## **Supporting Information**

In Situ Raman Studying the Microstructure and Function of Fe<sup>IV</sup> Species in Advanced Oxidation Process

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# Test S1 Synthesis of Au@SiO<sub>2</sub>@Fe-SACs, Au@SiO<sub>2</sub>@NC, SiO<sub>2</sub>@Fe-SACs, NC-Fe-SACs and Au@Pt NPs

Synthesis of 120nm Au@SiO<sub>2</sub>. Firstly, the synthesis of 120nm Au@SiO<sub>2</sub> was inspired by the literatures (Jian Feng Li et al., 2012)<sup>1</sup>: Initially, we synthesize 120nm Au NPs. 100 ml of chloroauric acid solution (0.01%) is added to a round-bottomed flask, boiled with stirring and refluxing. Subsequently quickly add 1.0 ml sodium citrate (1wt%) to the boiling solution and continue boiling the solution for 30 minutes. The solution is then cooled to room temperature. Put 4.0 ml of solution containing Au seeds (about 40 nm in diameter at this point) into a round-bottomed flask and add 53 ml of Milli-Q water. Add 0.9 ml sodium citrate (1wt%), stir for 3 minutes, then add 0.9 ml chloroauric acid (1wt%), stir for 8 minutes. Slowly drop 1.4 ml hydroxylamine hydrochloride (10 mM) into a round-bottomed flask at a rate of 1 drop every 10s and stir at a speed of 2000 r.p.m. Stirring for 1 hour at room temperature results in 120 nm Au NPs. Secondly, 120nmAu NPs are coated with SiO<sub>2</sub> shell. Place 15ml of 120nm Au NP solution in a round-bottom flask and dilute to 30ml. Add 0.5 ml APTES (0.5 mM) to the flask and stir for 20 minutes. 2.8ml sodium silicate solution (0.54% wt%, adjusted to pH~10.2 with orthophosphoric acid) was added into Au solution and stirred at room temperature for 3min. Stir the flask in a 90°C water bath for 1 hour. The resulting solution is placed in an ice bath to stop the reaction. The solution was transferred to a 1.5ml centrifuge tubes and centrifuged at 600g for 10 min. Pour out the supernatant, then add 1.5 ml of Mili-Q water and re-disperse the SHINs.

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Centrifuge tube at 600g for 10 min. Decant the supernatant to obtain clean,

concentrated  $Au@SiO_2$  from the bottom of the tube.

Synthesis of Au@SiO<sub>2</sub>@NC-Fe. The coated with Fe-SAC was inspired by the literatures (Haifeng Wang et al., 2022)<sup>2</sup>: Add 0.1 mL of ammonia (25%) to a mixture of 13ml of water and 3ml of ethanol. Then, 2 mL 0.015M tannic acid solution was added into the above solution, followed by 1mL 3.7wt% formaldehyde solution, and stirred for 30min. Subsequently, the Au@SiO<sub>2</sub> substrates obtained in the above steps was added, and stirred for 24 h. Add 200 $\mu$ L 0.1mM Fe(NO<sub>3</sub>)<sub>3</sub> solution and stir for 12h. The products were collected by centrifugation, washed and freeze-dried. Thereafter, the composite material was pyrolyzed in ammonia atmosphere at 600°C for 2h, and the pyrolyzed material was soaked in 0.1M diluted hydrochloric acid to remove excess Fecontaining impurities. Finally wash and collect materials to obtain Au@SiO<sub>2</sub>@NC-Fe loaded with Fe-SAC coating.

**Synthesis of Au@SiO<sub>2</sub>@NC.** By the same preparation method of Au@SiO<sub>2</sub>@NC-Fe, Au@SiO<sub>2</sub>@NC is obtained without adding Fe(NO<sub>3</sub>)<sub>3</sub> solution.

**Synthesis of SiO<sub>2</sub>@Fe-SACs and NC-Fe-SACs.** First, prepare SiO<sub>2</sub> spheres. Initially, 9 mL ammonia (28%) and 16.25 mL anhydrous ethanol are separately added to 24.75 mL H<sub>2</sub>O and stirred at a rate of 1200 r.p.m. to form Solution A. Concurrently, 4.5 mL tetraethyl orthosilicate (TEOS) is mixed with 45.5 mL ethanol to create Solution B. Solution B is then swiftly introduced into Solution A, taking care to prevent contact with the walls of the container. After 1 minute, the stirring speed is reduced to 400 r.p.m., and the mixture is allowed to react at room temperature for 2 hours. The product is then cleaned with ethanol and 5 mL of APTES is added for amination, after which it is set aside for further use. Subsequently, the same method used for loading Fe-SACs onto Au@SiO<sub>2</sub> is employed to prepare SiO<sub>2</sub>@NC-Fe-SACs. Finally, the SiO<sub>2</sub> is etched away using hydrofluoric acid (HF) to yield the NC-Fe-SACs.

