

## Supplementary Information

### **In situ formation of red/black phosphorus modified SiO<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> multi-heterojunction for enhanced photocatalytic degradation of organic contaminant**

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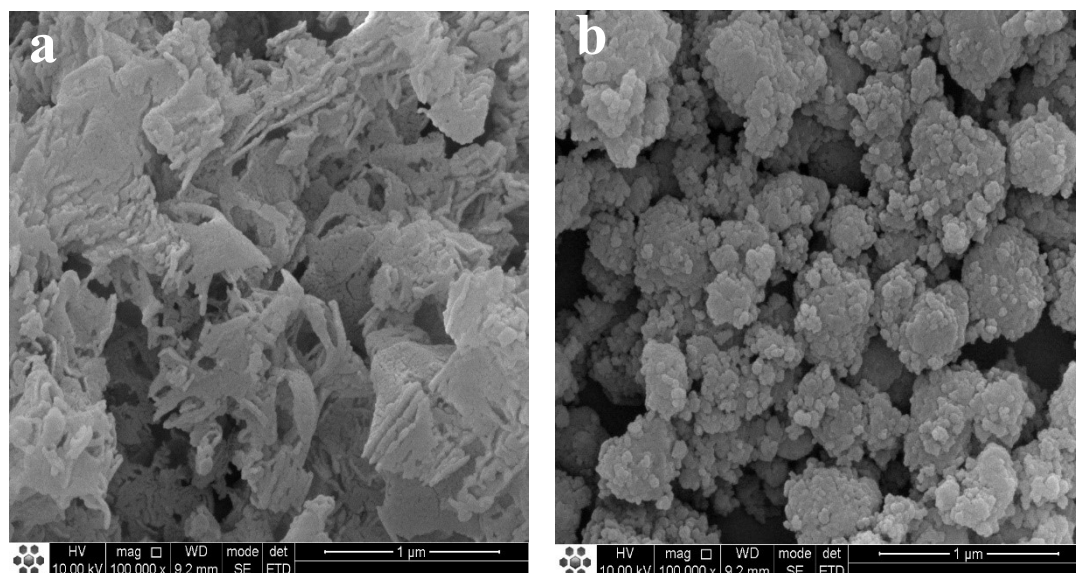
1. Electrochemical test: Electrochemical test was conducted using electrochemical workstation (CHI760E). A conventional three-electrode system was used for testing: the working electrode was connected to the prepared sample and the Ag/AgCl was used as the reference electrode and the platinum network was used as the counter electrode. The electrolyte added is 0.1mol/L NaSO<sub>4</sub>. And can be used in conjunction with the automatic cycle switching system of the device for testing. For the test of I-t curve and EIS, the lower limit of voltage is 0.1V and the upper limit of voltage is 0.3 V, which is relatively stable for the environment of test samples. The alternating current (AC) power supply is 220 V.

The tests for motchotky curves were consistent with the electrochemical stations used for the I-t curve tests, and the test voltages were selected from -3 to 3 V. The test frequency is 2000 Hz. In such an environment, the test performance of the material is stable.

For UV-vis testing of all powder materials, under visible light, a 300 W xenon lamp is used. The wavelength range of the test is 200-800 nm. BaSO<sub>4</sub> is used as a base material. The test material is located in the central surface of BaSO<sub>4</sub>.

2. Preparation of BP/RP heterojunction: BP/RP heterojunction is prepared by heat and pressure generated by high rotational speed. The purified RP and agate balls were added in the preparation process and put into the agate tank with a volume of 50 cm. The ratio of balls and powder was 30:1. The time of the ball milling was 6h and 12h under the experimental conditions of 450 r/min. It is sealed in a sealed stainless-steel tank and vacuumed for 1h.

