Fe-g-C_3N_4-Catalyzed Oxidation of Benzene to Phenol Using Hydrogen Peroxide and Visible Light

Xiufang Chen, Jinshui Zhang, Xianzhi Fu, Markus Antonietti, and Xinchen Wang*

Supporting Information:

Synthesis of Fe-g-C_3N_4: Fe-g-C_3N_4 was prepared according to the reported procedure.[6c] In a typical preparation, 1 g dicyandiamide mixed with 5 mL D.I. water was heated and stirred at 100 °C with different amounts of $FeCl_3$ added (e.g., 0.1g $FeCl_3$ for 10%-Fe-g-C_3N_4). The mixed solution was continually heated at 100 °C to remove water. The resulting reddish mixtures were then heated at 600 °C for 4 h under flowing nitrogen atmosphere, followed by naturally cooling to room temperature under the nitrogen gas. A detailed physical characterization of Fe-g-C_3N_4 was reported elsewhere.[6c]

Synthesis of SBA-15: Mesoporous silica SBA-15 was obtained using Pluronic P123 and tetraethylorthosilicate (TEOS) following the method reported in literature.[S1] In a typical preparation, 20.0 g of Pluronic P123 was dissolved in 150 g of water and 600 g of 2 M HCl solution with stirring at 35 °C. Then 42.5 g of TEOS was added into that solution with stirring at 35 °C for 20 h. The mixture was aged at 80 °C for 2 days without stirring. The powder was recovered by filtration and dried at 70 °C overnight. It was further calcined at 500 °C for 8 h at a ramping rate of 1 °C/min.

Synthesis of Fe-g-C_3N_4/SBA-15: Fe-g-C_3N_4/SBA-15 was prepared as follows: different amounts of dicyandiamide dissolved in 15 mL D.I. water mixed with $FeCl_3$ (e.g., 0.2 g dicyandiamide and 0.02 g $FeCl_3$) and stirred at 100 °C. Then 1.0 g SBA-15 was added into the mixture. The resultant mixture was continually stirred at 100 °C to remove water. Finally, the mixture was calcined at 600 °C for 4 h under flowing nitrogen gas, followed by naturally cooling to room temperature under the nitrogen gas. The sample was denoted as *x*-Fe-g-C_3N_4/SBA-15 with *x* standing for the initial dicyandiamide/SBA-15 mass ratio.

Characterization: X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance diffractometer with CuKα1 radiation (λ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS) data were obtained on Thermo ESCALAB250 instrument with a monochromatized AlKα line source (200

W). All binding energies were referenced to the C1s peak at 288.2 eV corresponding to a C-N-C coordination in g-C_3N_4. Atomic absorption spectroscopy (AAS) was performed with a Varian Spectra AA 220 atomic absorption spectrometer, which was used to determine the leached Fe in solution during reaction. The UV/vis diffuse reflectance spectra were performed on a Varian Cary 500 Scan UV-visible system. Nitrogen adsorption-desorption isotherms were collected at 77 K using a Micromeritics Tristar 3000 automated gas adsorption analyzer. FTIR spectra were recorded on a BioRad FTS 6000 spectrometer. Transmission electron microscopy (TEM) was recorded on a Jeol JEM 2100 microscope.

Electrochemical measurements: Electrochemical measurements were conducted with a BAS Epsilon Electrochemical System in a conventional three electrode cell, using a Pt plate as the counter electrode and Ag/AgCl electrode (3 M KCl) as the reference electrode. The working electrode was prepared by spreading the slurries of Fe-g-C_3N_4 (5 mg powder in 100 μL diluted Nafion (1 wt %) in ethanol) over 0.25 cm^2 of indium tin oxide (ITO) glass substrate. Then the film was dried in air. The Cyclic voltammetry (CV) measurement was carried out in a Na_2SO_4 (0.2 M) electrolyte, which was purged with nitrogen gas for 2 h prior to the measurements. The CV data were also measured in a mixture of 0.2 M Na_2SO_4 and 10 mM H_2O_2.

