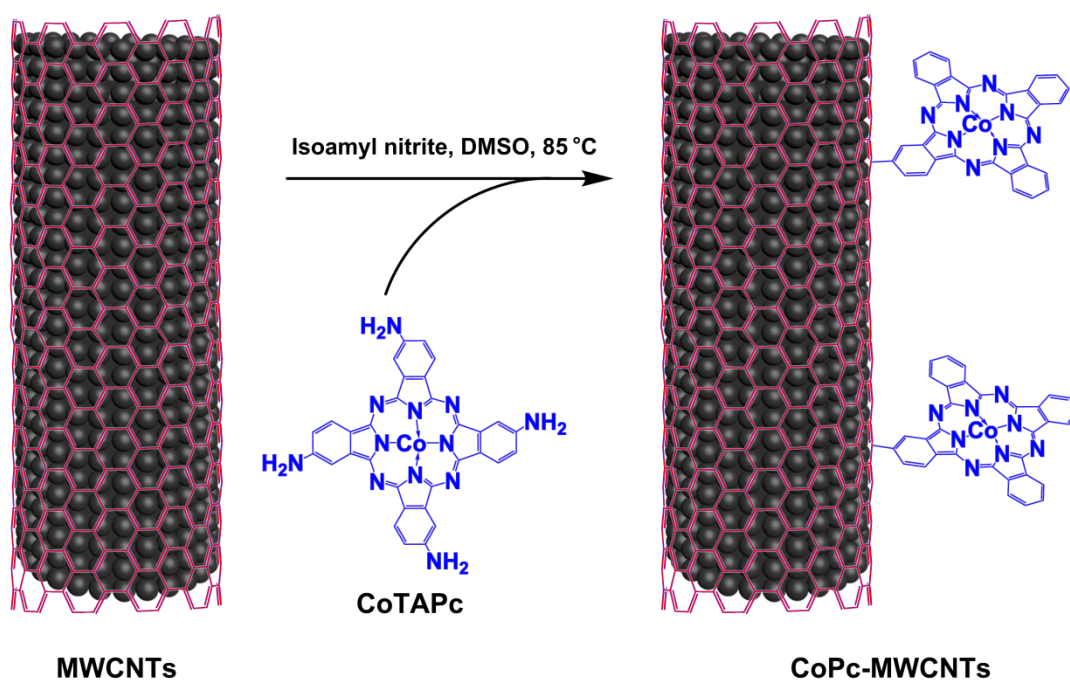E-mail:luwy@zstu.edu.cn(W. Lu); wxchen@zstu.edu.cn(W. Chen)

Fig. S1. The molecular structure of C.I. Acid Red 1 (AR1).

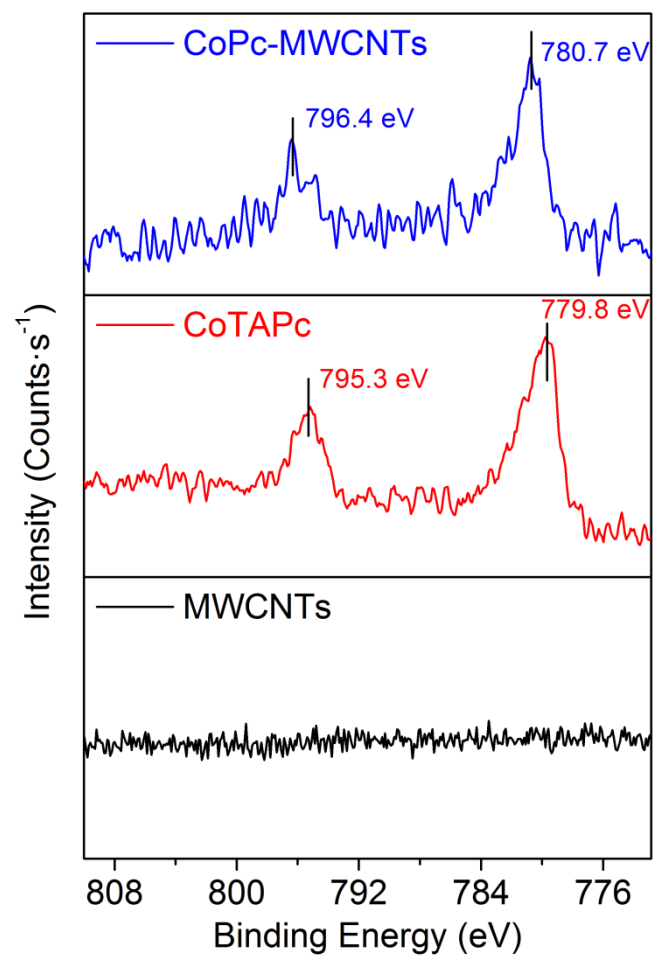**Fig. S2**. The synthesis of CoPc-MWCNTs.