3. SEM analysis: from the Fig. S1a, the two-dimensional structure of g-C<sub>3</sub>N<sub>4</sub> can provide large specific surface area, which is favorable for the reaction. After introducing of SiO<sub>2</sub>, the nanosheets of g-C<sub>3</sub>N<sub>4</sub> and nanoparticles of SiO<sub>2</sub> can be clearly observed in Fig. S1b. The g-C<sub>3</sub>N<sub>4</sub>/ SiO<sub>2</sub> lamellar becomes smaller and forms more pores. Commercial RP is a kind of relatively large material (Fig. S1c), the layer is thicker, after 12h ball milling can be found to be significantly smaller, and the surface is rough (Fig. S1d). Such a structure is helpful for the composite of materials. SEM-elemental mapping (Fig. S1e) discloses a uniform distribution of C, N, Si and P throughout the BP/RP-g-C<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> sample. The elements in the sample are evenly distributed. In addition, the energy-dispersive X-ray spectroscopy (EDS) spectrum reflects that the content of each element and the presence of BP/RP-g-C<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> sample (Fig. S2).



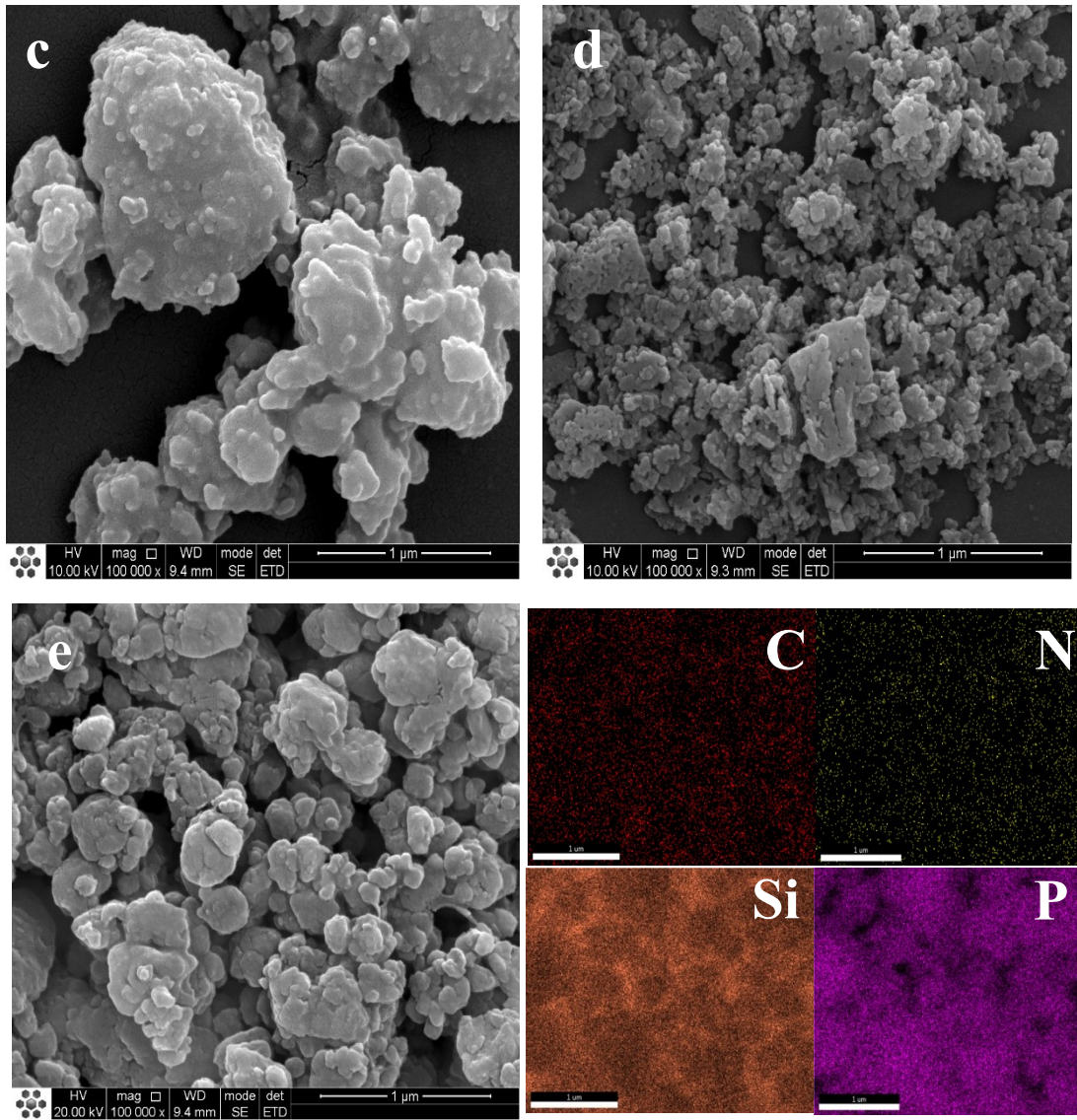


Fig. S1 (a-d) SEM images of  $g-C_3N_4$ ,  $g-C_3N_4/SiO_2$ , RP and BP/RP, (e) SEM of BP/RP- $g-C_3N_4/SiO_2$  and Elemental mapping images of C, N, Si and P.

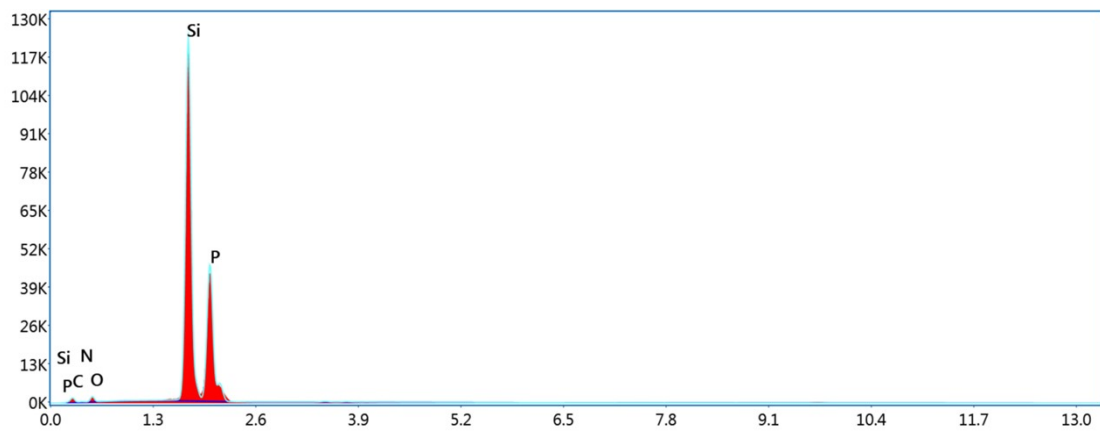


Fig. S2 EDS spectrum of BP/RP- $g-C_3N_4/SiO_2$ .

Tab.S1 BET Surface Area, Pore Volume, Pore Diameter of g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> and BP/RP-g-C<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub>.

catalyst	Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Pore Diameter (nm)
