Polymeric Aromatic N-Oxide: A Novel Kind of Metal-Free Photocatalyst

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Electronic Supplementary Information (ESI)

Experimental details:

I. Synthesis of polyimide and CNP(C_3N_4)

Polyimide was synthesized by the following way: melamine and 1,2,4,5-benzenetetracarboxylic anhydride (PMDA) were put into a crucible according to the molar ratio of 1:1. And a cover was used to make this crucible semi-closed. Then the crucible was heated to 598 K at the heating rate: 7 K/min. When temperature reached 598 K, it was kept for 4 hours (Fig. S1). After that, polyimide was stirred in about 50 ml H_2O/ 1 g polyimide at 333 K and filtered to get the solid. Finally, the solid was dried at 373 K over night.

CNP was also synthesized in the same way with melamine as reactants and the crucible was heated to 723 K (Fig. S3)[1].

II. Synthesis of PINO and CNPNO

2 g of polyimide and 10 ml CH_3COOH and 20 ml of 30% H_2O_2 was mixed. Then sealed the system to semi-closed, heated it to 333 K and kept for 3 hours under stirring condition. After that, the mixture was filtered and solid was washed with pure

water, till the flavor of CH_3COOH could not be smell. Then the solid was dried at 393 K over light.

CNPNO was also synthesized using the same method with CNP as reactants, but the reaction time is 24 hours.

III. Photodegradation of MO

MO solution was prepared in 0.05 mol/L NaH_2PO_4, 0.05 mol/L H_3PO_4 and 0.05 mol/L NaCl buffer solution.

Certain amount of catalyst (polyimide, PINO: 0.100 g, CNP and CNPNO: 0.010 g) was dispersed in 100 ml of 5 mg/L MO solution in Pyrex reactor. After stirring in the dark for 0.5 h, visible light irradiation was provided by a 300 W Xe lamp with a 420 nm cut-off filter. Along the experiment, the reactor was kept at 298 K by water bath.

N_2 control experiment was conducted in the same way except N_2 was pumped into the Pyrex reactor from the beginning of the experiment.

Wavelength dependence experiments were conducted on PINO under light irradiation by using different monochromatic filter (420, 450, 475, 500, 550 nm) each time, and the irradiation time was 3 hours.

IV. Adsorption experiments

Adsorption of methyl orange:

Preparation of methyl orange: methyl orange used as adsorbent was diluted using the MO used in photodegradation with water at the ratio of 1:1.

0.500 g of catalyst was added to 40 mL of MO solution and stirred. Certain amount of mixture was extracted to analyze at a fixed interval.

Adsorption of magneson I:

Preparation of saturated magneson I: excessive magneson I was dispersed in 1000 mL of water and 0.1 mol of NaH_2PO_4 was added, then the mixture were stirred for 2 hours at 333 K. When the mixture cooled down to room temperature, they were filtered; the solution was kept and placed over night.

0.100 g of catalyst was added to 40 ml of saturated magneson I and stirred. Solution was extracted at regular intervals. The extracted mixture was centrifugated and the concentration of the solution is decided by UV-Visible spectrometer.

V. Characterization

Fourier transform infrared spectra were acquired on NEXUS870.

X-ray diffraction measurement was performed on Rigaku RINT2000.

UV-Visible diffuse reflection spectra was measured on Shimadzu UV2550 and converted from reflection to absorbance using Kubelka-Munk method.

Photoluminescence spectra were collected Varian Cary Eclipse with excitation wavelength at 200 nm.

X-ray photoelectron spectra were recorded on PHI5000 VersaProbe.

Elemental Analysis was performed on Vario MICRO and all the samples were dried at 393 K over night before test.

Computational details:

All calculations were performed with Gaussian 03 program. B3LYP/6-31G method was used to optimize the model of polyimide and PINO. HOMO and LUMO are constructed with GaussView based on the calculation results.

HF/6-31g was used to optimize the model and acquire the energy of LUMO and HOMO according to the reference[2].