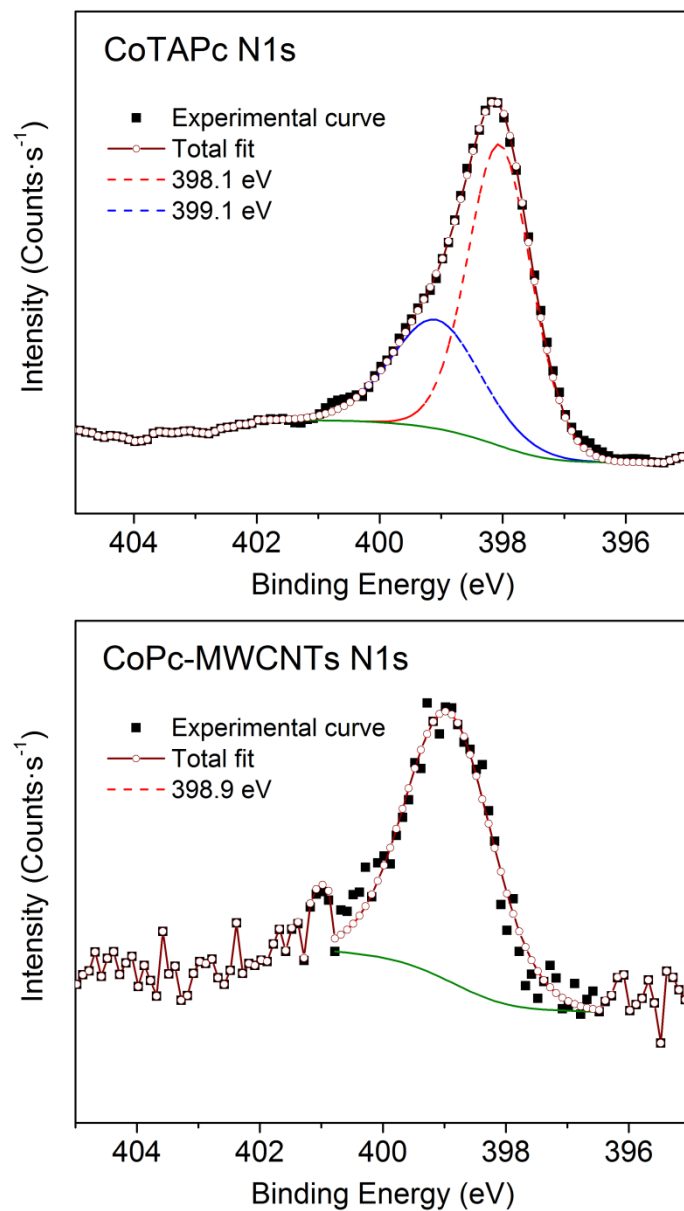**Fig. S3.** XPS Co 2p spectra of MWCNTs, CoTAPc and CoPc-MWCNTs.