g-C <sub>3</sub> N <sub>4</sub>	32.482	0.2683	12.36
g-C <sub>3</sub> N <sub>4</sub> /SiO <sub>2</sub>	70.291	0.843	12.98
BP/RP-g-C <sub>3</sub> N <sub>4</sub> /SiO <sub>2</sub>	96.603	0.94	13.214

4. The experiment shows that when the amount of SiO<sub>2</sub> is 150 mg, 200 mg, 300 mg, 400 mg, 500 mg and 600 mg, the proportion of SiO<sub>2</sub> in the heterostructure obtained by calcination is 0.547, 0.564, 0.649, 0.771, 0.832 and 0.857. Experiment of adding mixed material BP/RP-g-C<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> with different proportions and ball milling for 6h: In the catalytic process, 2 mg catalyst was selected to degrade 60 mg/L RhB, and the effect is shown in the Fig. S3. On the one hand, adding SiO<sub>2</sub> can promote the formation of heterogeneous structure (low concentration of SiO<sub>2</sub> can form relatively uniform, but high concentration of SiO<sub>2</sub> can easily cause the phenomenon of substance stratification, g-C<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub> not completely form heterogeneous structure, on the surface of g-C<sub>3</sub>N<sub>4</sub> will hinder light absorption, affecting the photocatalytic effect). On the other hand, the presence of SiO<sub>2</sub> will form a mesoporous structure with g-C<sub>3</sub>N<sub>4</sub>, which is also a structure that can promote photocatalysis. The size of porosity will affect the effect of photocatalysis. In the case of low SiO<sub>2</sub>, the pores formed are relatively uniform. Moreover, the formed mesoporous also plays a role in promoting the formation of



active substances ( $h^+$ ).