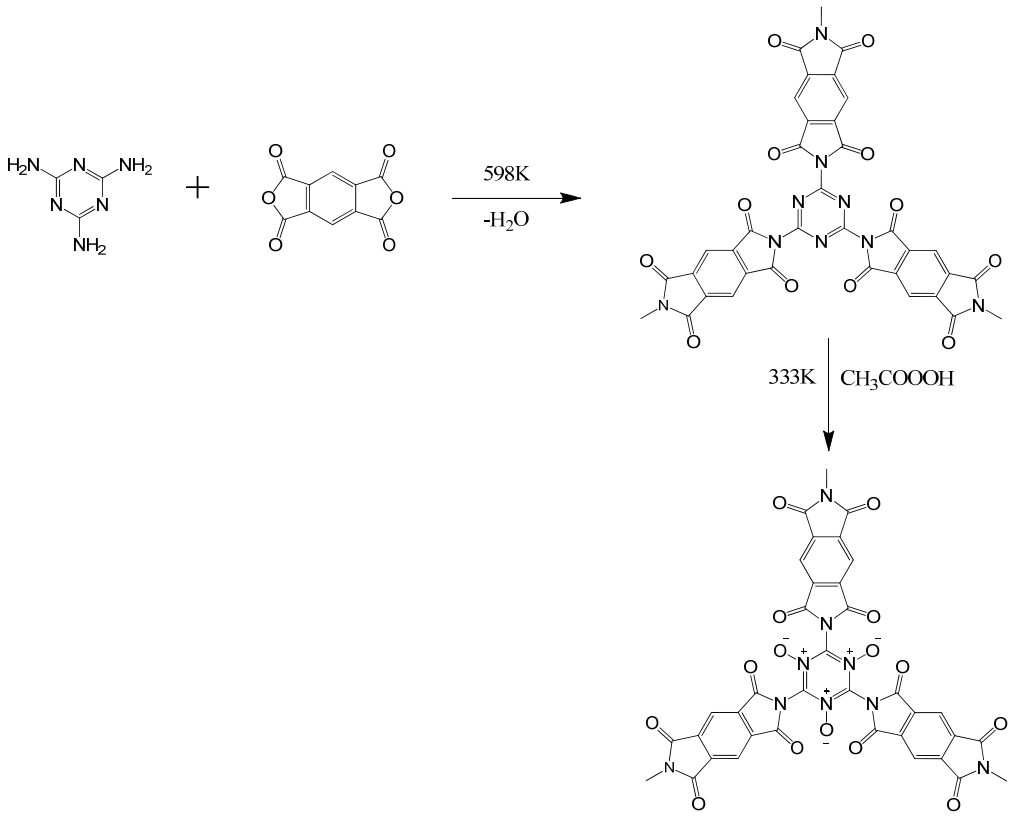

Fig. S1 Synthesis of polyimide and PINO.

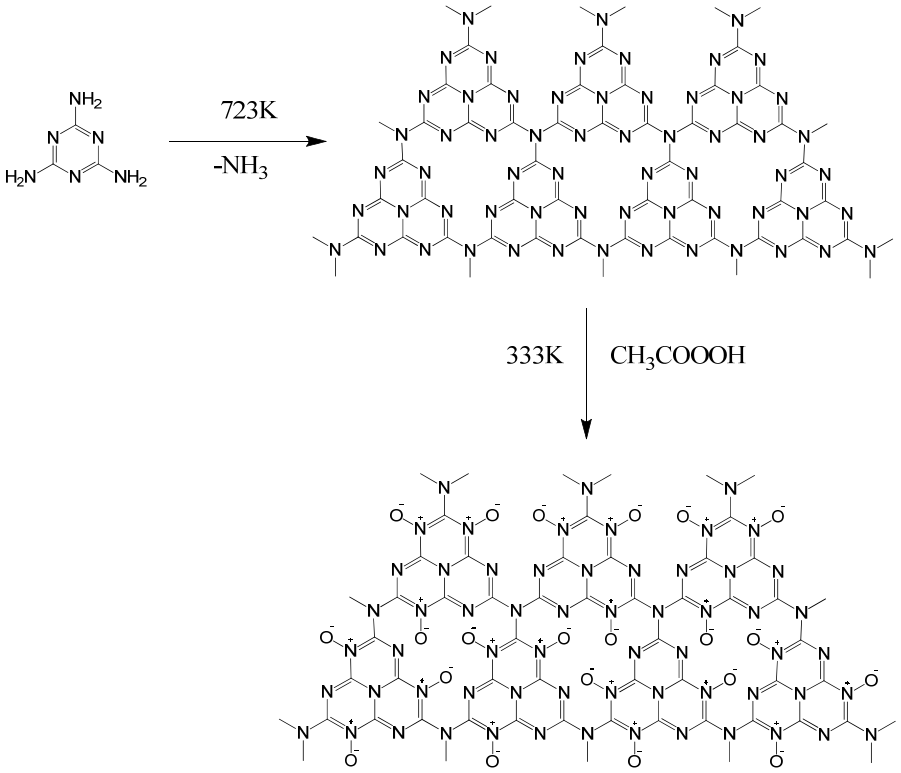

Fig. S2 Synthesis of C_3N_4 and CNPNO.

