

Supporting information:

High photocatalytic activity of 'clicked' iron phthalocyanine conjugated with carbon nanofibers

Zhenjun Chang,* Jing Zeng

College of Materials Science and Engineering, Jiangsu University of Science and
Technology, Zhenjiang, Jiangsu 210001, People's Republic of China

E-mail: zjchang@just.edu.cn

Materials

Polyacrylonitrile (PAN, $M_w = 70,000$) was purchased from Sinopec Petrochemical (Shanghai) Company Ltd. The alkyne-FePc was prepared according to our previous report.¹ Sodium azide (NaN_3 , 99%) and N,N,N',N',N'' -pentamethyldiethylenetriamine (PMDETA) were purchased from Alfa Aesar and used without further purification. Copper(I) bromide (CuBr , 99%), N,N -dimethylformamide (DMF), iodine monochloride (ICl), acetonitrile, and all other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received.

Experimental section

Preparation of carbon nanofibers (CNFs)

The PAN nanofibers were prepared according to our previous work.² In a characteristic example, PAN was first dissolved in DMF to prepare a 7 wt% solution. A typical electrospinning setup was used for this experiment. The PAN/DMF solution was loaded into a syringe fitted to a syringe pump. The positive terminal of a high voltage DC power supply of 30 kV was connected to the metallic needle of the syringe. The distance between the needle tip and collector was 20 cm. Then, PAN nanofibers were prepared. The PAN nanofibers were placed in a tube furnace and stabilized in air to 270 °C at a heating rate set at 3 °C min^{-1} , followed by holding at 270 °C for 1 h. Then they were carbonized in

nitrogen at 1000 °C at a heating rate of 5 °C min⁻¹, and held at 1000 °C for 30 min. The CNFs were thus obtained.

Synthesis of azide-decorated CNFs (CNF-N₃)

The CNF-N₃ was fabricated according to a previous work.^{3,4} 0.06 g of sodium azide was added to 30 mL of acetonitrile, and stirred at 0 °C for 30 min. Then, 0.039 g of iodine monochloride was added to the previous solution under stirring at 0 °C for 15 min. The carbon nanofibers were immersed in the reaction solution for 1, 2, 4 h, respectively. CNF-N₃ was obtained after washing with chloroform and methanol followed by drying overnight at 50 °C in a vacuum oven.

Click coupling of CNF-N₃ and propargyl phthalocyanine iron (Alkyne-FePc)

CNF-N₃ was suspended in 30 mL of DMF solution, and the solution was deoxygenated by bubbling with nitrogen for at least 30 min. Then an excess amount of alkyne-FePc, CuBr (0.23 g, 1.6 mmol), and PMDETA (0.27 g, 1.6 mmol) under N₂ flow were added to CNF-N₃/DMF solution. The reaction took place at room temperature for 24 h. CNF-FePc was washed with DMF and water to remove noncovalently bonded molecules, then was dried at 50 °C for 12 h in a vacuum oven.

Characterization

The microstructures of the grafted nanofibers, which were gold-sputtered prior to observation, were observed with a JSM-5600LV scanning electron microscope at an accelerating voltage of 10 kV. The morphology of FePc on the CNFs was measured on a Philips Tecnai-12 transmission electron microscope. Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet NEXUS-670 spectrometer with KBr pellets. X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos AXIS HIS spectrometer using a monochromatized Al K α X-ray source (1486.6 eV photons). The pressure in the analysis chamber was maintained at 10⁻⁶ Pa or less during each measurement. Surface elemental stoichiometries were determined from the sensitivity-factor-corrected spectral area ratios and were reliable within $\pm 10\%$. The photocatalytic activity experiments on

the obtained samples to understand the decomposition of an aqueous RhB solution were carried out using a self-made vessel as the photoreactor under visible-light irradiation. The concentration of RhB was determined using a UV-vis spectrophotometer (CARY Bio-100) by monitoring the changes in the main absorbance centered at about 553 nm. A 300 W Xenon lamp with a 420 nm cut-off filter was used for excitation. The humidity of the laboratory was about 60 %.

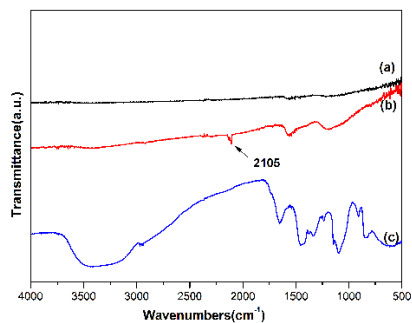


Fig. S1 FT-IR spectra obtained for (a) CNFs, (b) CNF-N₃ and (c) CNF-FePc.

nanofibers.

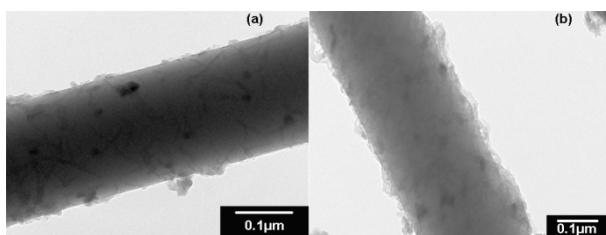


Fig. S2 TEM image of CNF-FePc with with different grafting yields (a) 5% and (b) 11%.

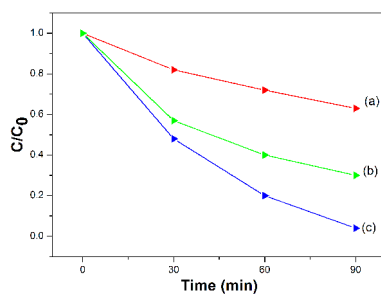


Fig.S3 Photodegradation of RhB in the presence of CNF-FePc with different grafting yields (a) 5%, (b) 11% and (c) 21%.

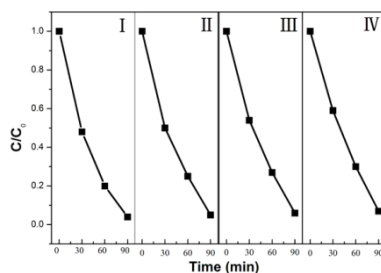


Fig. S4 Results of recycling experiments for the study of the degradation of RhB under similar conditions.

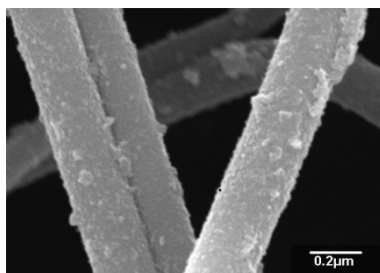


Fig. S5 SEM image of CNF-FePc after four-cycle experiments.