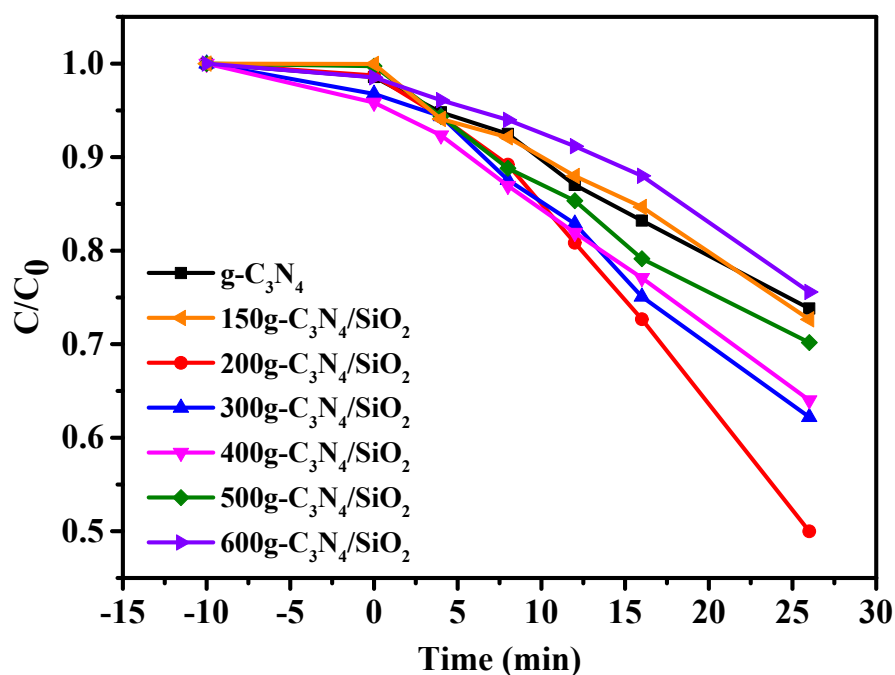


Fig.S3 Degradation of RhB by catalyst.

After adding different proportions of RP for ball milling for 6h, the rotating speed was 450 r/min. Later, it was found that the catalytic effect of adding 40% of RP was the best up to 86%, while for other catalytic materials, their catalytic effect could not reach this efficiency.

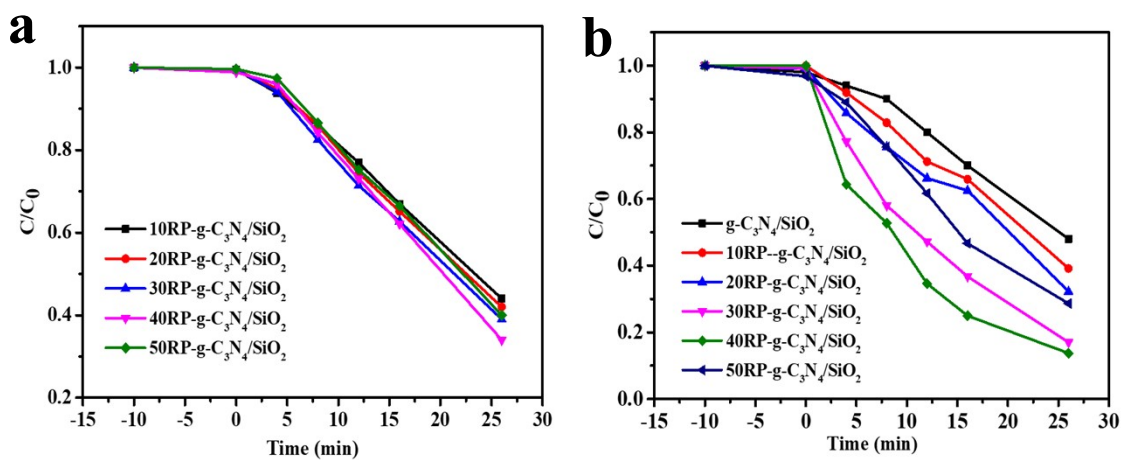


Fig.S4 (a)The catalyst milled for 3h degraded RhB, (b) the catalyst milled for 6h degraded RhB.

