

## Supporting Information

### **Visible-light-driven Photoreforming of Poly(ethylene terephthalate) Plastics via Carbon Nitride Porous Microtube**

Shuhui Guo, Yuanyong Huang, Di Li, Zhongkai Xie, Yujing Jia, Xiaojie Wu, Dongbo Xu\*, Weidong Shi\*

*<sup>a</sup> School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212013, PR China.*

\*Corresponding authors: xudb39@ujs.edu.cn, swd1978@ujs.edu.cn.

# 1. Experimental Procedures

## 1.1. Materials and Chemical reagents:

Fluorine-doped tin oxide (FTO) coated glasses as substrates were purchased from Zhuhai Kaivo Electronic Components Co., Ltd. China. Sodium hydroxide (NaOH), ethylene glycol, absolute ethanol and acetic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Naphthol solution (5 wt %), glyoxal (40%), melamine and L-arginine was purchased from aladdin. Glycolic acid (98%), p-phthalic acid (99%), and formic acid were purchased from Shanghai Macklin Biochemical Co., Ltd. China. Purified water was purchased from Hangzhou Wahaha Group Co., Ltd. Poly-(ethylene terephthalate) (powder, 375  $\mu\text{m}$ ) was purchased from Zhonglian Plastic Chemical Co.

## 1.2. Synthesis of bulk carbon nitride (BCN):

In a typical synthesis, the bulk carbon nitride was prepared by heating 1 g of melamine which was put in a ceramic boat at 500 °C for 90 min under a nitrogen atmosphere with the heat rate of 3 °C·min<sup>-1</sup>.

## 1.3. Synthesis of supramolecular precursors (L-ArgM<sub>x</sub>):

This synthesis refers to a previously reported procedure with a slightly modified, all chemicals used are analytical-grade reagents with no need for further purification<sup>1</sup>. First, 1.008 g (8.00 mmol) of melamine was added into 80 mL of distilled water with rapid stirring for 30 min at 80 °C. Then,  $x \times 8.00$  mmol of L-Arg was put into the above solution ( $x$ , equal to 0.10, 0.12, 0.14, 0.16, 0.18, or 0.20, refers to the molar ratio of L-Arg to melamine). Next, the mixed solution was stirred for 1 h at 80 °C. Last, the hot solution was transferred to a 100 mL Teflon-lined autoclave immediately and heated at 180 °C for 24 h. After cooling to room temperature, the resulting solid flocs were washed from the turbid liquid by centrifugation and dried at 60 °C for 2 days. The solid product was named as L-ArgM<sub>x</sub>.

## 1.4. Synthesis of CN<sub>x</sub>PM:

L-ArgM<sub>x</sub> was calcined in a tubular furnace under the same condition as the BCN. Subsequently, the obtained solid was ground into a fluffy powder and treated with 0.1 M NaOH solutions with stirring for 6 h. Last, the solid products were washed with DI water by centrifugation until the liquid supernatant became neutral (pH 7) and then were dried at 60 °C for 12 h. The final products were

donated as CN<sub>x</sub>PM.

### 1.5. Substrate Pretreatment:

According to the previous report, PET powders were washed with DI water and ethanol several times first and then were dried at 60 °C for 1 day. 12.5 g of PET powders (50 mg·mL<sup>-1</sup>) were soaked in 250 mL of 2 M NaOH aqueous in a sealed vial for 24 h at 40 °C with stirring at 300 rpm<sup>2</sup>.

### 1.6. Nuclear Magnetic Resonance (NMR) Spectroscopy:

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were collected on either a 400 MHz Bruker spectrometer and 600 MHz Agilent spectrometer. The samples after PR were prepared in 1 M NaOH in pure water with the sample concentrations of 25 mg·mL<sup>-1</sup>.

### 1.7. Quantitative <sup>1</sup>H NMR Spectroscopy:

Samples (typically 400 μL) were dissolved in D<sub>2</sub>O (typically 200 μL) and 5 mg of maleic acid was added in the above solution as the internal standard substance. The quantity of analyte (*m<sub>analyte</sub>*) in the sample was calculated via eq1:

$$m_{analyte} = \frac{I_{analyte} N_{standard} M_{analyte}}{I_{standard} N_{analyte} M_{standard}} m_{standard} \quad (1)$$

Where *I<sub>analyte</sub>* is the integral of the analyte peak, *N<sub>analyte</sub>* the number of protons corresponding to the analyte peak, *M<sub>analyte</sub>* the molar mass of the analyte, and *m<sub>standard</sub>* the known mass of the standard in the sample<sup>2</sup>.

### 1.8. Physicochemical characterization

X-ray diffraction (XRD) was conducted on the D/MAX-2500 diffractometer (Rigaku, Japan). Fourier Transform Infrared (FT-IR) was recorded on the Thermo Scientific Nicolet iS5 (America). The transmission electron microscopy (TEM) was recorded on the Tecnai G2 F30 S-TWIN (America) with an accelerating voltage of 120 kV. The specific surface area was determined with a MicroActive for ASAP2460 surface area and porosity analyzer according to the Brunauer-Emmett-Teller (BET) method. X-ray photoelectron spectroscopy (XPS) data were collected by the Thermo Fisher Scientific ESCALAB 250Xi (American). The solid-state <sup>13</sup>C nuclear magnetic resonance (NMR) information was collected on the Agilent model 600 MHz spectrometer. The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were acquired by the Shimadzu UV-2450

spectrophotometer. The fluorescence lifetime was determined by recording the time-resolved fluorescence emission spectra on a fluorescence spectrophotometer (Edinburgh Instruments, FLS-980). Electron paramagnetic resonance (EPR) was executed at a Bruker model A300 spectrometer at room temperature. The time-resolved PL spectra were tested by the Edinburgh fls1000. The Raman spectra was determined by Horiba LabRAM HR Evolution (Japan).

### **1.9. Photoelectrochemical and Electrochemical measurements**

The photoelectrochemical analysis was operated by the CHI-852C (Chenhua, China) electrochemical workstation with a conventional three-electrode setup and employed to measure the transient photocurrent behavior of the photocatalysts, where the prepared electrodes were immersed in a sodium sulfate electrolyte solution (0.5 M, pH 6.8), Pt wire and Ag/AgCl electrode (saturated KCl) acting as the working, counter, and reference electrode, respectively. In a typical process, 20 mg of prepared catalysts were dispersed in a 3 mL ethanol solution adding into the 100  $\mu$ L of Naphthol. Afterwards, the as-prepared solution was ultrasonicated continuously 30 min. Then, the slurry was gradually coated onto a clean 1 cm  $\times$  2 cm fluorine-doped tin oxide (FTO) glass electrode using a spin coater (MODEL KW-4A, Shanghai, China). Photocurrent measurements were recorded by a 300 W Xenon lamp. All measurements were performed at ambient temperature.

### **1.10. Photocatalytic measurements**

Typically, 20 mg catalysis was dispersed in 25 mL pure water, and then another 25 mL substrate was added to the ascribed solution. The resulting mixture was ultrasonicated for 10 min. The prepared samples were added to the 200 mL Pyrex top-irradiation reactor and capped with a rubber septum. The system was purged by argon bubbling for about 20 min and the temperature was carefully maintained at around 20  $^{\circ}$ C during the experiment. Next, the system was stirred continuously and illuminated by using a 300 W Xenon arc lamp equipped with a cutoff filter ( $\lambda > 420$  nm). Afterward, the generated H<sub>2</sub> data were collected by GC7920-TA chromatograph (Beijing Zhong Jiao Jin yuan Technology Co. Ltd China.) equipped with a molecular sieve 5  $\text{\AA}$  column with argon as the carrier gas (99.999%).