Catalytic Test: Fe-g-C_3N_4 (50 mg) was milled and then suspended in a mixture of acetonitrile (4 mL), benzene (0.8 mL, 9 mmol), water (4 mL), and hydrogen peroxide (30 wt%, 0.51 mL, 5 mmol). The resulting biphasic system was stirred at 60 ^oC for 4 h in the dark. At the end of the reaction, ethanol (5 mL) was poured into the mixture at 4 ^oC for quenching the reaction and to turn the biphasic system to a single-phase one. To carry out the photochemical reaction, a 500 W Xenon lamp together with a 420 nm cut-off filter was used as a visible light source for the irradiation of reaction system, with otherwise the same experimental conditions as those in the dark. The products of the reactions were analyzed by a gas chromatograph (HP6890) and GC-MS with toluene as the internal standard. H_2O_2 concentration was determined by colorimetric titration method based on the formation of a yellow colored complex Ti(IV)-H_2O_2, using a UV/Vis spectrophotometer at 410 nm.[S2] Briefly, the $Ti(SO_4)_2$ test reagent was prepared by digesting 1 g TiO_2 with 100 mL H_2SO_4 (98 wt. %) for 20 h at 155 ^oC.

The solution was diluted to 500 mL with distilled water and filtered prior to use. The reaction solution (105 μL) was added to 2.5 mL $Ti(SO_4)_2$ reagent and diluted to 25 mL with distilled water. Then the solution was analyzed using a Lambda 2 UV/Vis spectrophotometer.

Table S1. Catalytic activities for direct phenol production from benzene by Fe-g-C_3N_4 based catalysts with(+)/without(-) visible light (λ>420 nm).

	Catalyst	*hv*	t (h)	Benzene Conv. (%)	H_2O_2 Conv. (%)	H_2O_2 Sel. (%)[a]
1	Fe-g-C_3N_4	-	4	1.8	99.1%	3.2
2	Fe-g-C_3N_4	+	4	4.8	100	8.3
3	Fe-g-C_3N_4/SBA-15	-	4	6.7	80.9	14.2
4	Fe-g-C_3N_4/SBA-15	+	4	11.9	97.6	20.7

[a] Moles of produced phenol/moles of reacted H_2O_2 × 100.

Table S2. Catalytic performances for the direct synthesis of phenol on Fe-g-C_3N_4 catalysts with different iron contents under visible light irradiation (λ> 420 nm).[a]

Catalyst	t (h)	Benzene Conv. (%)	TOF×100 (h^{-1})[b]
5%-Fe-g-C_3N_4	4	1.8	15.4
10%-Fe-g-C_3N_4	4	4.8	43.1
20%-Fe-g-C_3N_4	4	2.5	24.5

[a] For reaction conditions, see Experimental Section.

[b] Turnover frequency: *n* (phenol) per *n* (melem units) per hour.

Table S3. Catalytic performances of g-C_3N_4 catalysts for the direct synthesis of phenol modified with different transition metals in the presence of visible light (λ> 420 nm).

Catalyst	t (h)	Benzene Conv. (%)	TOF×100 (h^{-1})
Fe-g-C_3N_4	4	4.8	43.1
Cu-g-C_3N_4	4	1.4	12.6
Ti-g-C_3N_4	4	0.1	1.0
Ni-g-C_3N_4	4	0.1	1.0
Zn-g-C_3N_4	4	0.1	1.0

Table S4. Textural and photocatalytic properties of Fe-g-C_3N_4/SBA-15 catalysts with different Fe-g-C_3N_4 content.[a]

Catalyst	S_{BET}[b] (m^2/g)	V_p[c] (cm^3/g)	D_p[d] (nm)	Benzene Conv. (%)	TOF×100 (h^{-1})[e]
0.1-Fe-g-C_3N_4/SBA-15	506	0.82	6.3	6.1	1257.0
0.2-Fe-g-C_3N_4/SBA-15	451	0.75	5.9	6.7	835.7
0.5-Fe-g-C_3N_4/SBA-15	319	0.58	5.8	4.5	198.7
1.0-Fe-g-C_3N_4/SBA-15	156	0.31	5.7	2.6	68.9
2.0-Fe-g-C_3N_4/SBA-15	34	0.07	3.9	1.5	25.2
SBA-15	556	0.86	6.3	0	-
Fe-g-C_3N_4	8	0.02	3.4	1.8	16.1

[a] In dark condition. For details, see Experimental Section.