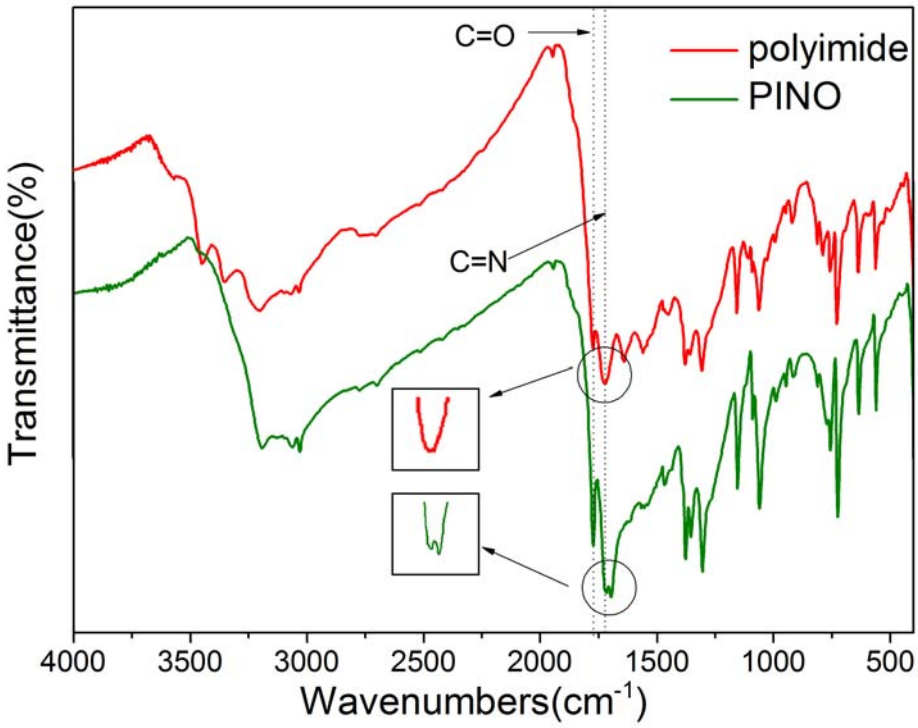

Fig. S3 FTIR spectra of polyimide and PINO

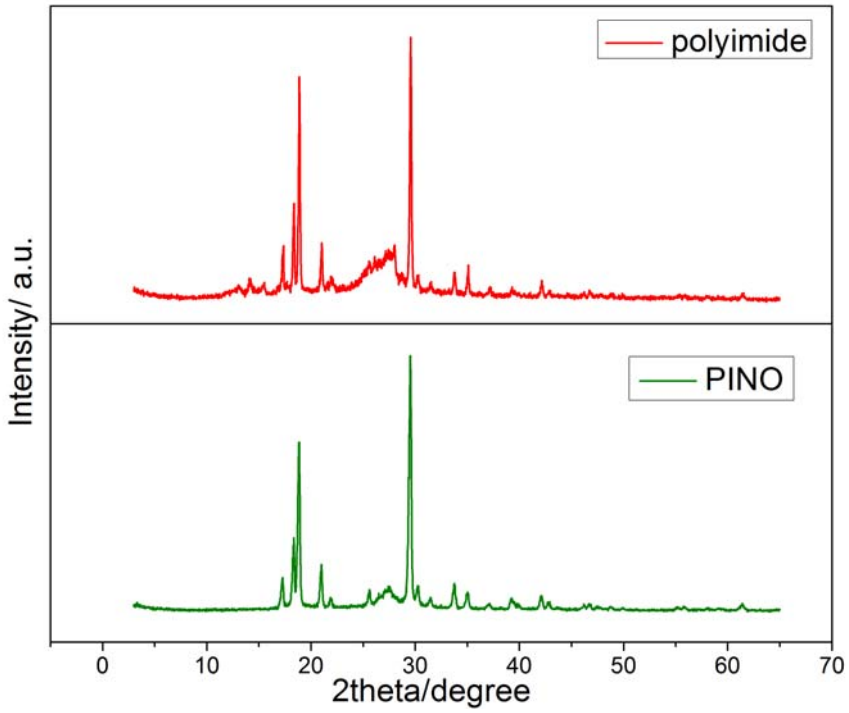

Fig. S4 XRD spectra of polyimide and PINO

Table S1 Elemental Analysis of polyimide and PINO

Sample	C	H	N	O
Polyimide	45.49%	2.14%	26.68%	25.69%
PINO	46.05%	2.04%	20.45%	31.46%

