

# Salt-Mediated Structural Transformation in Carbon Nitride: From Regulated Atomic Configurations to Enhanced Photocatalysis

Kechen Zhang <sup>1,2</sup>, Changxin Liu <sup>1,2</sup>, Qiang Liu <sup>1,2</sup>, Zheyang Mo <sup>1,2</sup> and Dawei Zhang <sup>1,2,\*</sup>

<sup>1</sup> Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

<sup>2</sup> School of Materials Science and Engineering, University of Science and Technology of China, Shenyang 110016, China

\* Correspondence: zdwchem@mail.ustc.edu.cn

## Preparation of standard solutions

To prepare the standard solutions for tetracycline (TC), phenol and rhodamine b (RhB), 50 mg·L<sup>-1</sup> TC water solution, 10 mg·L<sup>-1</sup> phenol water solution and 10 mg·L<sup>-1</sup> RhB water solution were first made. Then, standard solutions with lower concentration were prepared through the dilution of high concentration solution (0.1, 0.5, 1, 5, 10, 20, 30, and 40 mg·L<sup>-1</sup> for TC; 0.1, 0.5, 1, 2, 4, 6, and 8 mg·L<sup>-1</sup> for phenol and RhB).

## Quantification of pollutants

Quantification of TC was performed on the high performance liquid chromatography (HPLC) system LC-20A (Shimadzu, Japan) equipped with SPD-20A UV-vis detector. The column used in the measurements was a Diamonsil C18(2) (5 μm particle size, 200 \* 4.6 mm). The chromatography was conducted at 25 °C. The mobile phase was methanol. The flow rate was 0.5 mL·min<sup>-1</sup>. In each measurement, 10 μL of standard solution or sample was injected. The effluent was monitored at 360 nm (used for quantification) and 254 nm. The area of peak with retention time of 9.5 min was used to determine the concentration.

Quantification of phenol was carried out by a colorimetric method [49]. 30 μL of 3.739 mol·L<sup>-1</sup> NH<sub>4</sub>Cl solution (2 g NH<sub>4</sub>Cl dissolved in 10 mL NH<sub>3</sub>·H<sub>2</sub>O), 60 μL of 0.098 mol·L<sup>-1</sup> 4-aminoantipyrine (C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>O) aqueous solution (0.2 g C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>O dissolved in 10 mL H<sub>2</sub>O) and 60 μL of 0.243 mol·L<sup>-1</sup> potassium ferricyanide (K<sub>3</sub>[Fe(CN)<sub>6</sub>]) aqueous solution (0.8 g K<sub>3</sub>[Fe(CN)<sub>6</sub>] dissolved in 10 mL H<sub>2</sub>O) were added to the standard solution or sample, which was then kept for 15 min at 25 °C. The concentration of phenol was determined by measuring the absorption at 502 nm on a UV-2550 UV-vis spectrometer (Shimadzu, Japan). The measurements were carried out at 25 °C. Two 3 mL quartz cuvettes were used in the measurements and the reference cuvette was filled with deionized water.

Quantification of RhB was carried out by measuring the absorption at 554 nm on the UV-vis spectrometer (The measurements conditions are similar with the quantification of phenol).

The calibration curves of TC, phenol and RhB are shown in Figure S6.

## ROSs capture:

Scavengers were used to uncover the reactive oxygen species (ROS) in the degradation: 50 μM K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> for quenching e<sup>-</sup>, 10 mM EDTA·2Na for quenching h<sup>+</sup>, 1 mM benzoquinone

(BQ) for quenching  $\cdot\text{O}_2^-$  and 0.2 mM EDTA·Fe(II) for quenching  $\text{H}_2\text{O}_2$ .