[b] BET Surface area.

[c] Pore volume.

[d] Average pore size determined by BJH method.

[e] Turnover frequency: *n* (phenol) per *n* (melem units) per hour.

Figure S1. Cycling runs in the photocatalytic oxidation of benzene to phenol in the present of H_2O_2 for 2 h under visible-light irradiation (λ> 420 nm).

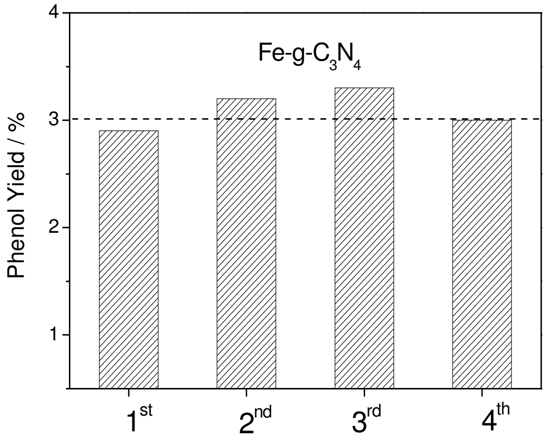


Figure S2. XPS spectra of Fe 2p for Fe-g-C_3N_4 before and after reaction. The Fe 2p3/2 binding energy of sample before and after reaction is both in the region of binding energy of the Fe(III) valence state (710.3-711.8 eV).

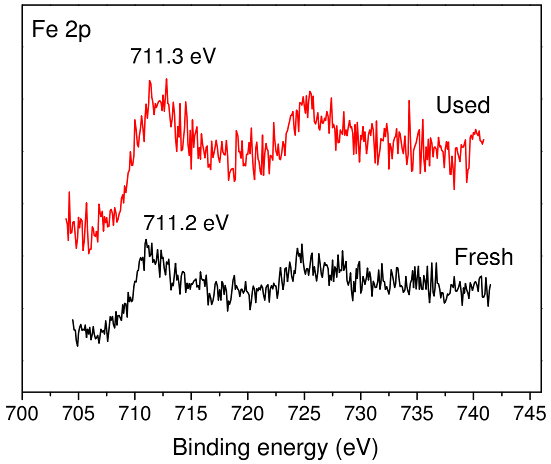
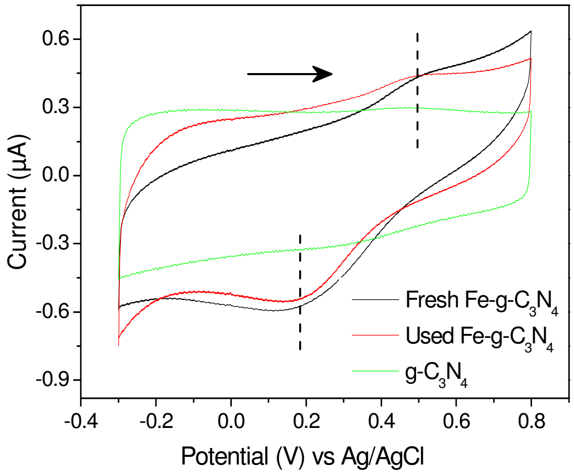


Figure S3. Cyclic voltammograms of Fe-g-C_3N_4 electrode in the absence (a) and presence of 10 mM H_2O_2 (b) in 0.2 M Na_2SO_4 aqueous solution.

(a)



(b)