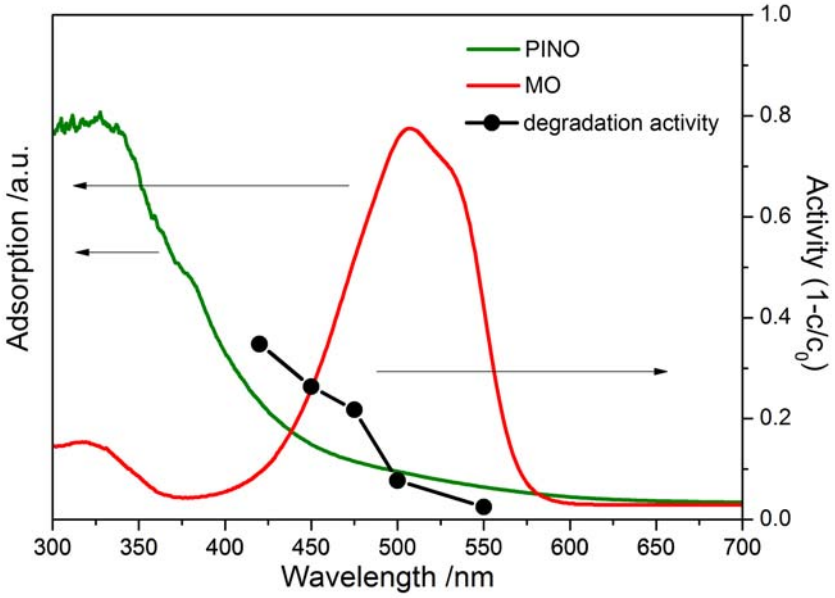

Fig. S5 UV-Visible spectra of PINO and MO and photodegradation rate with different monochromatic filter.