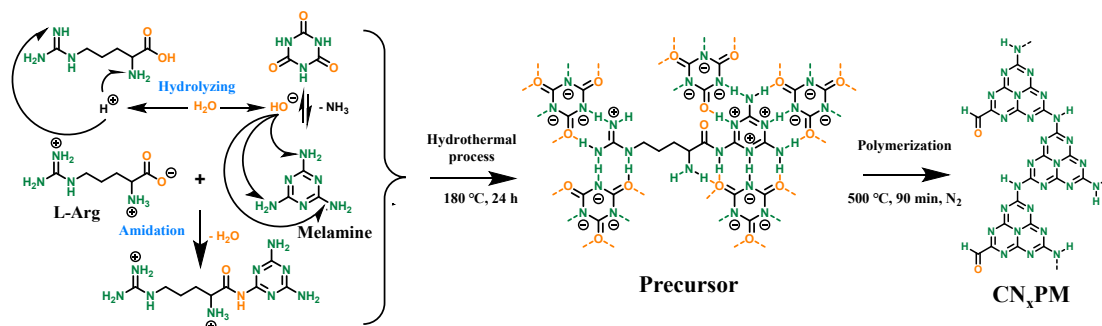


Fig. S1. The synthetic path of  $\text{CN}_x\text{PM}$ .

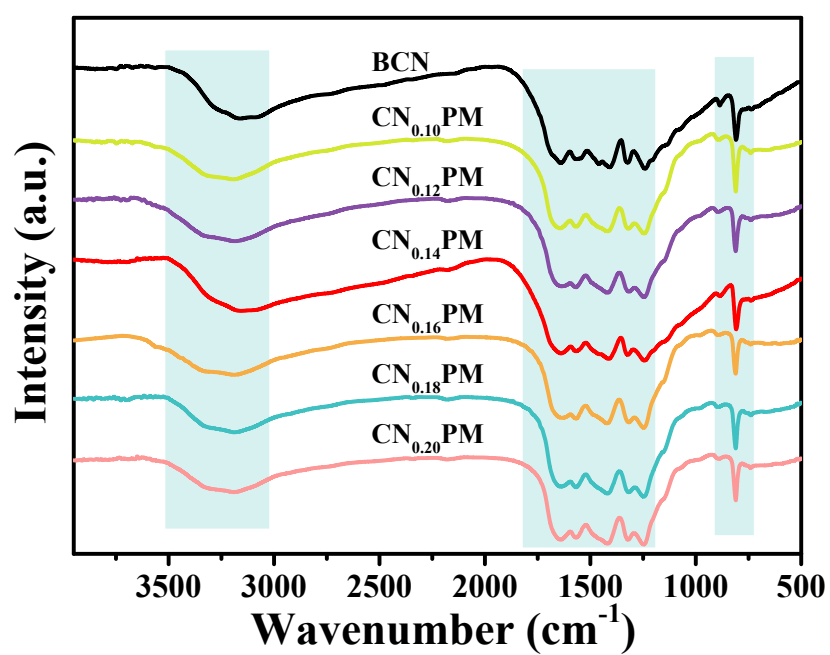
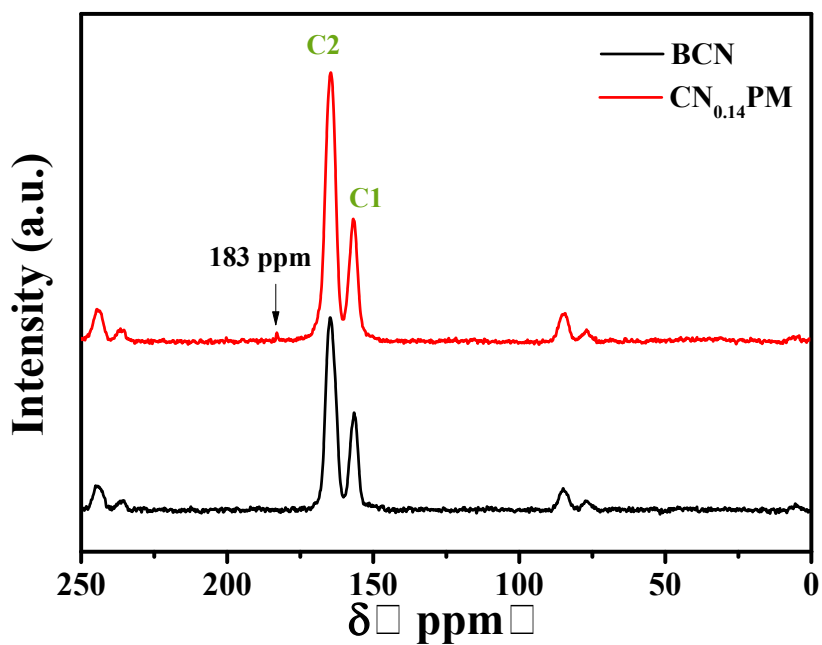
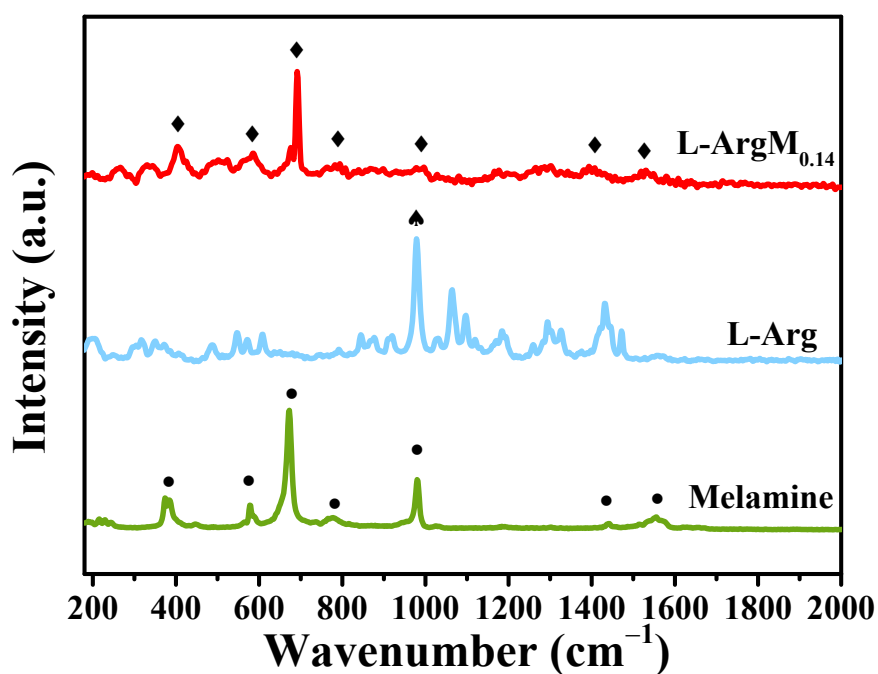


Fig. S2. FT-IR spectra of  $\text{CN}_x\text{PM}$  and BCN.