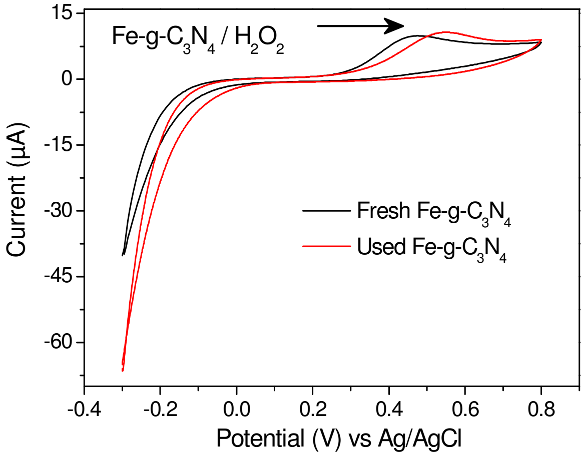
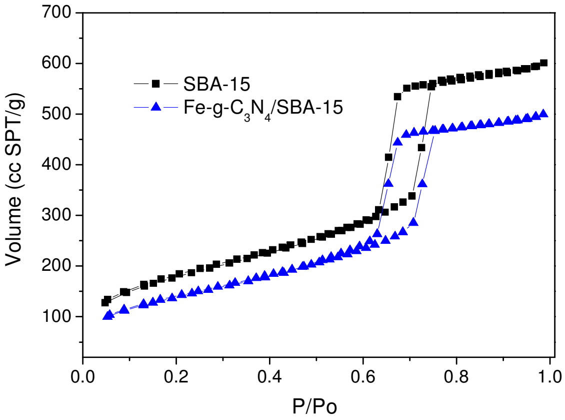


Figure S4. N_2 sorption isotherms (a) and pore distribution curve (b) of SBA-15 and 0.2-Fe-g-C_3N_4/SBA-15.

(a)



(b)

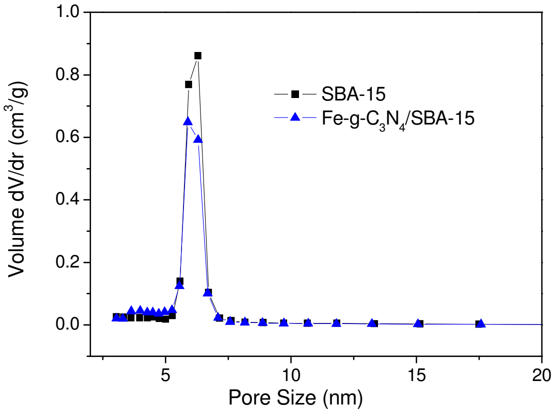


Figure S5. FTIR spectra of Fe-g-C_3N_4/SBA-15 catalysts with different Fe-g-C_3N_4 content. All the samples show features at 1200 to 1680 cm^{-1} that are characteristic of aromatic CN heterocycles and also the breathing mode of the triazine units at 800 cm^{-1}.[S3]

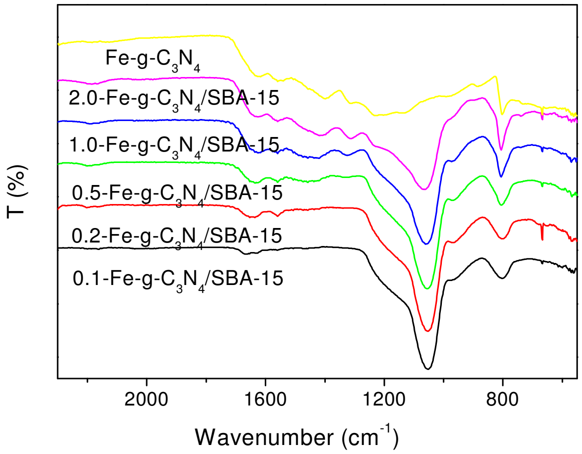


Figure S6. Low-angle XRD pattern of Fe-g-C_3N_4/SBA-15 catalysts with different Fe-g-C_3N_4 content.

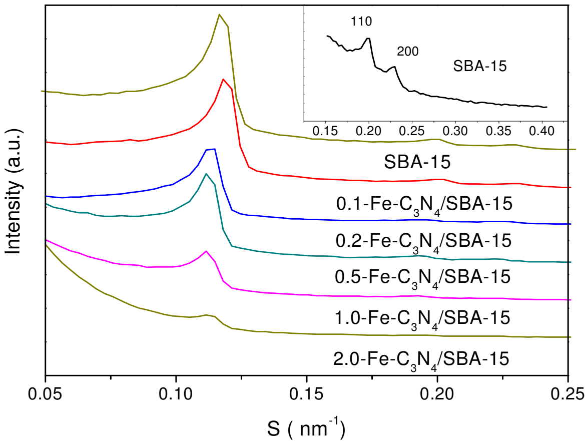


Figure S7. Diffuse reflectance UV-Vis spectra of Fe-g-C_3N_4/SBA-15 catalysts with different Fe-g-C_3N_4 content.

