

# Covalent modification of iron phthalocyanine into skeleton of graphitic carbon nitride and its visible-light-driven photocatalytic reduction of nitroaromatic compounds

Jiajia Qian <sup>2,#</sup>, Ying Liu <sup>3,#</sup>, Weiran Zheng <sup>1,\*</sup>, Baocheng Zhou <sup>3</sup>, Xiaoping Dong <sup>3,\*</sup>

<sup>1</sup>*Institute of Agro-product Safety and Nutrition, Zhejiang Academy of Agricultural Sciences, Hangzhou 310021, China*

<sup>2</sup>*Jiaxing Eco-Environmental Monitoring Center of Zhejiang Province, Jiaxing, 314000, China*

<sup>3</sup>*Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, China.*

<sup>#</sup> *These authors contributed equally*

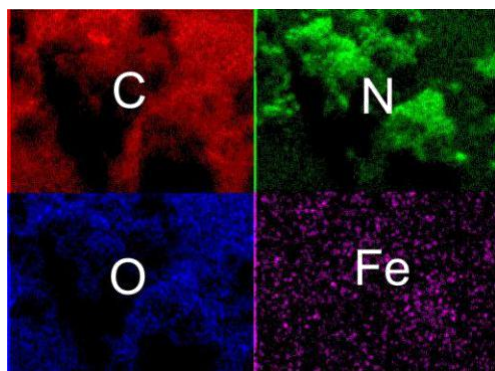
<sup>\*</sup> *Corresponding authors: [rancki@163.com](mailto:rancki@163.com) (W. Zheng); [xpdong@zstu.edu.cn](mailto:xpdong@zstu.edu.cn) (X. Dong)*

## 1. Synthesis of carboxyl functionalized FePc

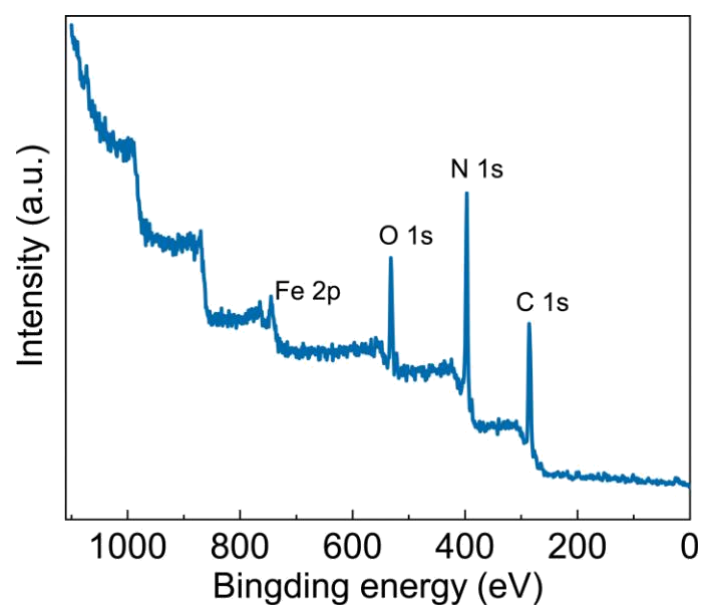
Carboxyl functionalized FePc (FePc-COOH) was obtained through a solid-state strategy according to the literature [1]. Typically, o-phthalic anhydride (8.46 g, 0.044 mol), iron (III) chloride hexahydrate (4.87 g, 0.018 mol), and ammonium molybdate ( $0.12 \text{ g}, 9 \times 10^{-5} \text{ mol}$ ) were mixed in an agate mortar, and then a small quantity of urea (15.00 g, 0.25 mol) was added and ground to powder. The resultant red solid was transferred into a beaker that was covered by a watch glass and then heated at  $140^{\circ}\text{C}$  in an oven for 0.5 h. After the bubbles disappeared in beaker, the temperature was further increased to  $190^{\circ}\text{C}$  for 5 h. The obtained dark blue material was ground into powder, and then was boiled in a saturated solution of HCl/NaCl (250 mL, 1M) for 1.5 h. After cooling it to room temperature, the solid was centrifuged, washed with deionized water, and dried in an oven overnight. The crude product, 500 mL NaOH solution (2 M) and 200 g NaCl were added to three-necked round-bottomed flask. The mixture was stirred by a magnetic stirrer and heated at  $95^{\circ}\text{C}$  for 10 h. Subsequently, the resulting mixture was dispersed into 1000 mL of water under magnetic stirring, followed by centrifugation and water washing for several times until the supernatant solution was colorless. Finally, a certain volume of 6 M HCl was dropwise added to adjust the pH of the collected supernatant solution to 2. The resulting precipitate was collected by filtration, washed thoroughly with deionized water and dried overnight, and we obtained FePc-COOH.