**Fig. S3.** the solid-state  $^{13}\text{C}$  NMR spectrums of BCN and  $\text{CN}_{0.14}\text{PM}$ . (Test time: 13 h, the MAS spinning frequency: 8000 Hz)



**Fig. S4.** Raman spectra of  $\text{L-ArgM}_{0.14}$ , L-Arg, and melamine.

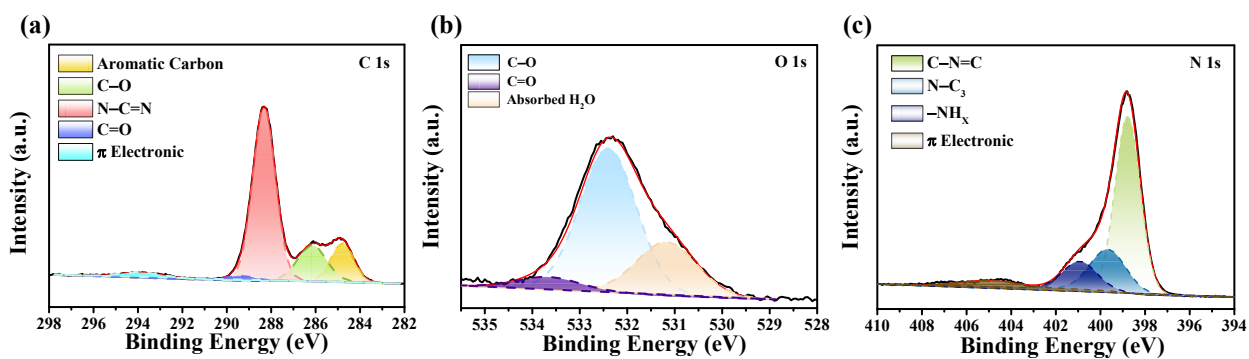


Fig. S5. C 1s, O 1s and N 1s XPS spectra of  $\text{CN}_{0.14}\text{PM}$  (a), (b), and (c).

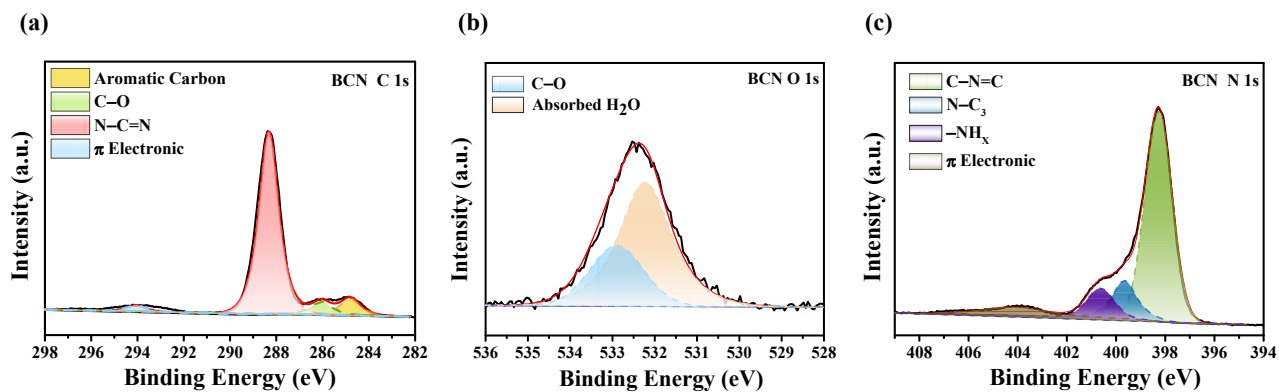
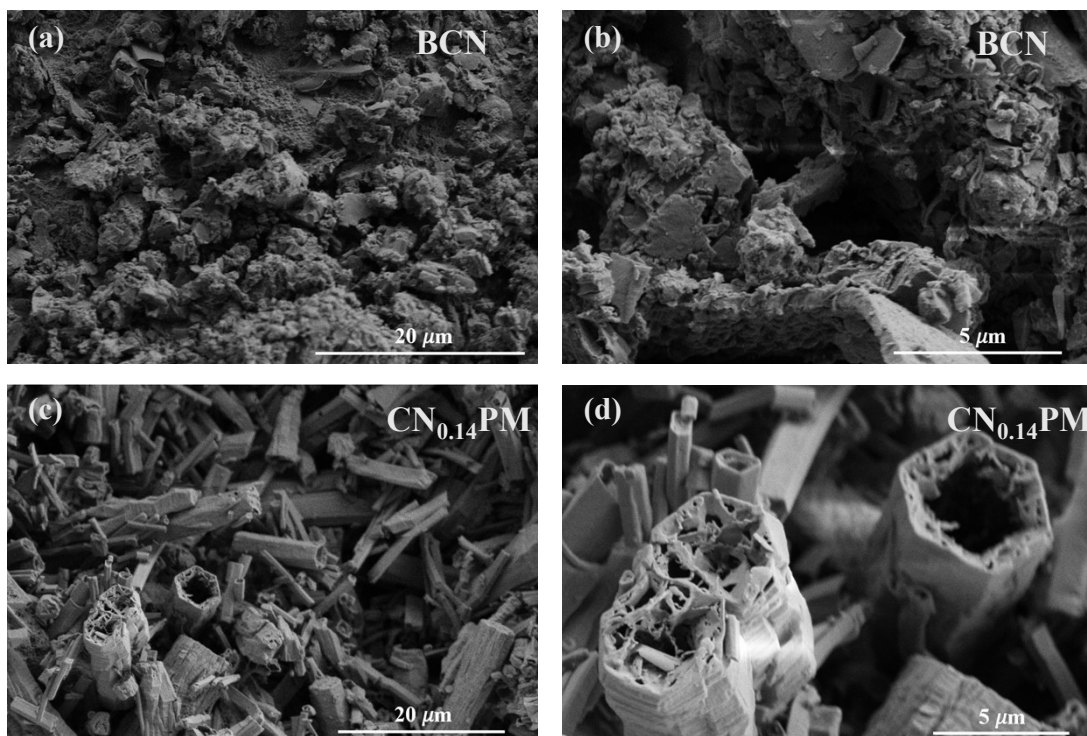
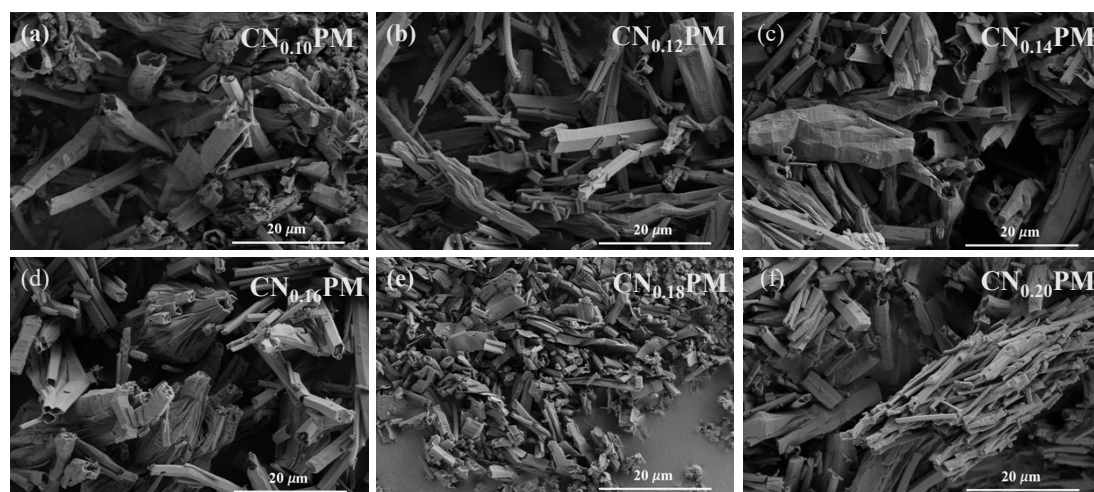


Fig. S6. C 1s, O 1s, and N 1s XPS spectra of BCN (a), (b), and (c).