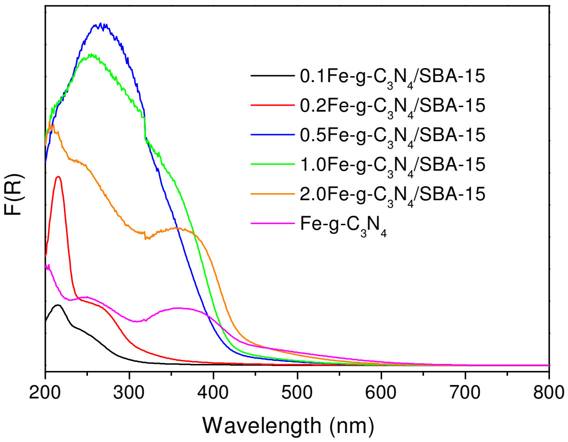
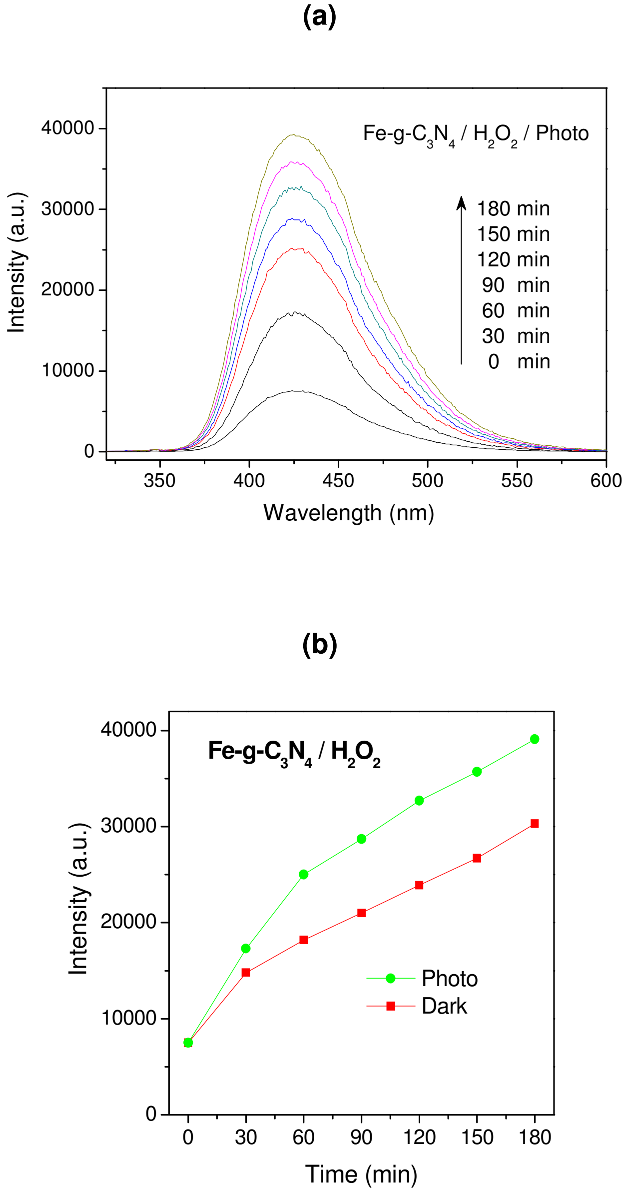


Figure S8. (a) The •OH-trapping PL spectra of suspensions containing Fe-g-C_3N_4/H_2O_2 (0.01 M) and TA and (b) plot of the induced PL intensity (at 426 nm) against reaction time in dark and under visible light irradiation. The generation of •OH radicals was investigated by the method of photoluminescence with terephthalic acid (TA-PL).[S4]



Reference:

[S1] Zhao, D. Y.; Huo, Q. S.; Feng, J. L.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.

[S2] Eisenberg, G. M. *Ind. Eng. Chem. Anal.* **1943**, *15*, 327.

[S3] Bojdys, M. J.; Müller, J.; Antonietti, M.; Thomas, A. *Chem. Eur. J.* **2008**, *14*, 8177.

[S4] Hirakawa T.; Nosaka, Y. *Langmuir*, **2002**, *18*, 3247.