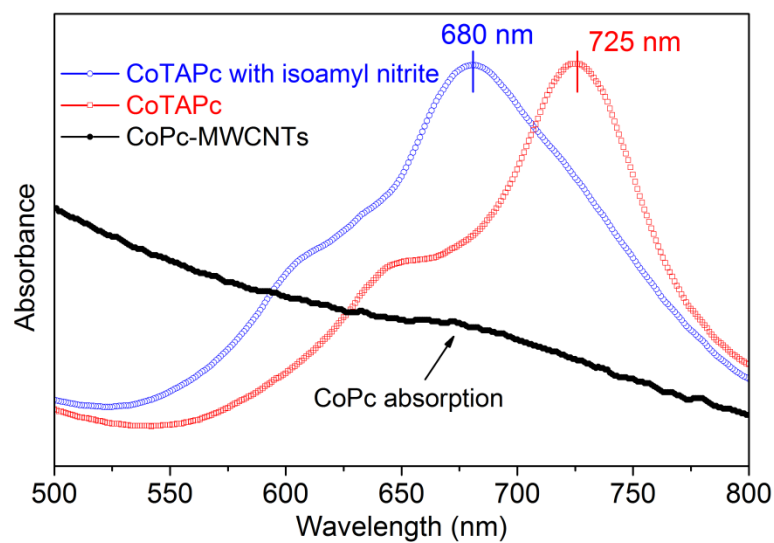**Fig. S4.** XPS N 1s spectra of CoTAPc and CoPc-MWCNTs.

Fig. S5. UV-vis spectra of CoTAPc, CoTAPc with isoamyl nitrite and CoPc-MWCNTs in
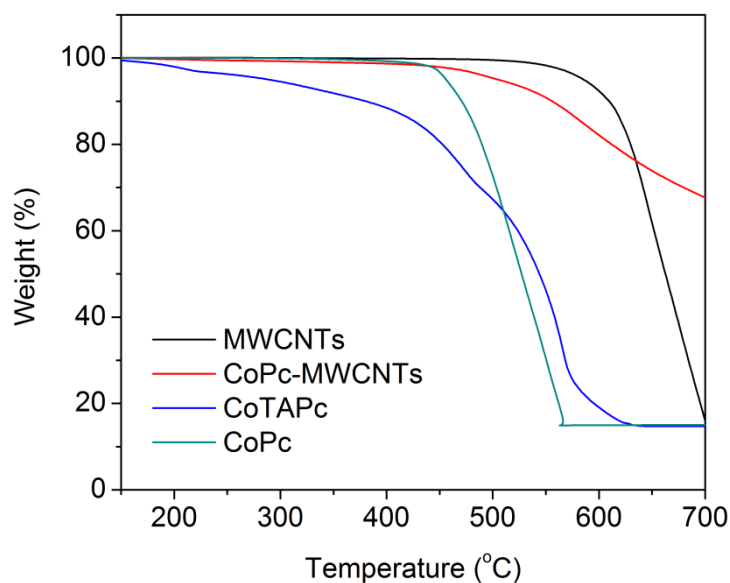
DMSO solution.

Fig. S6. Dynamic thermogravimetric analytical curves of CoPc, CoTAPc, MWCNTs and CoPc-

MWCNTs obtained in air.

Thermal stability was investigated by dynamic thermogravimetric analysis (TGA, Mettler

Toledo TGA/DSC1) at a heating rate of 20 °C/min using air as carrier gas.