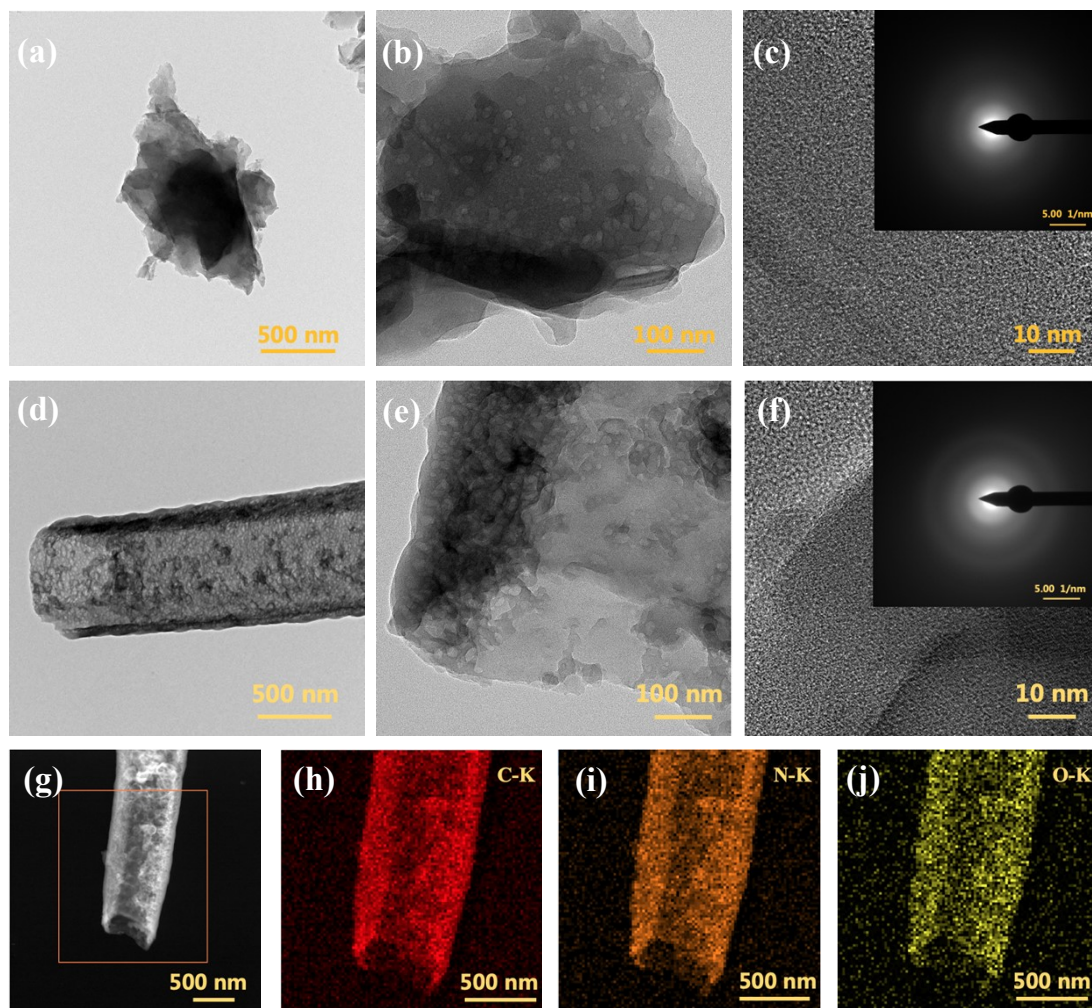


**Fig. S7.** SEM image of BCN (a,b) and CN<sub>0.14</sub>PM (c,d).

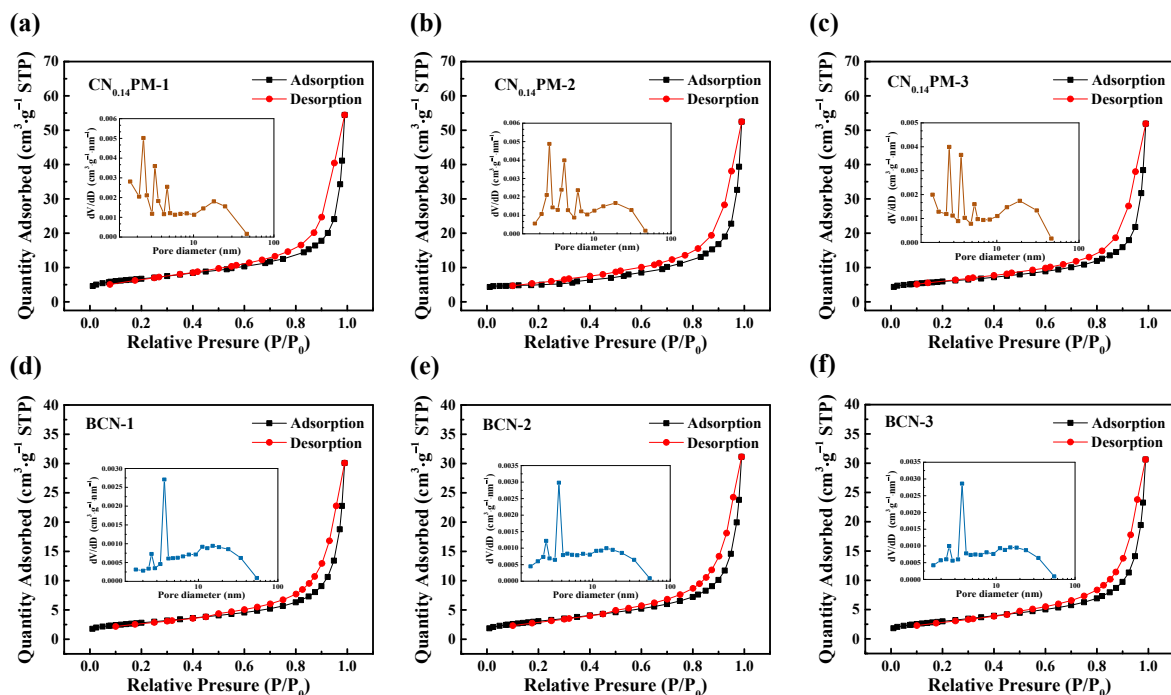


**Fig. S8.** SEM image of CN<sub>0.10</sub>PM (a), CN<sub>0.12</sub>PM (b), CN<sub>0.14</sub>PM (c), CN<sub>0.16</sub>PM (d), CN<sub>0.18</sub>PM (e) and CN<sub>0.20</sub>PM (f).





**Fig. S9.** (a, b, d, e) TEM and (c, f) HRTEM images of BCN (a, b, c) sample and  $\text{CN}_{0.14}\text{PM}$  (d, e, f); (g) high angle annular dark-field (HAADF) scanning TEM image for the  $\text{CN}_{0.14}\text{PM}$ ; (h-j) the elemental mapping images carbon, nitrogen and oxygen of  $\text{CN}_{0.14}\text{PM}$ .