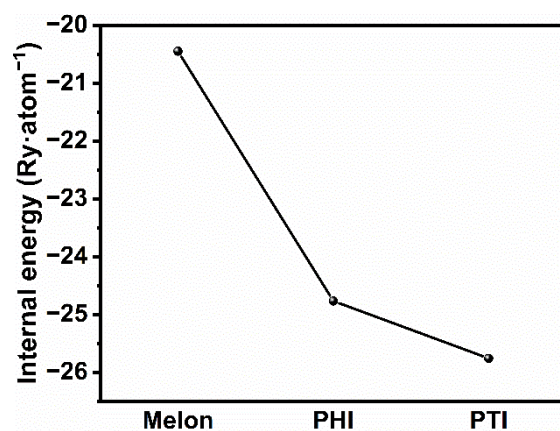


Figure S1. Internal energy of melon, PHI and PTI calculated by DFT.

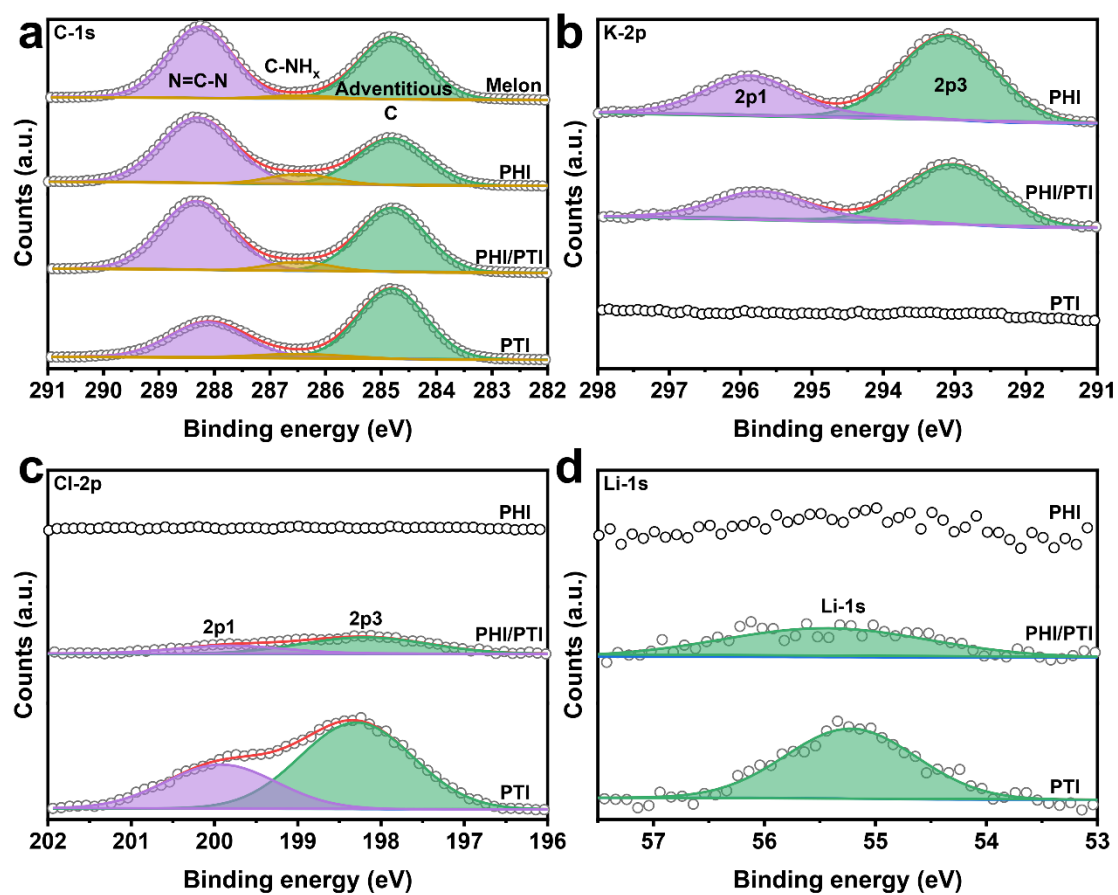
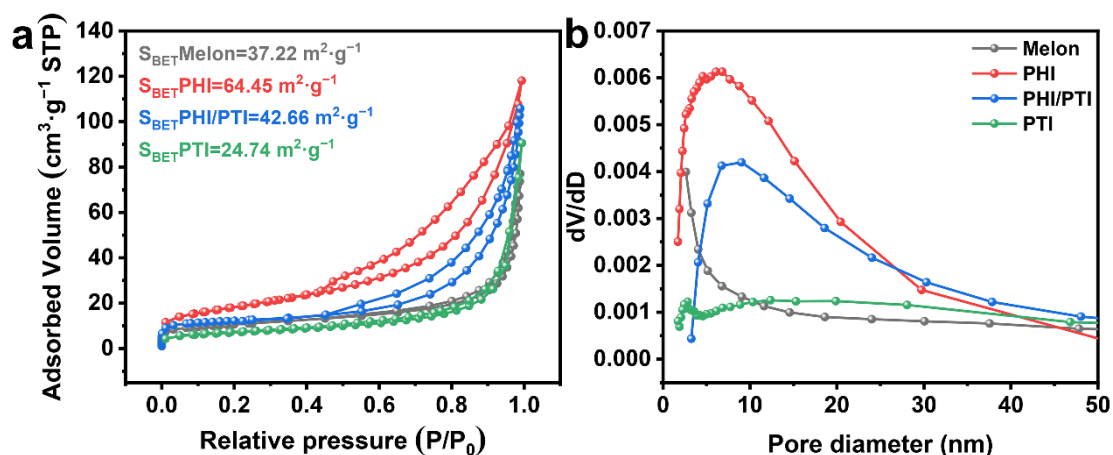
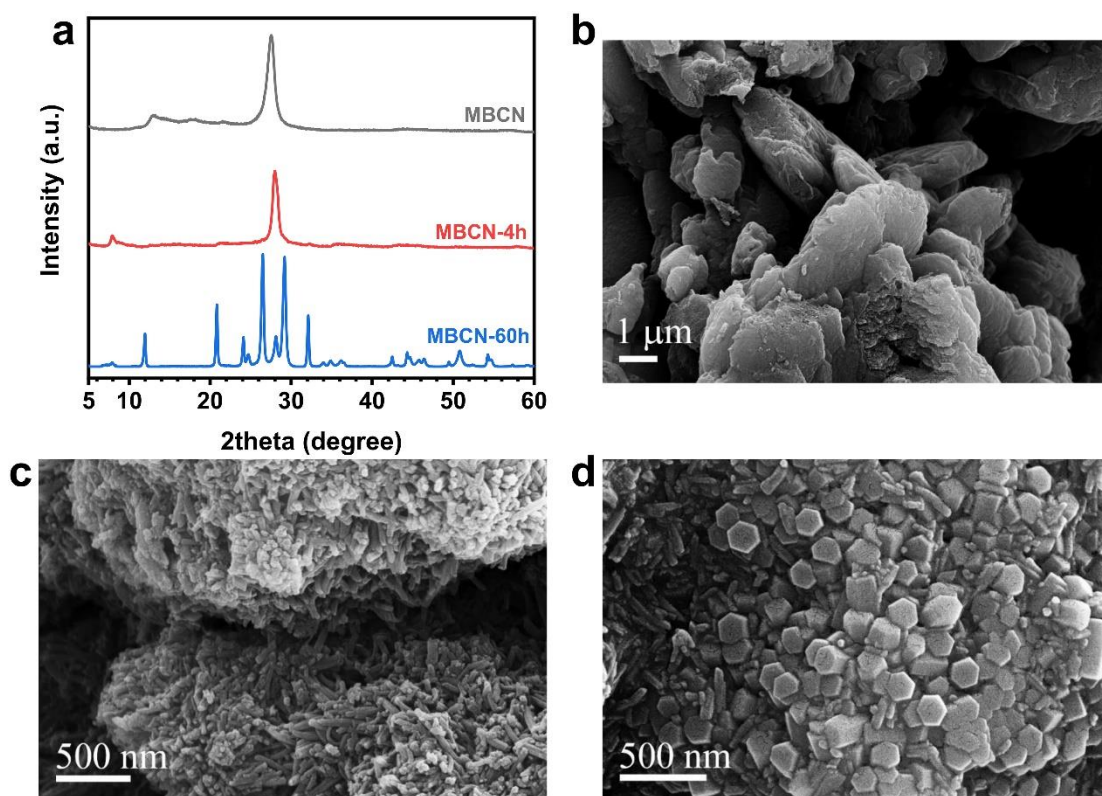


