Spiderweb-inspired all-weather CoS quantum dots confined in N-doped carbon for boosted sulfate radical evolution

*Jie Ding^a, Ying-Bo Zhu^a, Yu-Long Ma^{*a}, Yong-Gang Sun^{*a}, Lei Wang^a, Li-Qiong*

Wang^a, Yuan-Yuan Li^a, Wen-Xin Ji^a, Zhi-Jun Yu^b

^a State Key Laboratory of High-efficiency Coal Utilization and Green Chemical

Engineering. College of Chemistry and Chemical Engineering, Ningxia University,

Yinchuan 750021, China.

^b School of Environment, Tsinghua University, Beijing 10084, China.

Corresponding author:

Yu-Long Ma

State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical

Engineering, College of Chemistry and Chemical Engineering, Ningxia University

Helanshan Rd. 539, Yinchuan 750021, China

E-mail: yulongma796@sohu.com (Yu-Long Ma)

Yong-Gang Sun

State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical

Engineering, College of Chemistry and Chemical Engineering, Ningxia University

Helanshan Rd. 539, Yinchuan 750021, China

E-mail: cassyg2015@163.com (Yong-Gang Sun)

Experimental details

Sulphur was purchased from Sigma-Aldrich (99.99%). Other chemical reagents were purchased from Aladdin Chemical Reagent Co., Ltd., and were used without further purification.

Preparation of ZIF-67@CNTs: The ZIF-67@CNTs were prepared via a typical hydrothermal method. First, 50 mg acid treatment of CNTs (Aladdin, >90%) dispersed in 50 mL N,N-dimethylformamide (DMF, Aladdin, 98%) with continuous stirring for 1 h. Second, 0.1 mol Co(NO₃)₂·6H₂O (Aladdin, 99%) was dissolved in the above dispersion with continuous stirring for 20 min. Third, 0.01 mol 2-methylimidazole (Aladdin, 99%) was added into the above solution and stirring for another 40 min. Then, the mixture was transferred to a Teflon-lined autoclave and maintained at 60 °C for 20 h. Finally, the obtained product was centrifuged with deionized water and ethanol for several times. The collected powder was dried at 80 °C overnight. ZIF-67 without CNTs as a control.

Preparation of CoS@CNTs: To get the CoS@CNTs, the obtained ZIF-67@CNTs and Sulphur were placed in a sealed ampoule bottle with weight ratio of 1:2. And then the materials were heated to 500 °C for 2 h in tubular furnace with a temperature increase rate of 2 °C min⁻¹ under argon atmosphere. After cooling to room temperature naturally, the final product was washed with deionized water and ethanol several times, respectively, and then dried in drying oven at 80 °C.

Preparation of CoS@CNTs with LPP: Dissolve the LPP material into the acetonitrile solution under magnetic stirring for 30 min. Next, a certain proportion of

catalyst slowly injected to the solution, and the resulting dispersion was stirred for 4 h for complete hydrolysis at 60 $^{\circ}$ C.

Catalytic activity test: BPA was selected as a target pollutant to evaluate the catalytic activity of catalytic, as it is a ubiquitous pollutant and an important intermediate in industrial processes. The degradation experiments were carried out in a batch mode using a threenecked flask (250 mL) at room temperature. In a typical experiment, catalytic was dispersed in BPA solution (50 mg/L, 150 mL) for 2 min. Then the degradation reaction was initiated by adding PMS under magnetic stirring. At predetermined time intervals, samples were withdrawn and filtered through 0.22 μ m membrane filters to remove suspended MOFs. Meanwhile, an aliquot of 1 M isopropyl alcohol was immediately added to quench the reaction, and then the concentration of BPA was analyzed. After reaction, CoS@CNTs was separated by filtration, washed with water and methanol, and then reused in a new reaction after being dried at 60 °C.



Figure S1 The HR-TEM image of CoS quantum dot nanoclusters.



Figure S2 XRD pattern of CoS/CNTs.



Figure S3 Raman spectra of CoS/CNTs.



Figure S4 BET results.



Figure S5 Adsorption performance of different catalysts.



Figure S6 Effect of Cl⁻ on BPA degradation.



Figure S7 Reaction rate constant of catalysts.



Figure S8 Nyquist EIS plot of catalysts.





Figure S9 The diagram of metal dissolution.