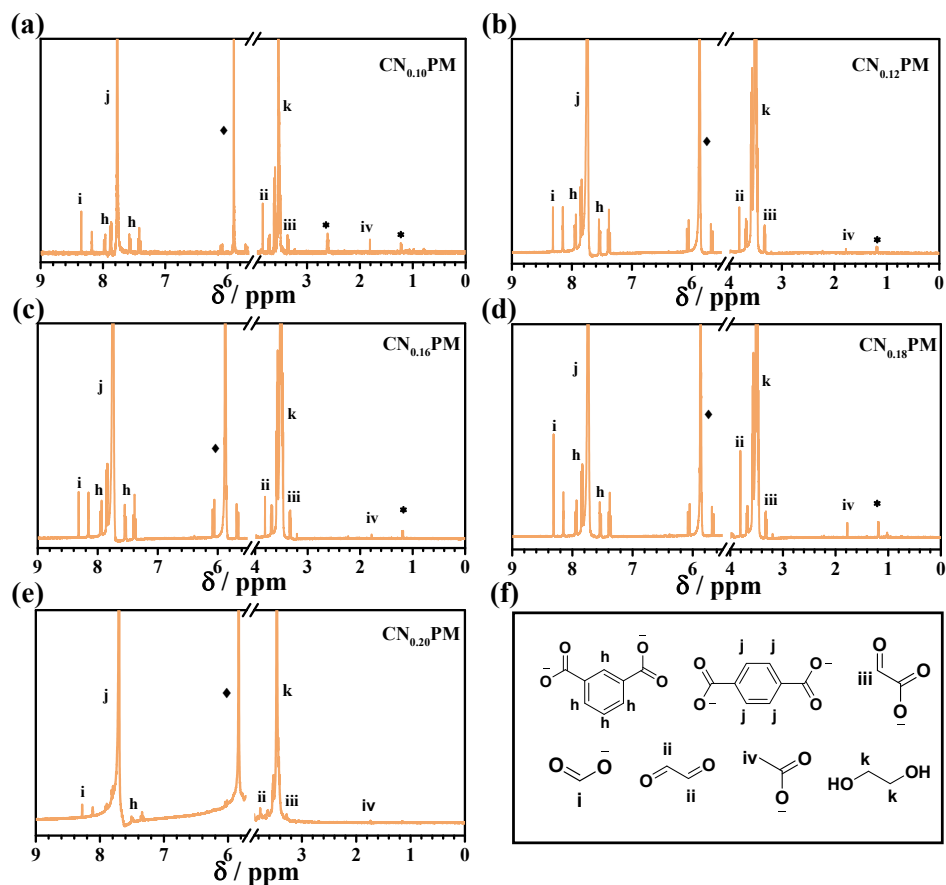


**Fig. S10.** Nitrogen adsorption-desorption isotherms of  $\text{CN}_{0.14}\text{PM}$  and BCN.

The nitrogen adsorption and desorption isotherms of BCN and  $\text{CN}_{0.14}\text{PM}$  were measured three times respectively, and the specific surface area and pore volume were average it over three separate measurements.

**Table S1** The physical properties of  $\text{CN}_{0.14}\text{PM}$  and BCN

Samples	$S_{\text{BET}}$ ( $\text{m}^2 \cdot \text{g}^{-1}$ )	Pore Volume ( $\text{cm}^3 \cdot \text{g}^{-1}$ )
$\text{CN}_{0.14}\text{PM-1}$	24.9152	0.084209
$\text{CN}_{0.14}\text{PM-2}$	20.0630	0.081177
$\text{CN}_{0.14}\text{PM-3}$	21.1902	0.080285
Average value	22.0561	0.081890
BCN-1	10.1130	0.046539
BCN-2	11.2217	0.048187
BCN-3	10.9226	0.047380
Average value	10.7524	0.047369



**Fig. S11.** The  $^1\text{H-NMR}$  spectra of (a)  $\text{CN}_{0.10}\text{PM}$ , (b)  $\text{CN}_{0.12}\text{PM}$ , (c)  $\text{CN}_{0.16}\text{PM}$ , (d)  $\text{CN}_{0.18}\text{PM}$  and (e)  $\text{CN}_{0.20}\text{PM}$  after 20 h simulated visible light irradiation; (f) Chemical structures and peak assignments; Peaks labeled with an asterisk (\*) are uncertain substance. Maleic acid was used as an internal standard. Photoreforming conditions:  $\text{CN}_x\text{PM}$  (20 mg), NaOH (1 M, 50 mL), PET substrate ( $25 \text{ mg}\cdot\text{mL}^{-1}$ ), irradiation ( $\lambda > 420 \text{ nm}$ ,  $20 \text{ }^\circ\text{C}$ ).

**Table S2.** Quantification of the organic oxidation products formed from PET after 20 h of photoreforming with CN<sub>x</sub>PM. Maleic acid was used as an internal standard.

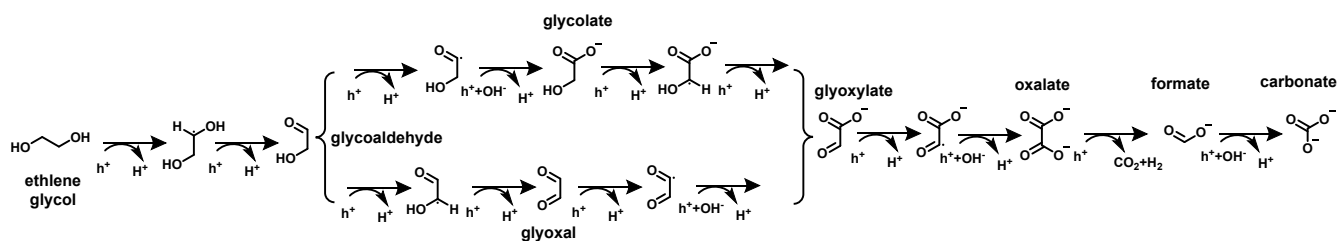
Catalyst	Substrate	Base	Time (h)	Organic compound quantity (nmol)		
				Acetate	Formate	Glyoxal
CN <sub>0.14</sub> PM	PET	1 M	20	860	10340	7320
CN <sub>0.10</sub> PM	PET	1 M	20	230	2068	862
CN <sub>0.12</sub> PM	PET	1 M	20	287	3446	2154
CN <sub>0.16</sub> PM	PET	1 M	20	287	2585	862
CN <sub>0.18</sub> PM	PET	1 M	20	888	1855	3757
CN <sub>0.20</sub> PM	PET	1 M	20	287	1730	2154

\*Photoreforming conditions: CN<sub>x</sub>PM (20 mg), NaOH (1 M, 50 mL), PET substrate (25 mg·mL), irradiation: ( $\lambda > 420$  nm), 20 °C.