## References

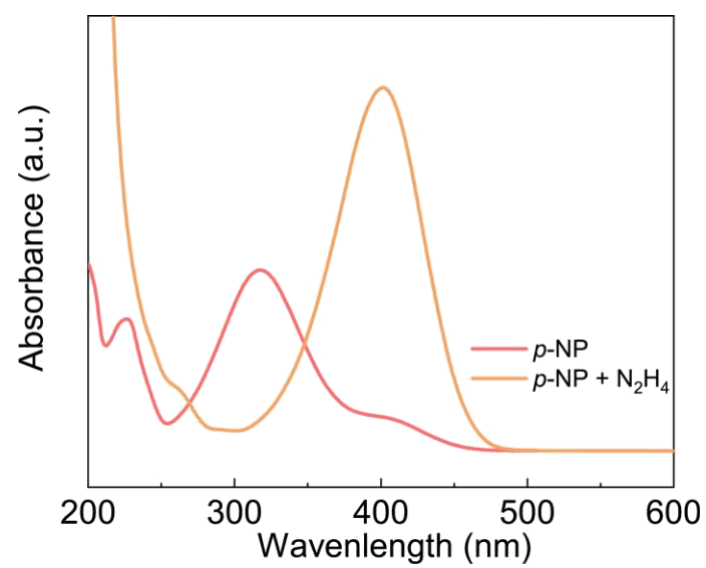
- [1] D. Christendat, M. David, S. Morin, A. Lever, K. Kadish, J. Shao, Synthesis and characterization of highly soluble hexadecachloro-and hexadecafluorophthalocyanine ruthenium (II) complexes, 9 (2005) 626-636.



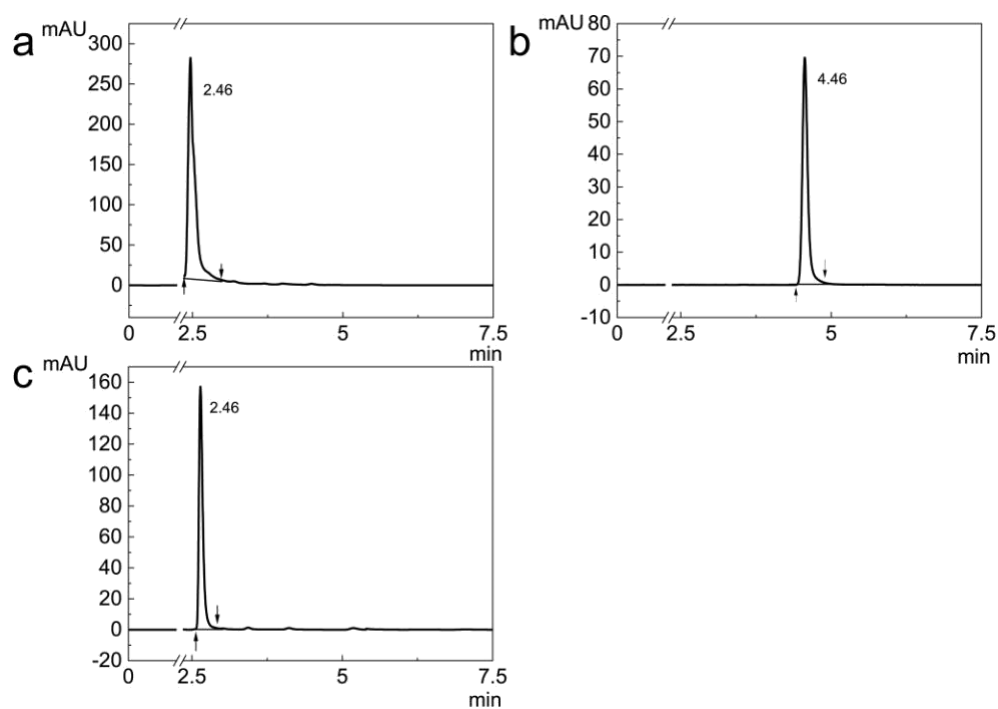
**Figure S1.** EDS element mapping of gCN-FePc-1.