Figure S6 shows the weight loss curves of CoPc, CoTAPc, MWCNTs and CoPc- MWCNTs

by TGA experiment using air as carrier gas. The oxidation of CoTAPc started at ~150 °C, while the weight loss of CoPc (without amino substituent groups) started from ~450 °C which exhibits higher thermal stability in air. This is due to the fact that the destruction of phthalocyanine ring with amino substituent groups take place more easily than that of the unsubstituted phthalocyanine. In addition, the oxidative decomposition of MWCNTs started at ~550 °C with a nearly compelete weight loss at ~710 °C. Importantly, the initial oxidation of CoPc-MWCNTs at ~450 °C is very similar to CoPc, and CoPc-MWCNTs exhibit better thermal stability than MWCNTs at temperatures as high as 850 °C. These results indicates that the direct bonding between CoPc and MWCNTs enhances the stability of them.
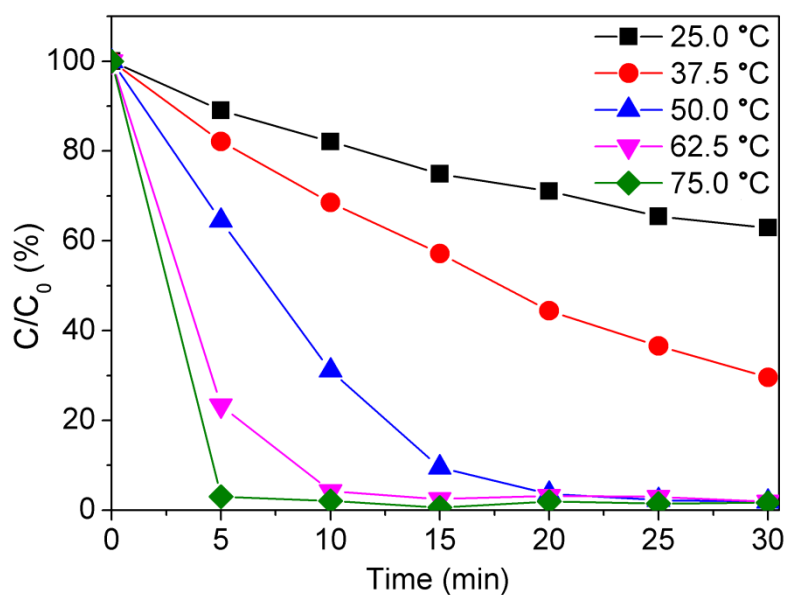

Fig. S7. Catalytic oxidation of AR1 (5×10^{-5}M) at different temperature. ([CoPc-MWCNTs]=0.2 g/L (containing 8.88×10^{-6} M of CoPc), [C_{12}-LAS]=5×10^{-3} M , [H_2O_2]=0.01 M, pH 7.55)
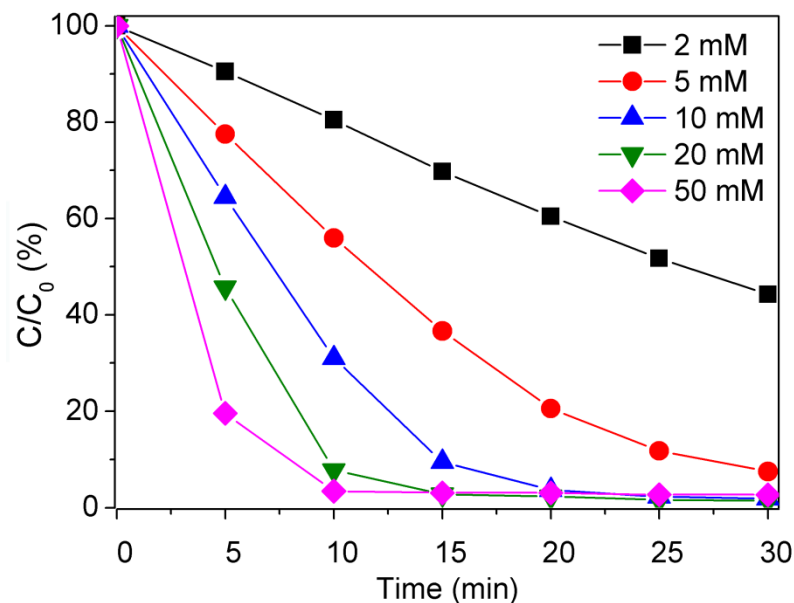
Fig. S8. Effect of H_2O_2 concentration on the catalytic oxidation of AR1 (5×10^{-5} M). ([CoPc-MWCNTs]=0.2 g/L (containing 8.88×10^{-6} M of CoPc), [C_{12}-LAS]=5×10^{-3} M, pH 7.55, 50 °C.)
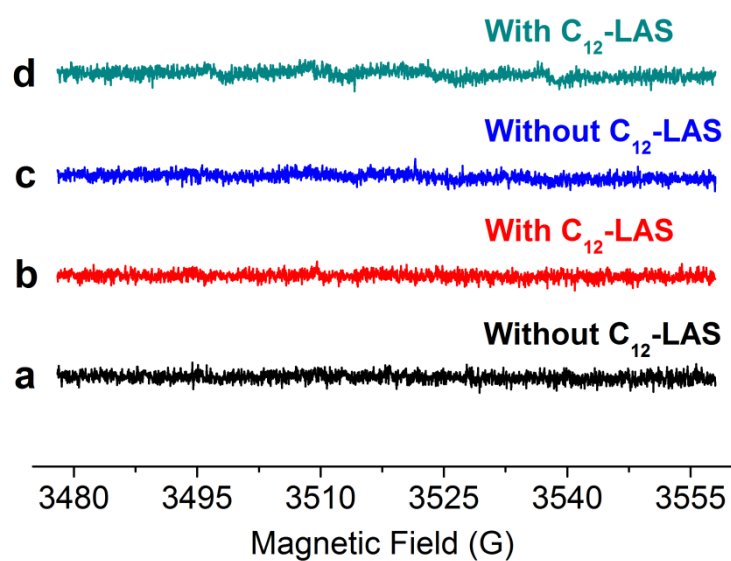