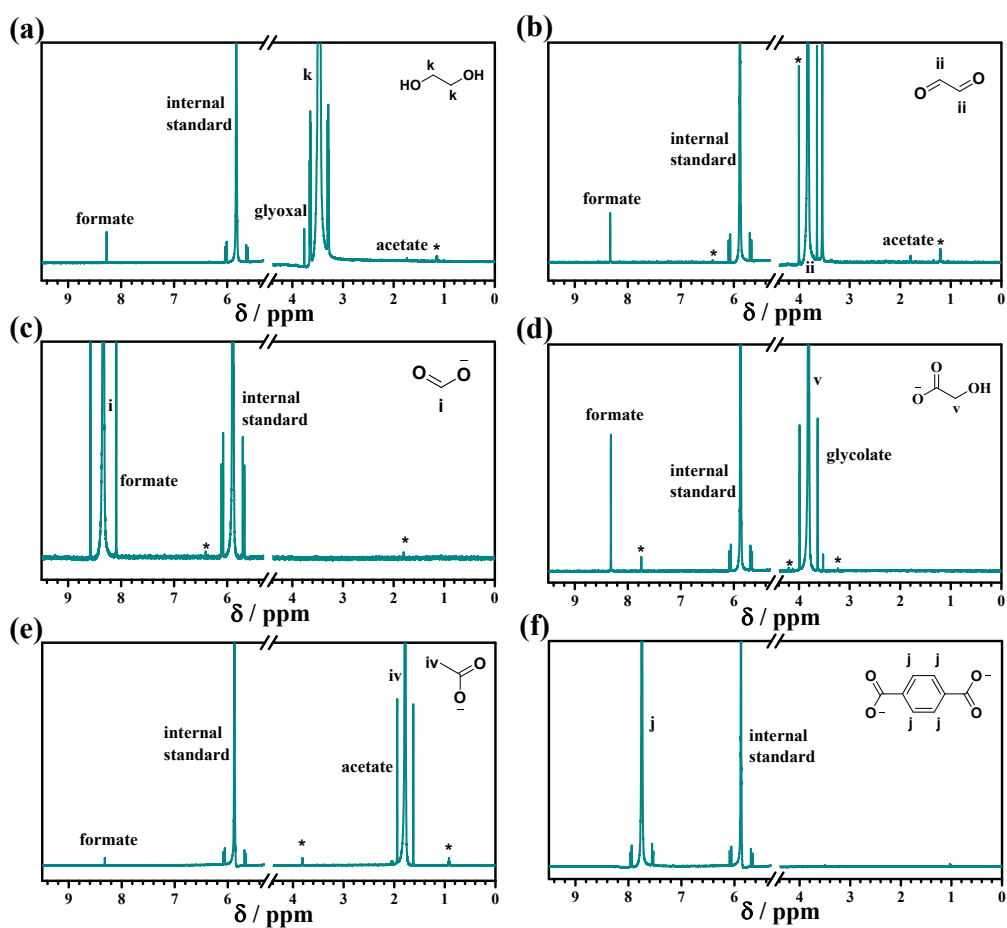
**Table S3.** Quantification (by <sup>1</sup>H-NMR spectroscopy) of PET after photoreforming.

Sample	Component	Ideal quantity of component (umol)	Measured quantity of component (umol)	Conversion (%)
PET	Ethylene glycol	52.04	30.8	59
	Terephthalate	52.04	37.48	72

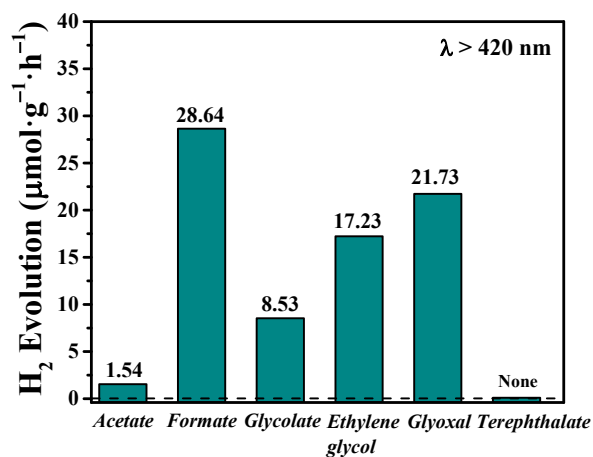
\*Photoreforming conditions: CN<sub>0.14</sub>PM (20 mg), NaOH (1 M, 50 mL), PET substrate (25 mg·mL), irradiation: ( $\lambda > 420$  nm), 20 °C.



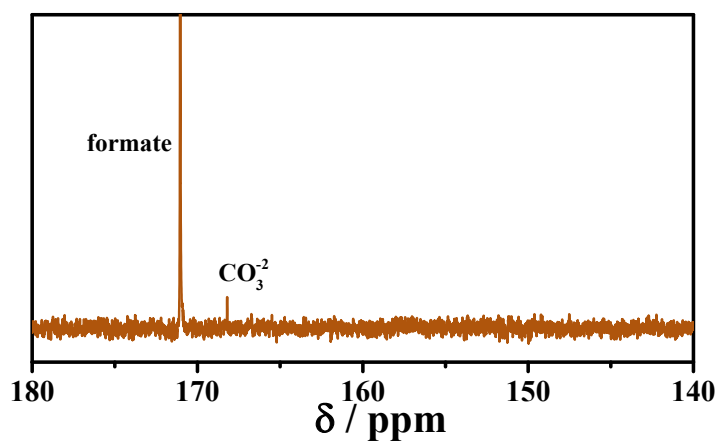
**Fig. S12.** Proposed reaction scheme for the photo-oxidation of ethylene glycol.



**Fig. S13.** The <sup>1</sup>H-NMR spectra of (a) ethylene glycol, (b) glyoxal, (c) formate, (d) glycolate, (e) acetate and (f) terephthalate after 20 h simulated visible light irradiation. Maleic acid was used as an internal standard. Photoreforming conditions: CN<sub>0.14</sub>PM (20 mg), NaOH (1 M, 50 mL), substrate (25 mg·mL<sup>-1</sup>), irradiation ( $\lambda > 420$  nm, 20 °C).



**Fig. S14.** Photoreforming of oxidation intermediates with CN<sub>0.14</sub>PM ( $\lambda > 420$  nm). Photoreforming conditions: CN<sub>0.14</sub>PM (20 mg), NaOH (1 M, 50 mL), substrate (25 mg·mL<sup>-1</sup>), irradiation ( $\lambda > 420$  nm, 20 °C).



**Fig. S15.** The <sup>13</sup>C-NMR spectra of formate after 20 h simulated visible light irradiation. Photoreforming conditions: CN<sub>0.14</sub>PM (20 mg), NaOH (1 M, 50 mL), substrate (25 mg·mL<sup>-1</sup>), irradiation ( $\lambda > 420$  nm, 20 °C).

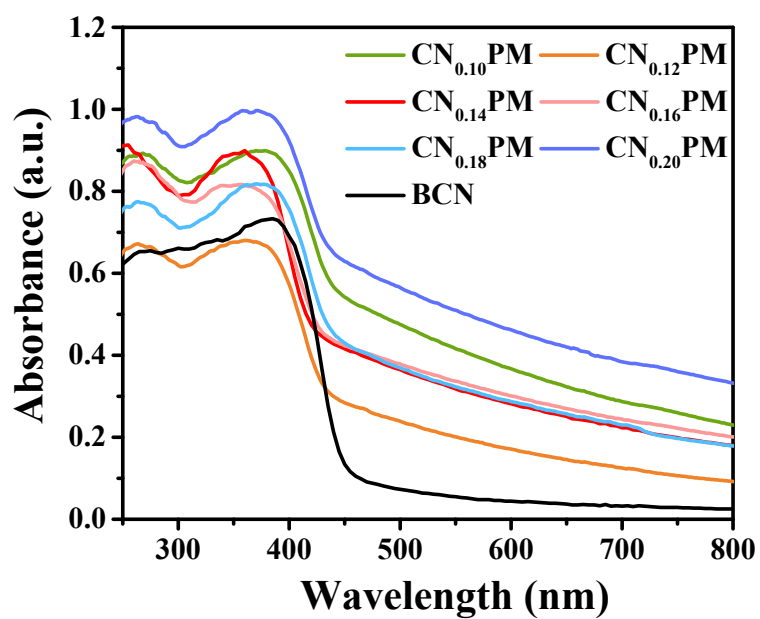


Fig. S16. UV-vis absorption spectra of  $\text{CN}_x\text{PM}$ .