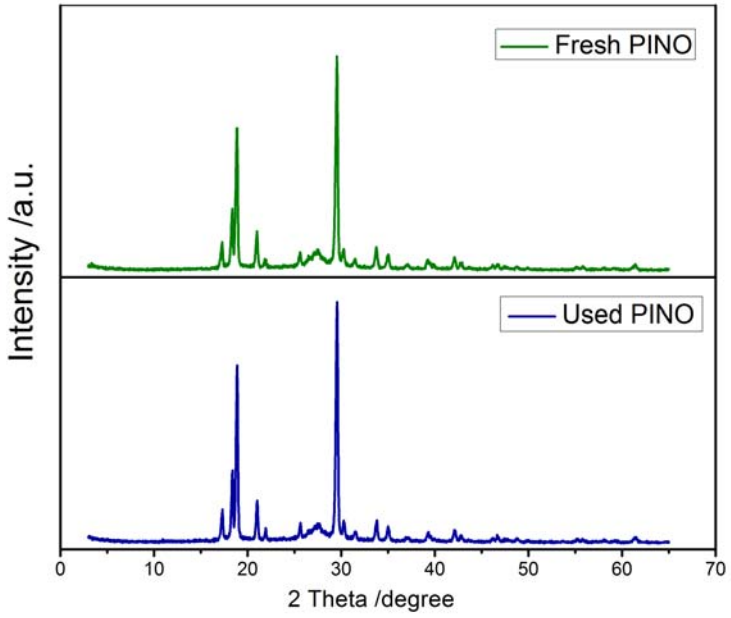

Fig. S6 XRD of fresh PINO and used PINO

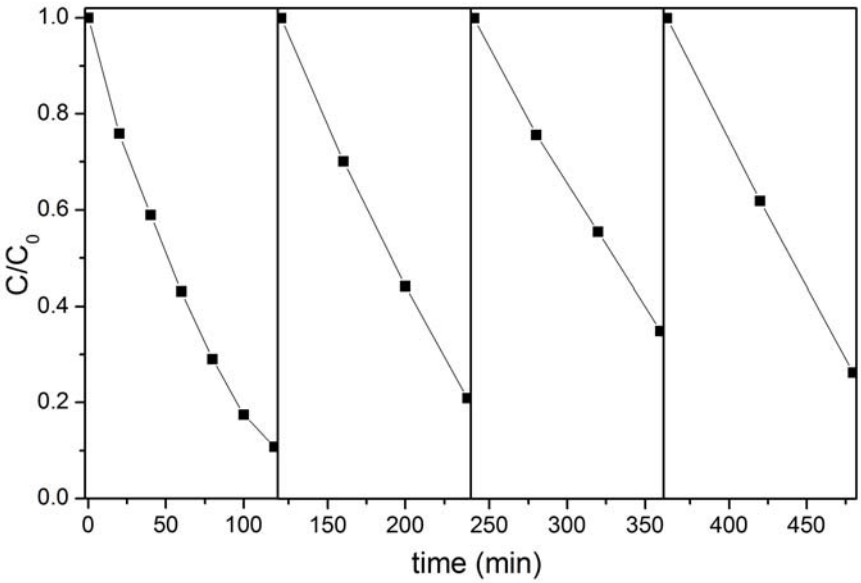

Fig. S7 Cyclic runs of MO degradation by PINO

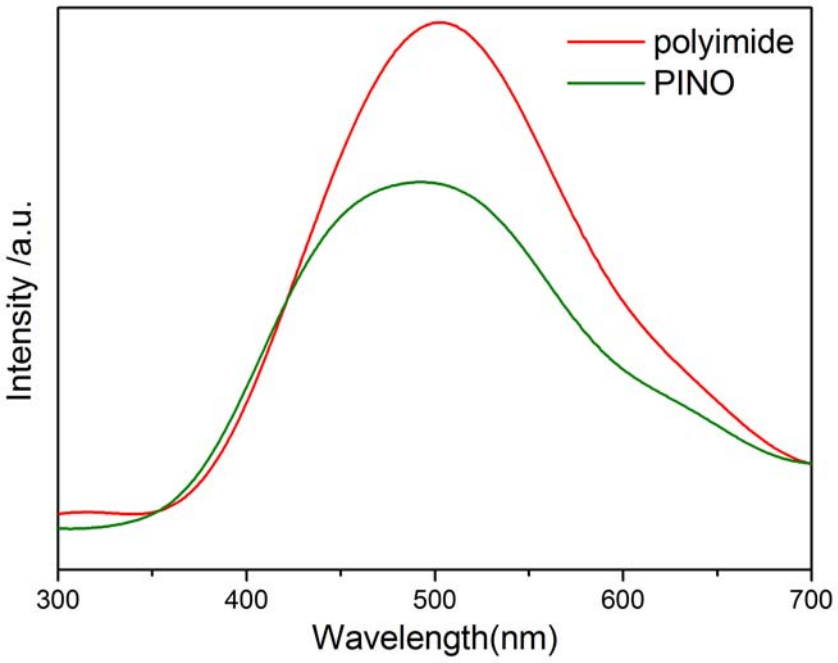

Fig. S8 Photoluminescence spectra of polyimide and PINO

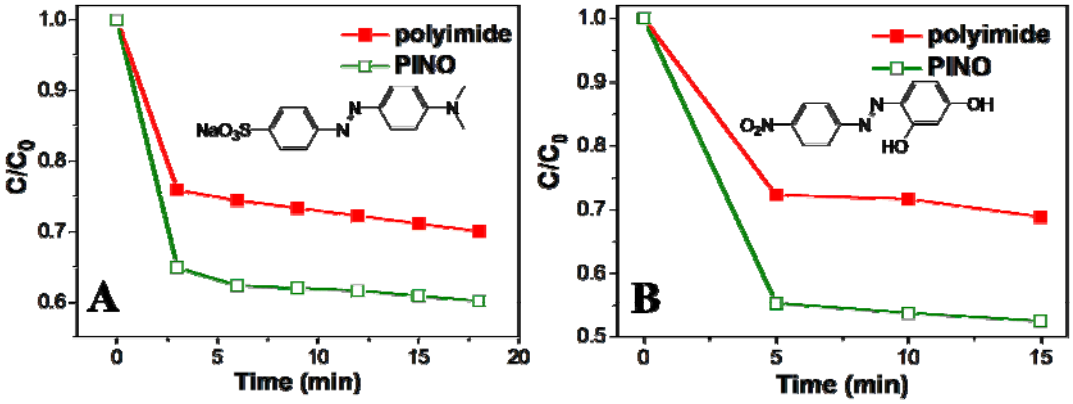

Fig. S9 Adsorption of (A) MO and (B) Magneson I on polyimide and PINO.