Figure S2. High resolution XPS profiles of the g-C<sub>3</sub>N<sub>4</sub> samples. (a): C-1s spectra. (b): K-2p spectra. (c): Cl-2p spectra. (d): Li-1s spectra.

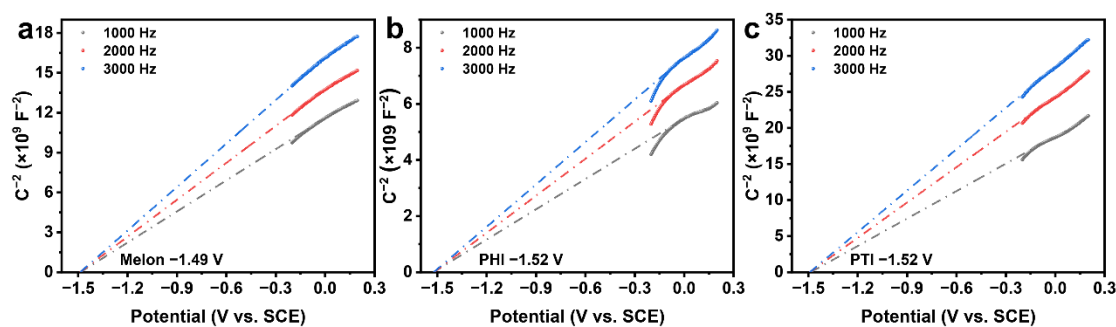


**Figure S3.** Microstructures of the g- $\text{C}_3\text{N}_4$  samples. (a):  $\text{N}_2$  adsorption-desorption isotherms. (b): Pore distribution.

To verify whether this structural transformation occurs only in urea-based g- $\text{C}_3\text{N}_4$ , we performed a similar experiment with melamine precursor. In detail, MBCN was prepared by heating melamine at  $550^\circ\text{C}$  for 4 h in air. Then MBCN was calcined in the environment of molten salts of mixed KCl and LiCl at  $550^\circ\text{C}$  under flow  $\text{N}_2$ . The as-obtained samples were labelled as MBCN- $x$ h ( $x=4$  and 60), in which  $x$  represents the treat time in molten salts. After the calcination, the samples were washed in hot water three times and then dried at  $60^\circ\text{C}$ .



**Figure S4.** Structures and morphologies of the MBCN-based samples. (a): XRD patterns. (b)-(d): SEM images of MBCN, MBCN-4h and MBCN-60h.