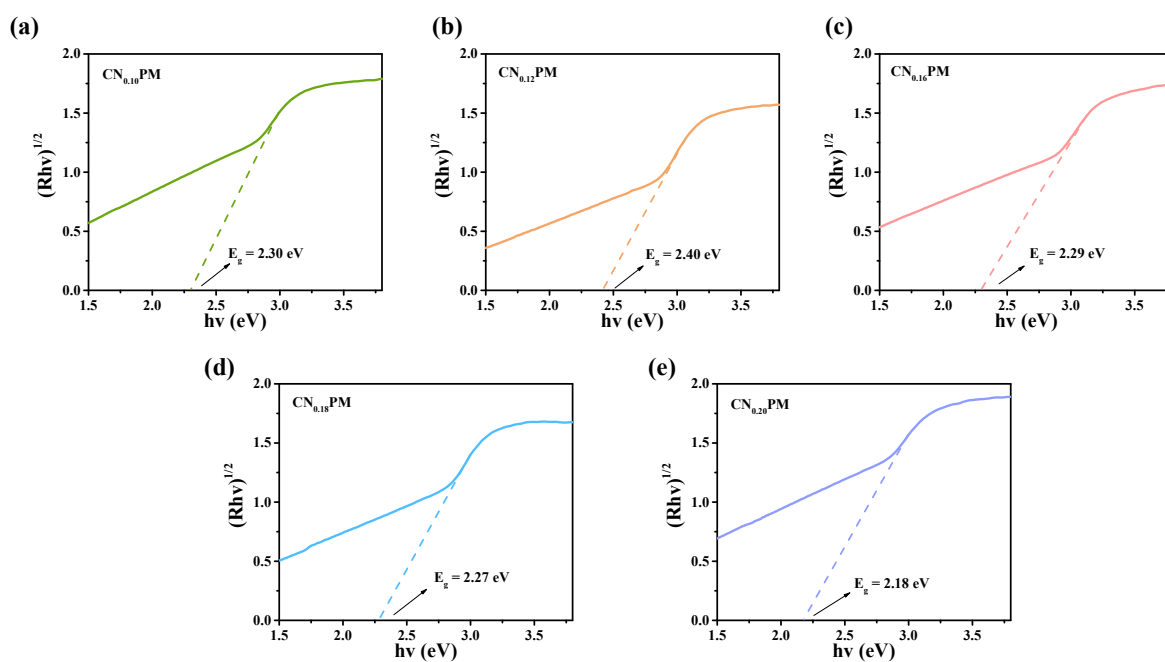


Fig. S17. Tauc plots of  $\text{CN}_x\text{PM}$  calculated by DRS.

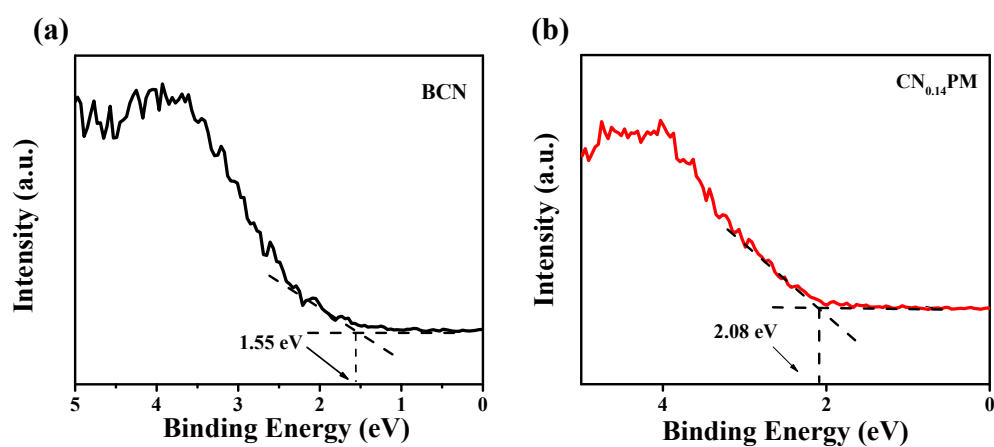


Fig. S18. The XPS valence band spectrum of BCN and  $\text{CN}_{0.14}\text{PM}$ .

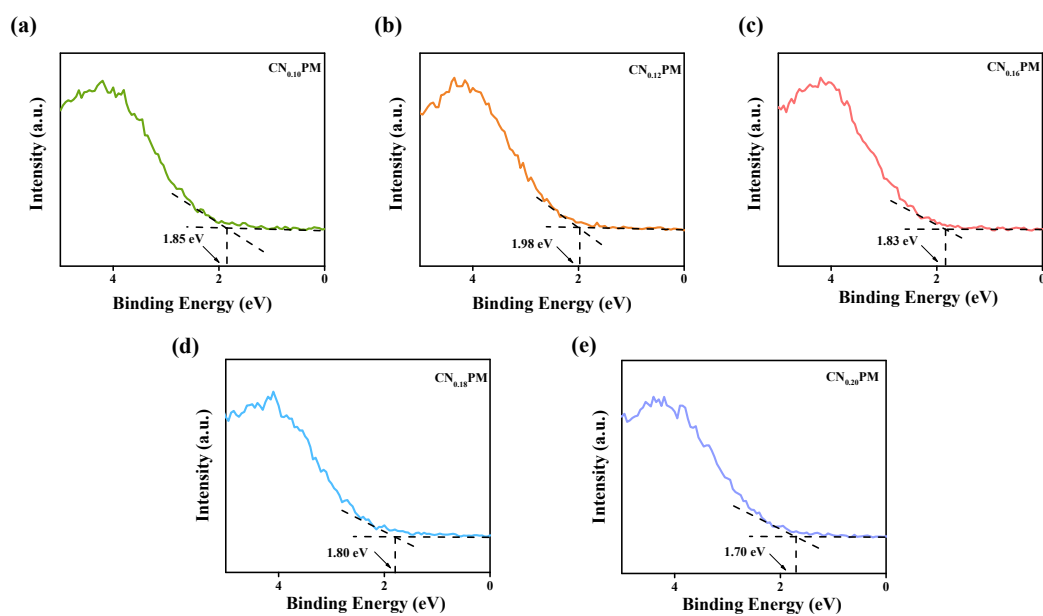


Fig. S19. The XPS valence band spectrum of  $\text{CN}_x\text{PM}$ .

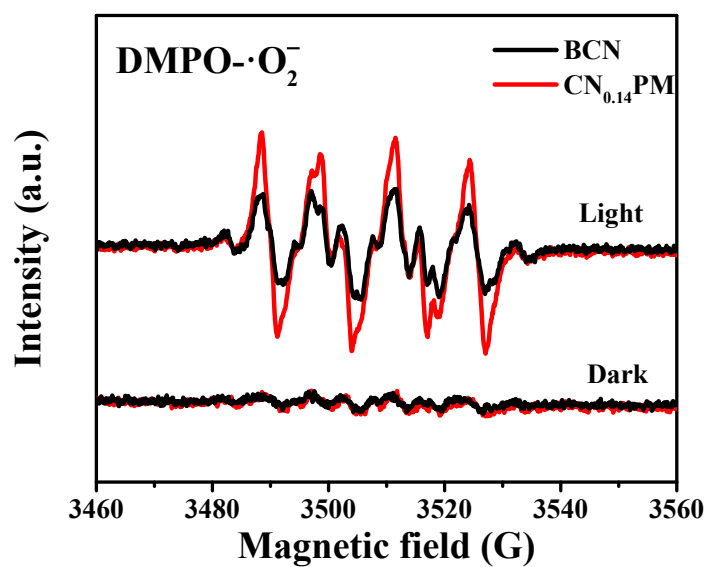




Fig. S20. DMPO spin-trapping EPR spectra in methanol dispersion for  $\text{DMPO}\cdot\text{O}_2^-$ .