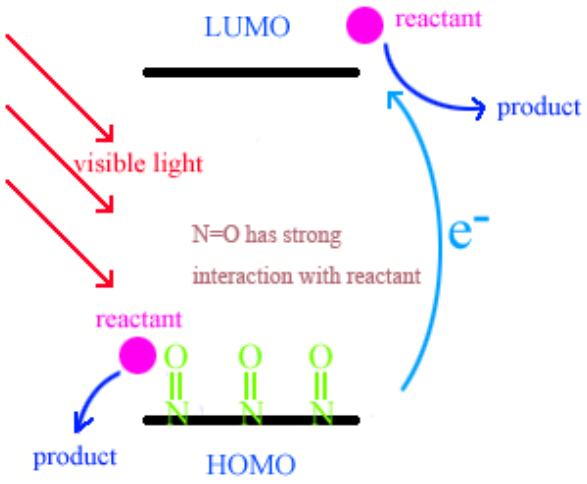

Fig. S10 Synergic effect in PINO

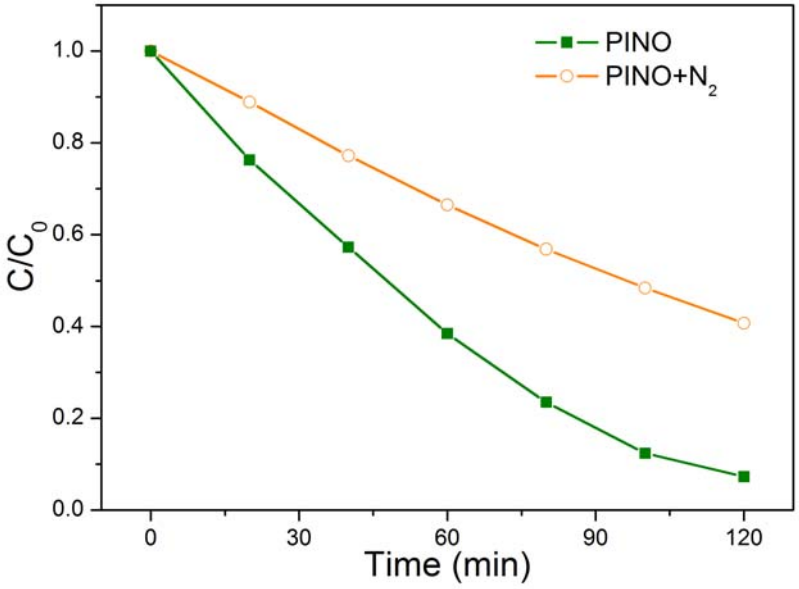

Fig. S11 Photodegradation of MO in air and N_2 atmosphere

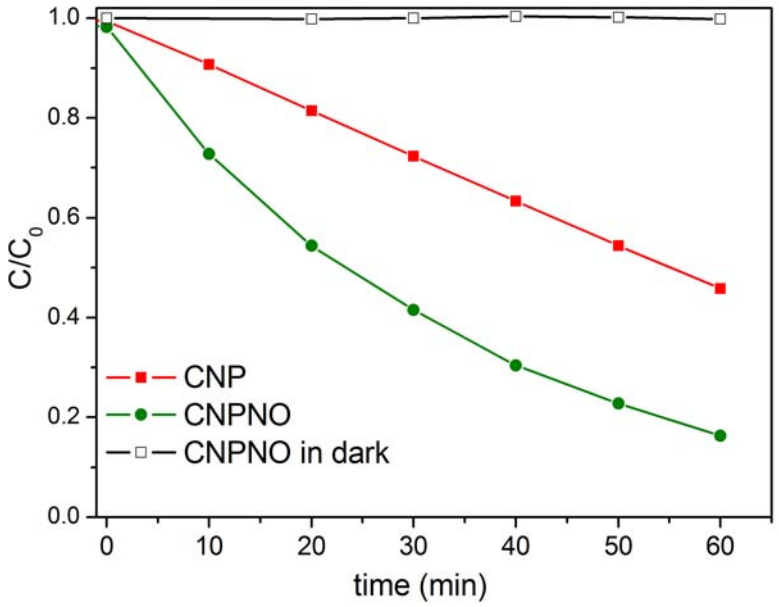

Fig. S12 Photodegradation of MO by CNP and CNPNO

Reference

1. S. C. Yan, Z. S. Li and Z. G. Zou, *Langmuir*, 2009, **25**, 10397-10401.