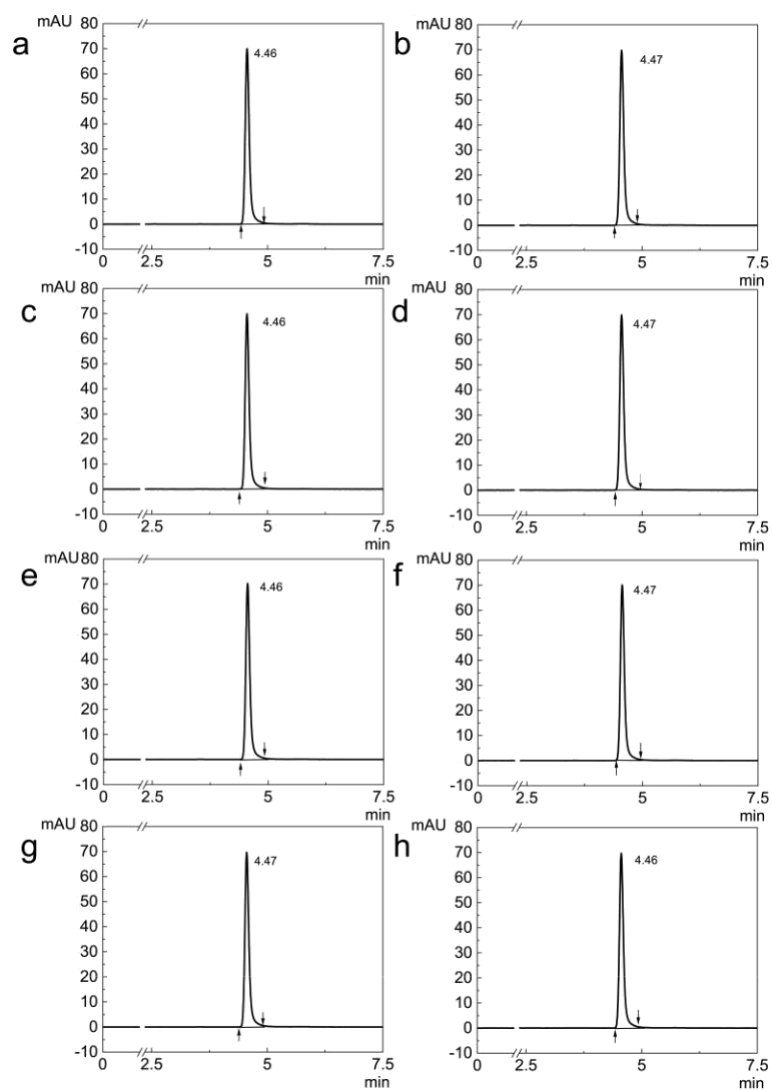
**Figure S2.** The XPS survey spectrum of gCN-FePc-1.



**Figure S3.** UV-vis absorption spectra of *p*-NP solution before and after adding N<sub>2</sub>H<sub>4</sub>.



**Figure S4.** The liquid chromatograms of *p*-NP solution after photocatalytic reaction (a), the initial *p*-NP solution (b) and the *p*-AP standard solution (c).



**Figure S5.** The liquid chromatograms of *p*-NP solutions before and after different treatments: only *p*-NP (**a** and **b**); with catalyst and  $\text{N}_2\text{H}_4$  (**c** and **d**); with catalyst and light (**e** and **f**); with  $\text{N}_2\text{H}_4$  and light (**g** and **h**).

**Table S1** The composition of *p*-NP solutions before and after different conditions analyzed by HPLC.

Reaction Condition	<i>p</i> -NP (Retention Time: 4.46 min)	<i>p</i> -AP (Retention Time: 2.46 min)
with catalyst, light and N <sub>2</sub> H <sub>4</sub>		√
only <i>p</i> -NP	√	
with catalyst and N <sub>2</sub> H <sub>4</sub>	√	
with light and N <sub>2</sub> H <sub>4</sub>	√	
with catalyst and light	√	

The experimental data in Table S1 are based on three repeated experiments.