The effect of ball milling for 12h on the degradation of RhB and OFL is as follows in Fig. S5. The experimental results show that with the increase of RP, the catalytic effect of xRP-g-C<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> increases first and then decreases, because the addition of RP increases the heterojunction and the active material. High concentration of RP in the process of ball mill, the formation of BP/RP-g-C<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> may be uneven, resulting in low catalytic effect.

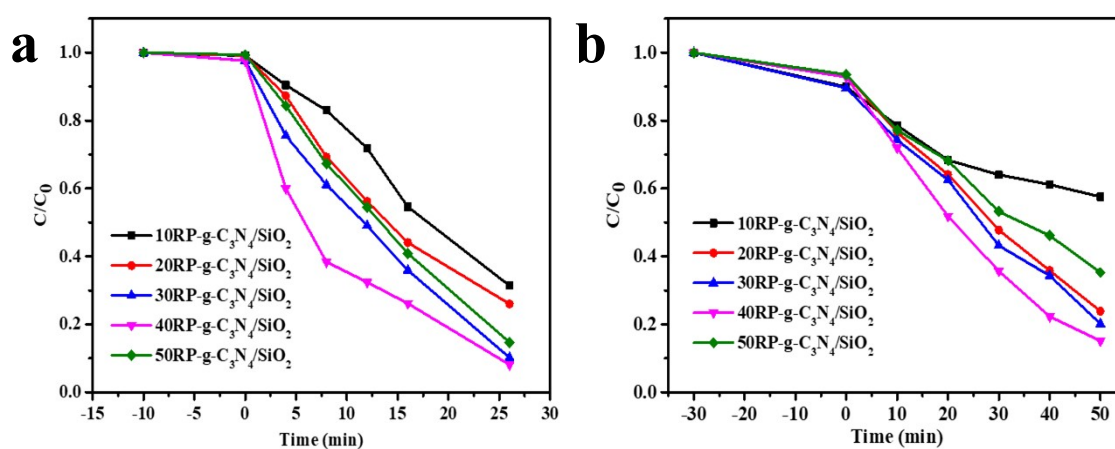


Fig. S5 (a) RhB degradation experiment, (b) OFL degradation experiment.

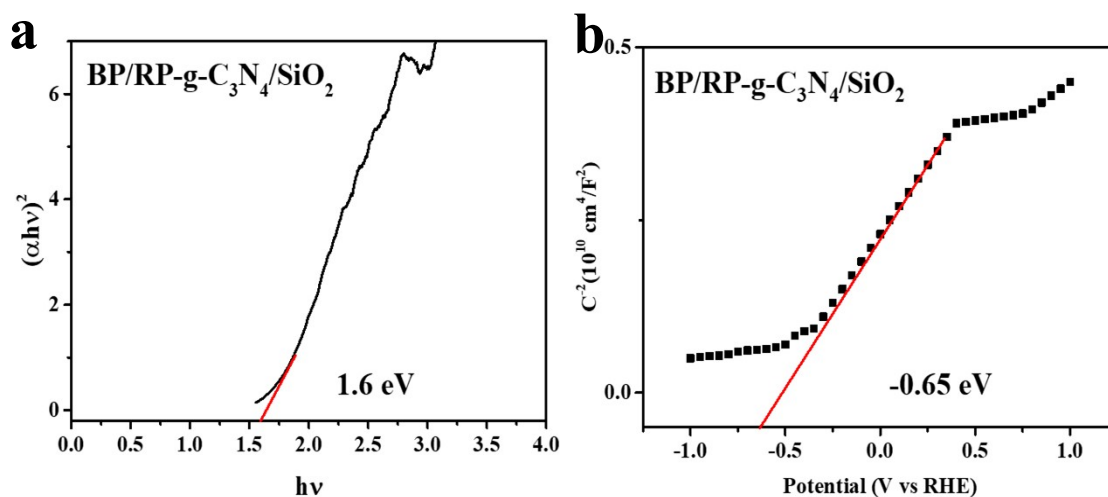


Fig. S6 (a) band gap test of BP/RP-g-C<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub>, (b) Mott-Schottky of BP/RP-g-C<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub>.