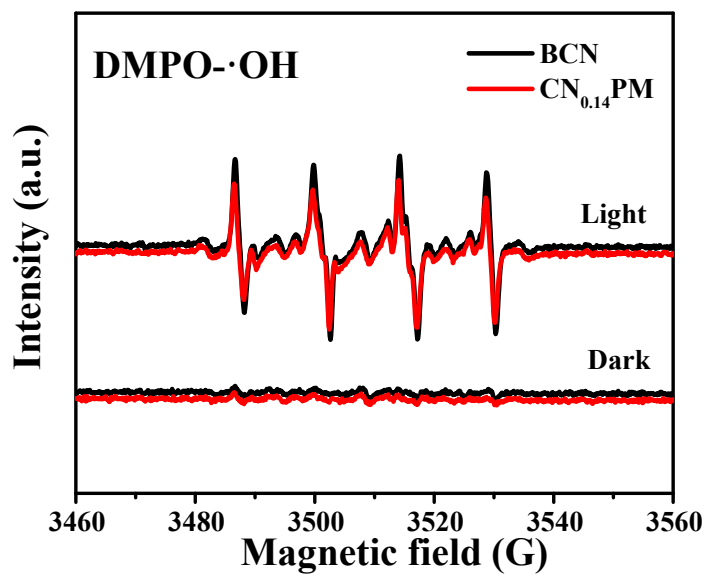


Fig. S21. DMPO spin-trapping EPR spectra in aqueous dispersion for  $\text{DMPO}\cdot\text{OH}$ .

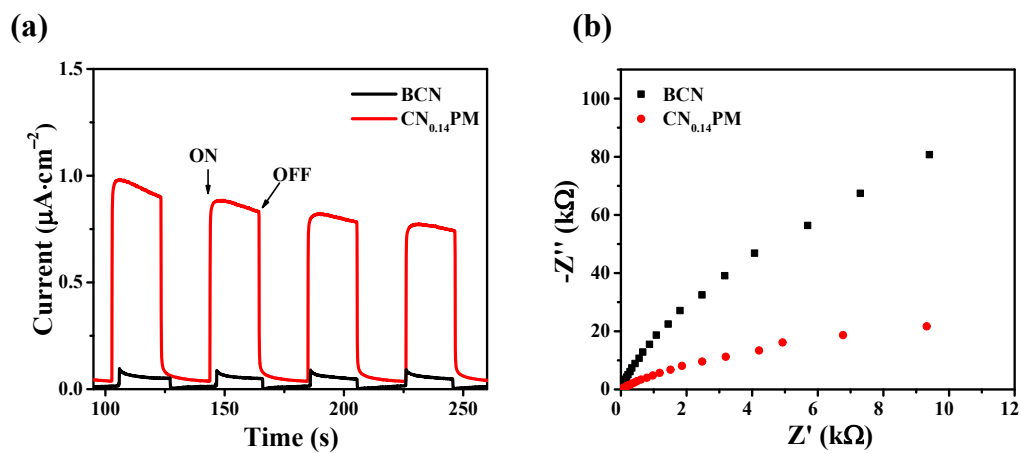


Fig. S22. (a) periodic on/off photocurrent response; (b) EIS Nyquist plots of BCN and  $\text{CN}_{0.14}\text{PM}$ .

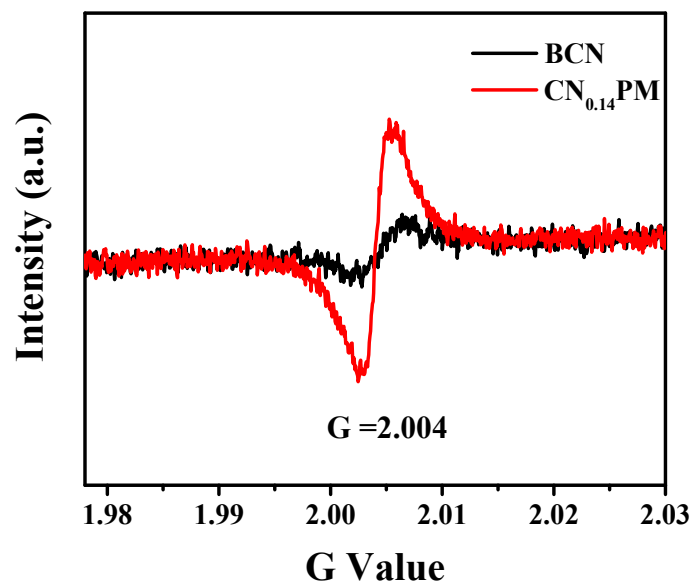


Fig. S23. Electron paramagnetic resonance (EPR) of BCN and  $\text{CN}_{0.14}\text{PM}$ .

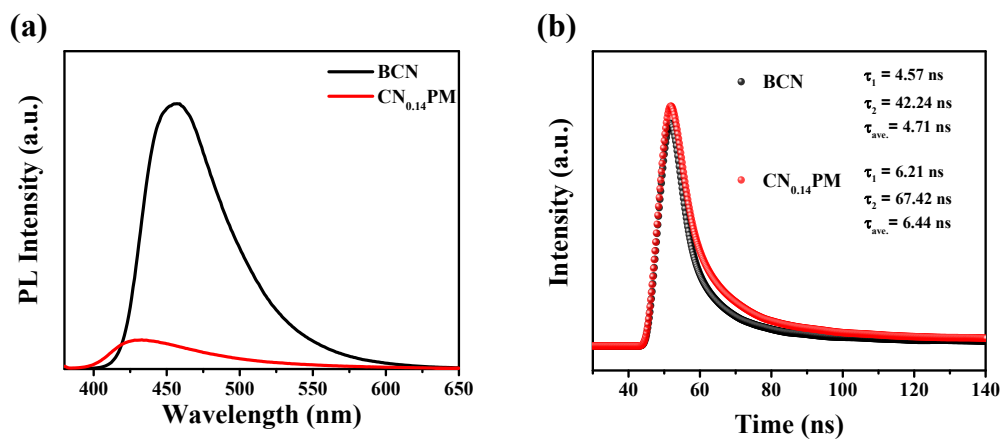
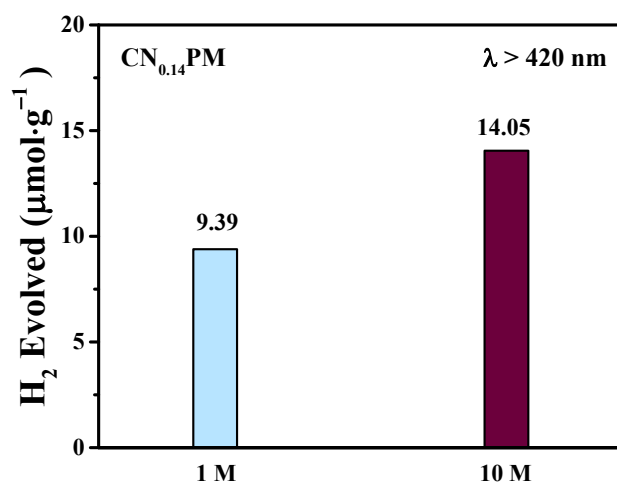


Fig. S24. (a) Steady-state PL spectra; (b) Fluorescence (FL) emission decay spectra.



**Fig. S25.** Photoreforming of PET with CN<sub>0.14</sub>PM at 1 M and 10 M NaOH.

1. B. Wu, L. Zhang, B. Jiang, Q. Li, C. Tian, Y. Xie, W. Li, H. Fu, *Angew. Chem. Int. Ed.*, **2021**, *60*, 4815-4822.
2. T. Uekert, H. Kasap, E. Reisner, *J. Am. Chem. Soc.*, **2019**, *141*, 15201-15210.