Synthesis of Au@Pt NPs<sup>3</sup>. The as-prepared 55 nm Au NPs solution (30 mL) was vigorously stirred in a round-bottom flask. Then 0.36 mL of H<sub>2</sub>PtCl<sub>6</sub> (1 mM) was added and the solution was heated to 80 °C. Under agitation, freshly prepared ascorbic acid (AA) solution (10 mM, 0.18 mL) was added dropwise with a speed of 80  $\mu$ L/min. After that, the thoroughly mixed solution was kept at 80 °C for 30 min and cooled to room temperature. The Au@Pt core-shell NPs were obtained by centrifugation (5500 rpm, 10 min) and washed with deionized water. The shell thickness and particle size of Au@Pt NPs were controlled by changing the amount of H<sub>2</sub>PtCl<sub>6</sub> added. The color of nanoparticle solution gradually changed from brown-red to gray-black with the increase of Pt shell thickness.

Instrument Name	Model	Manufacturer
High-Performance	Agilent 1200	Agilent Technologies Inc.
Liquid Chromatography		
Pure Water Apparatus	Milli-Q IQ7000	Sartorius AG, Germany
Ultrasonic Cleaner	KQ-600DE	Anqing Bohui Ke Yi
		Information Technology Co.,
		Ltd.
Electric Constant	DGC-9140A	Beijing Huanuotaihe
Temperature Drying		Instruments & Equipment Co.,
Oven		Ltd.
Freeze Dryer	ALPHA 14/LDplus	Beijing Wuzhou Oriental
		Science and Technology
		Development Co., Ltd.
Field Emission Scanning	SU-8000 Hitachi	Hitachi High-Technologies
Electron Microscope		Corporation, Japan
High-Resolution	JEM-2100F	Hitachi High-Technologies
Transmission Electron		Corporation, Japan
Microscope		
X-ray Photoelectron	Thermo Scientific	Thermo Fisher Scientific Inc.
Spectroscopy Analyzer	ESCALAB 250	
X-ray Diffractometer	Bruker D8	Bruker Corporation, Germany
Magnetic Stirrer	RH digital	Beijing Ming Si Pu Rui
		Technology Co., Ltd.
pH Meter	FE28	Beijing Ming Si Pu Rui
		Technology Co., Ltd.
Electronic Scale	ME802E	Beijing Ming Si Pu Rui
		Technology Co., Ltd.
Centrifuge	Sigma 3-18K	Sartorius AG, Germany

Table S1. The specific models and information of the instruments

Table S2. The Main DFT Data Table of NC, C-N<sub>4</sub>-Fe<sup>2+</sup>, C-N<sub>4</sub>-Fe<sup>4+</sup>=O, C-N<sub>4</sub>-Fe<sup>4+</sup>-O-O

Model	Frequency	Raman Intensity	Vibrational Modes
1	349.52	517.9803	C-C bond stretching
			vibration
2	457.88	442.6497	C-C bond stretching
			vibration
3	836.78	151.9812	torsional vibrations of C-C
			bond
4	1218.25	6684.6402	C-C bond stretching
			vibration
5	1368.69	1611.8039	C-C bond stretching
			vibration of the D-band
6	1608.92	17969.2229	C-C bond stretching
			vibration of the G-band

Table S2.1 The Main DFT Data Table of NC

Table S2.2 The Main DFT Data Table of C-N<sub>4</sub>-Fe<sup>2+</sup>

Model	Frequency	Raman Intensity	Vibrational Modes
1	180.83	99.5571	Fe-N bond stretching
			vibration
2	310.88	297.3125	Fe-N bond stretching
			vibration
3	455.33	27.4559	C-C bond stretching
			vibration
4	835.48	79.2575	torsional vibrations of C-C
			bond
5	1352.21	3573.4826	C-C bond stretching
			vibration of the D-band
6	1588.93	570.4071	C-C bond stretching
			vibration of the G-band

#### Table S2.3 The Main DFT Data Table of C-N<sub>4</sub>-Fe<sup>4+</sup>=O

Model	Frequency	Raman Intensity	Vibrational Modes
1	191.83	658.1212	Fe-N bond stretching
			vibration
2	335.18	464.8936	Fe-N bond stretching
			vibration
3	448.27	411.1725	C-C bond stretching
			vibration
4	837.54	213.5634	Fe-O bond stretching

			vibration
5	1349.73	11909.4828	C-C bond stretching
			vibration of the D-band
6	1562.28	6838.2723	C-C bond stretching
			vibration of the G-band

### Table S2.4 The Main DFT Data Table of C-N<sub>4</sub>-Fe<sup>4+</sup>-O-O

Model	Frequency	Raman Intensity	Vibrational Modes
1	220.58	115.1207	Fe-O bond stretching
			vibration
2	312.01	372.5786	Fe-N bond stretching
			vibration
3	1094.80	561.2416	O-O bond stretching
			vibration
4	1306.71	3599.487	C-C bond stretching
			vibration of the D-band
5	1604.21	6888.5981	C-C bond stretching
			vibration of the G-band



Figure S1. SERS spectra of DMPI-Au and DMPI-Au@SiO2@Fe-SACs



Figure S2. WT-EXAFS signals on Fe-K-edge for NC-Fe-SAC



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 $Au@Pt + H_2O_2$  and  $Au@SiO_2@Fe-SACs + Au@Pt + PMS$ .

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