Fig. S9. DMPO spin-trapping EPR spectra in AR1 (5×10^{-5} M) aqueous (curve a and b) and ethanol (curve c and d) solution with and without C_{12}-LAS after reaction for 100s. ([CoPc-MWCNTs]=0.2 g/L (containing 8.88×10^{-6} M of CoPc), [C_{12}-LAS]=5×10^{-3} M , [H_2O_2]=0.01 M, [DMPO]=0.02 M, pH 7.55, 50 °C)
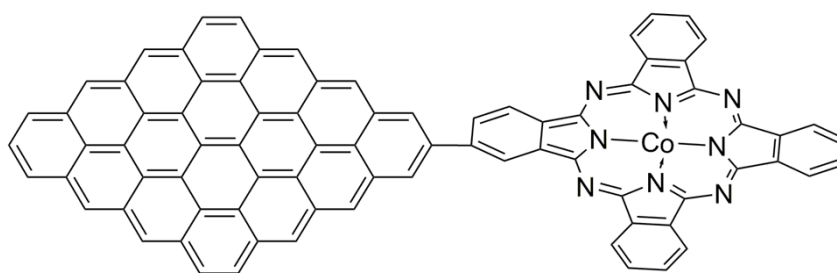
Fig. S10. The simplified model of CoPc-MWCNTs for the DFT calculation at the B3LYP/6-31G

level of theory using graphite as a coronene-like planar sheet due to the stacked graphite structure

of MWCNTs.

The DFT calculations with the B3LYP/6-31G method presented in Fig. 10 and Tables S1

were performed using the Gaussian program[1].

Table S1. Calculated bond lengths for the energy minimized DFT models of the formed cobalt-

oxo intermediates in CoTAPc-MWCNTs system with or without LAS.

Cobalt-oxo intermediates in CoPc-MWCNTs	Total spin	Bond lengths (Å)		
		Co-O (SO_3^-)	Co-O	Co-N
Without LAS	S=1/2	/	1.7428	1.95210
				1.94311
				1.95467
				1.94333
With C_2-LAS	S=1/2	2.00347	1.79965	1.95315
				1.95361
				1.95682
				1.95750
With C_{12}-LAS	S=1/2	1.99004	1.80032	1.96039
				1.95375
				1.95828
				1.95362

Reference:

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R.

Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji,

M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr. J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*; Gaussian, Inc.: Wallingford CT, 2009.