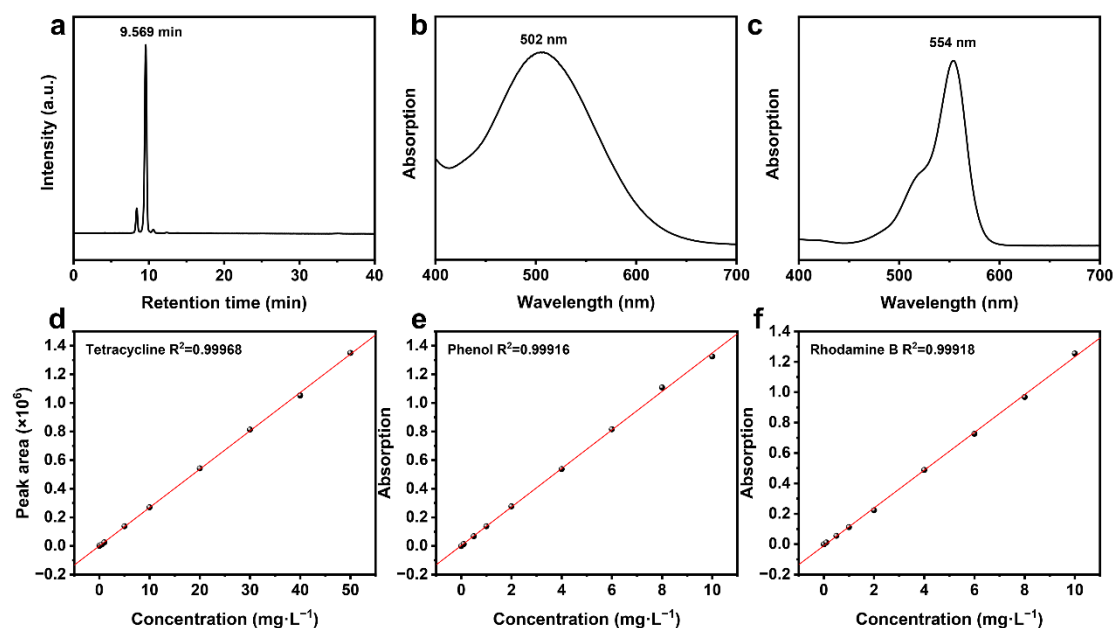


**Figure S5.** MS plots of (a): melon, (b): PHI and (c): PTI.

**Table S1.** Fitting parameters for the time-resolved PL of melon, PHI and PTI.

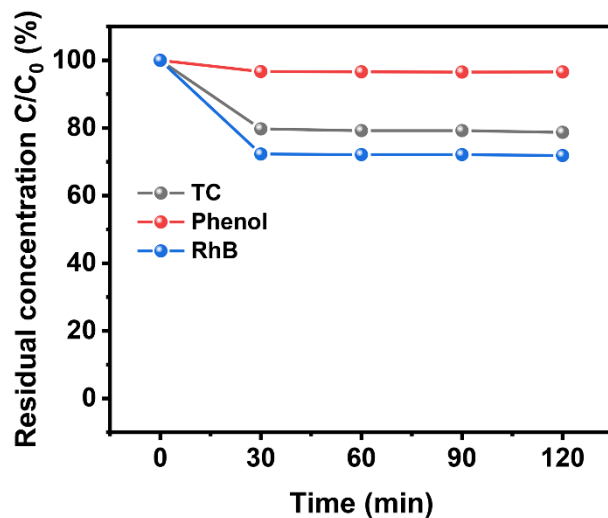
| Sample | $\tau_1$ [ns] | $\tau_2$ [ns] | $B_1$ | $B_2$ | $\tau$ [ns] |
|--------|---------------|---------------|-------|-------|-------------|
| Melon  | 2.25          | 8.68          | 1543  | 925   | 6.74        |
| PHI    | 0.93          | 5.71          | 2416  | 426   | 3.41        |
| PTI    | 1.93          | 6.90          | 1800  | 698   | 4.82        |

All calibration curves showed good linearity ( $R^2 > 0.999$ ) over the test range ( $0.1 \sim 50 \text{ mg} \cdot \text{L}^{-1}$  for TC;  $0.1 \sim 10 \text{ mg} \cdot \text{L}^{-1}$  for phenol and RhB). Limit of quantification were  $0.5 \text{ mg} \cdot \text{L}^{-1}$  for TC and  $0.1 \text{ mg} \cdot \text{L}^{-1}$  for phenol and RhB.