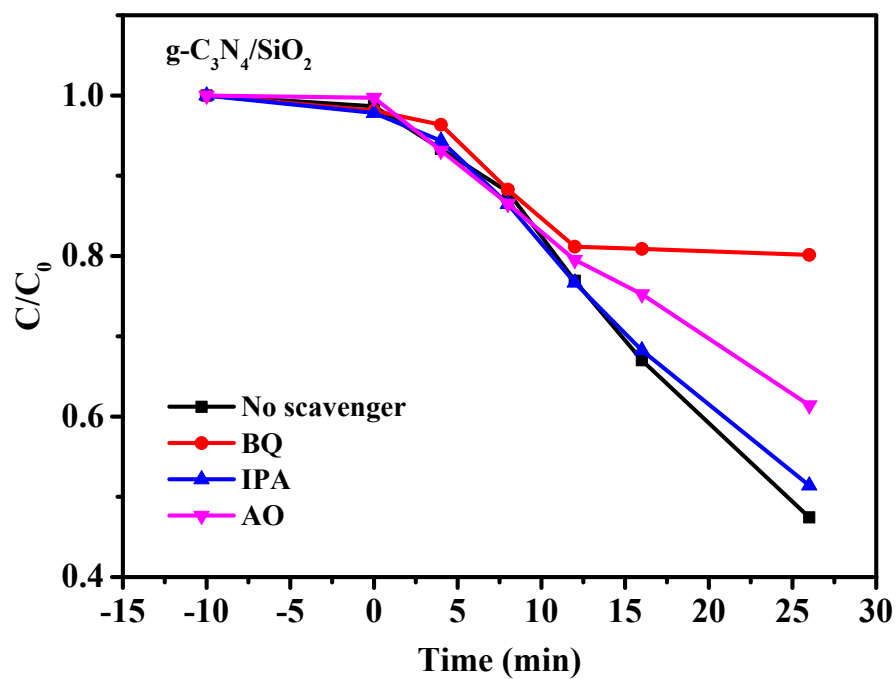


Fig. S7 g-C<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> degradation RhB active substance capture experiment.

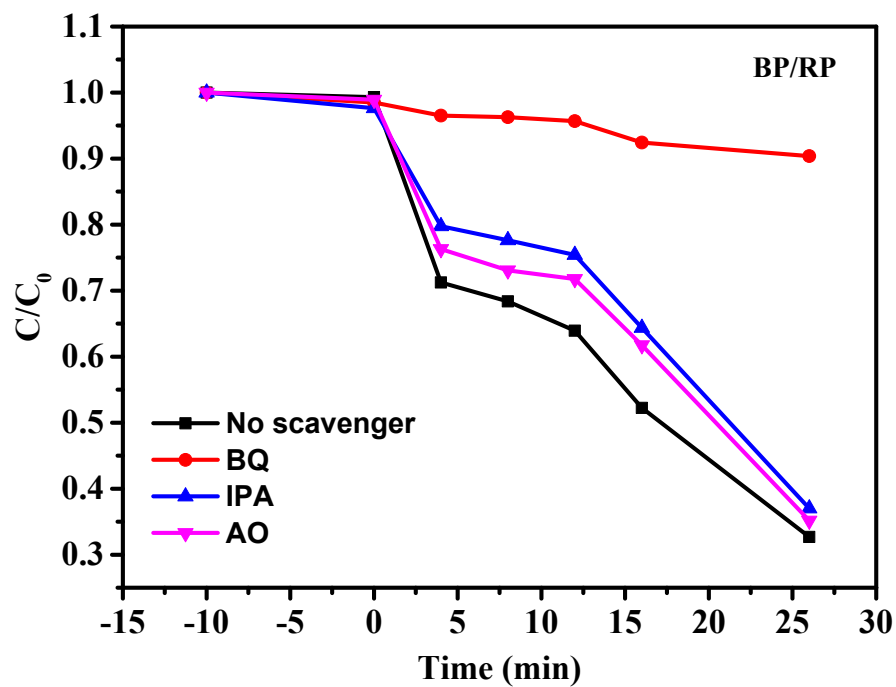


Fig. S8 BP/RP degradation RhB active substance capture experiment.