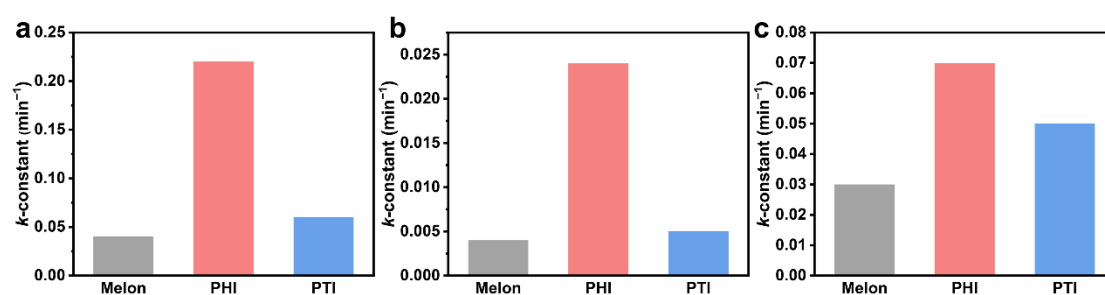


**Figure S6.** (a): Chromatograph of TC ( $50 \text{ mg} \cdot \text{L}^{-1}$ ) standard solution. (b-c): UV-vis absorption spectra of phenol ( $10 \text{ mg} \cdot \text{L}^{-1}$ , After colorimetric reaction) and RhB ( $10 \text{ mg} \cdot \text{L}^{-1}$ ) standard solution. (d-f): Calibration curves of TC, phenol, and RhB.

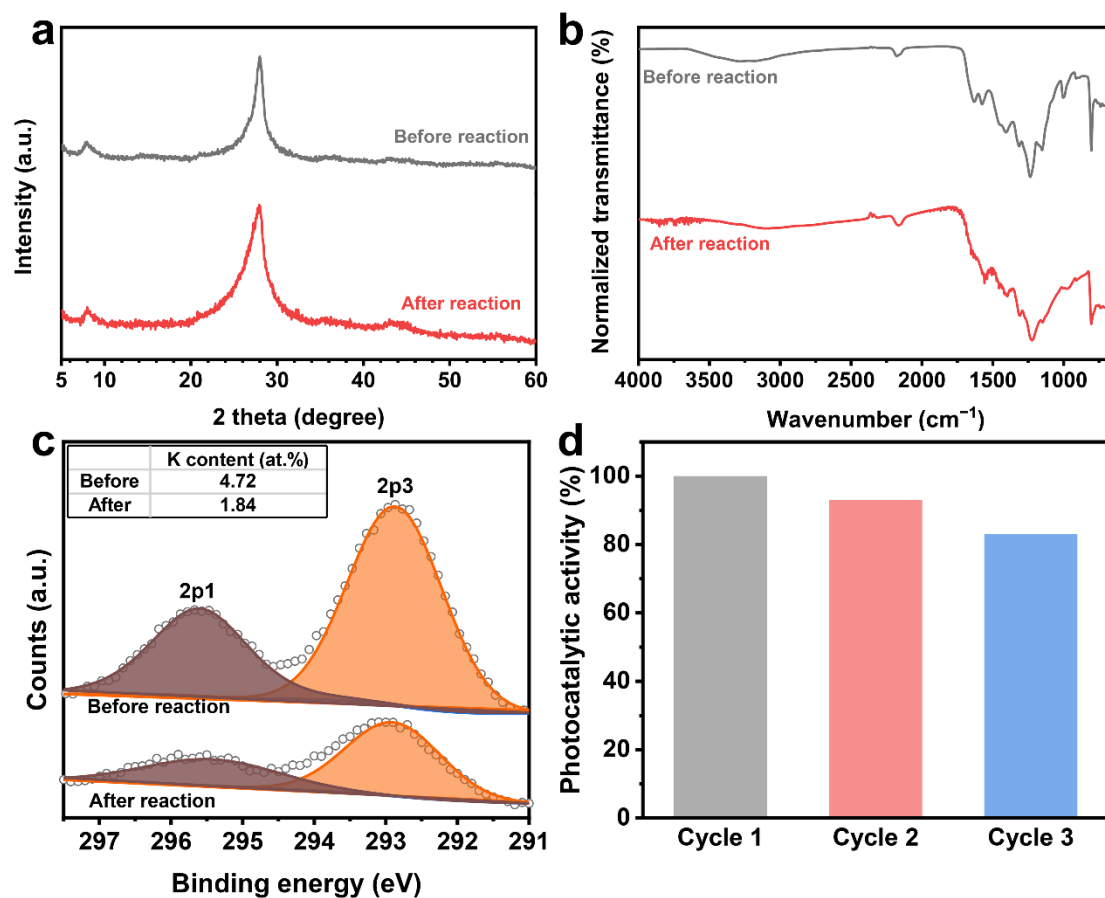
It is clear that, the residual concentration of pollutants exhibited no distinct reduction after 30 min adsorption in dark, demonstrating the equilibrium of adsorption-desorption can be reached after 30 min reaction in dark.



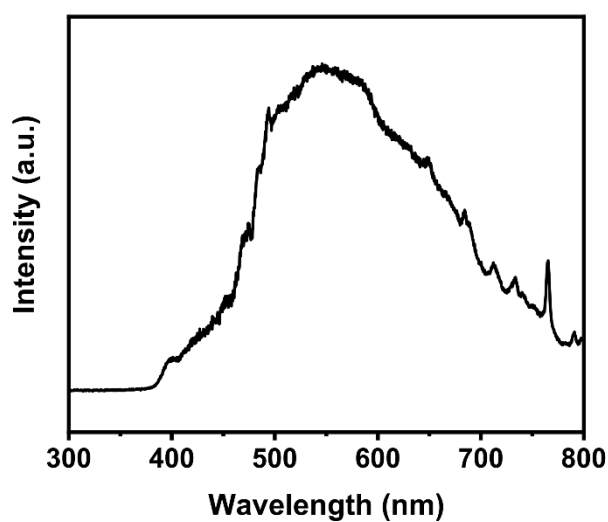
**Figure S7.** Kinetics of adsorption-desorption tests of photocatalyst-pollutants solution in dark.



**Figure S8.** Rate constants for the photocatalytic degradation of (a): TC, (b): phenol and (c): RhB.

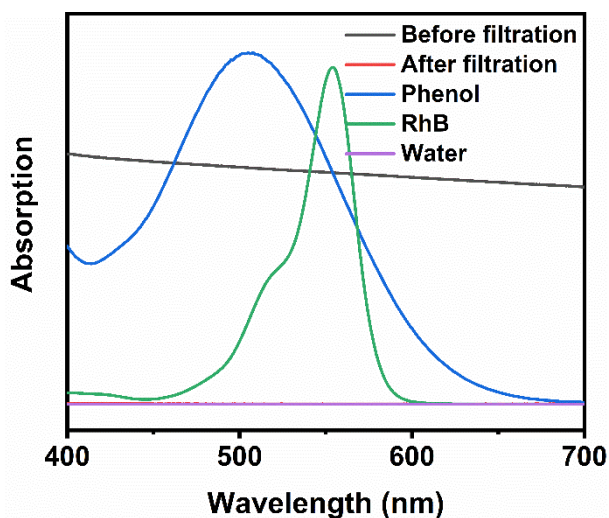


**Figure S9.** Stability tests of PHI photocatalyst for the degradation of TC. (a)-(c): XRD patterns, FTIR spectra and K-2p spectra before and after the reaction. (d): Cyclic tests.



**Figure S10.** Emission spectrum of PLS-SXE 300D Xe lamp equipped with AM1.5 G filter. (Obtained from Perfectlight Sci&Tech, China).

When the water solution of photocatalyst was filtered, the absorption of liquid was barely detected compared to phenol and RhB solutions, demonstrating the 0.22  $\mu\text{m}$  filter (Nylon 66, 13 mm diameter) could reach a good separation of the solids in the samples.



**Figure S11.** UV-vis absorption spectra of pure water, RhB solution ( $10 \text{ mg}\cdot\text{L}^{-1}$ ), phenol solution ( $10 \text{ mg}\cdot\text{L}^{-1}$ , after colorimetric reaction) as well as photocatalyst solution before and after filtration.

## References

49. Lacoste, R.; Venable, S.; Stone, J. Modified 4-aminoantipyrine colorimetric method for phenols. Application to acrylic monomer. *Anal. Chem.* **1959**, *31*, 1246-1249.