

## Supporting Information

The specific surface areas of  $\alpha$ -S and  $\alpha$ -S/ $C_3N_4$  heterojunctions are determined. The specific surface areas of  $\alpha$ -S,  $S_1$ ,  $S_2$  and  $S_3$  are 3.79, 17.6, 21.7 45.2 and 58.0  $m^2/g$ , respectively. Surface area of the photocatalyst can provide active reaction sites and the adsorption positions of the reactants. In general, photocatalysts with big specific area can exhibit high photocatalytic ability. And the exact causal relationship of the specific surface area and the photocatalytic ability will be discussed in the following research.

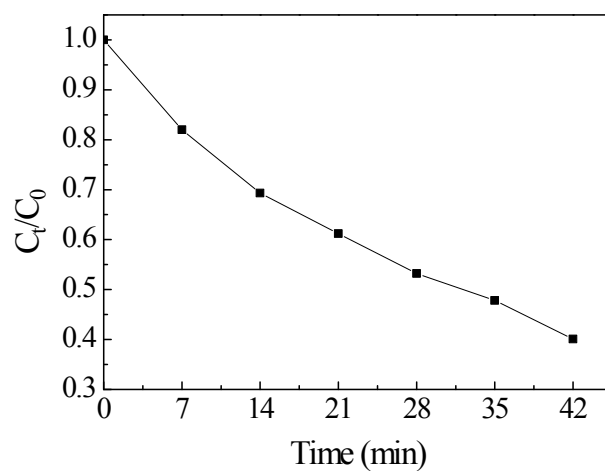


Figure S1  $C_t/C_0$  of the RhB concentration versus reaction time in photocatalytic degradation with ultra-thin  $C_3N_4$  nanosheet under visible light illumination.

## Oxidizing species

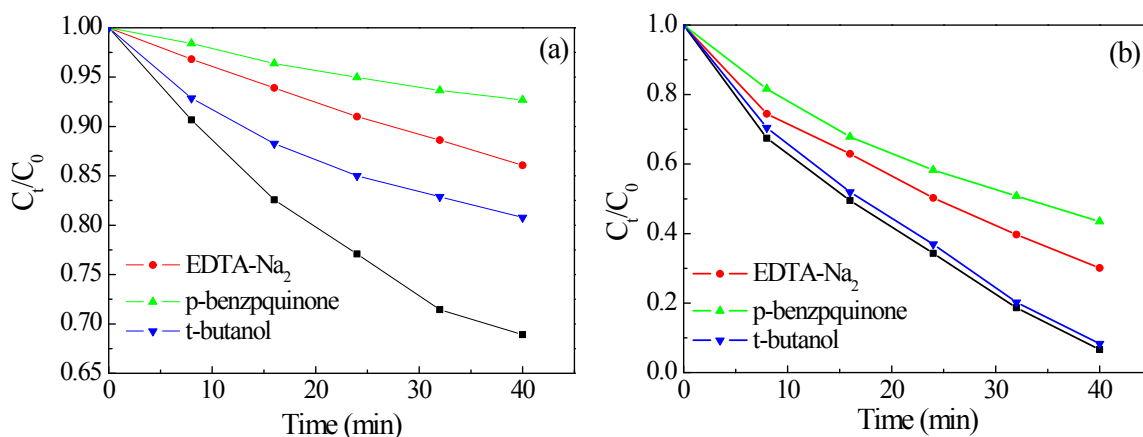


Figure S2  $C_t/C_0$  of the RhB concentration versus reaction time for photocatalytic degradation with

(a)  $\alpha$ -S and (b)  $\text{S}_2$  added different scavengers under visible light illumination.

To probe the oxidizing species in the photocatalytic degradation of RhB with  $\alpha$ -S, EDTA- $\text{Na}_2$ , *p*-benzquinone and TBA, efficient holes,  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  radicals scavengers, are separately added in the solution. The degradation rate of RhB is obviously decreased with the addition of each scavengers, indicating that holes,  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  radicals are all the potential reactive species in the process of the photocatalytic degradation of RhB (Figure S2 (a)). Due to the positive VB potential of  $\alpha$ -S (2.4 eV vs. NHE) to the standard redox potential of  $\cdot\text{OH}/\text{OH}^-$  (1.99 eV vs. NHE), the photogenerated holes can react with surface absorbed  $\text{OH}^-$  to generate  $\cdot\text{OH}$ , which then can oxidize RhB. Because the CB potential of  $\alpha$ -S (-0.4 eV vs. NHE) is negative than the standard redox potential of  $\text{O}_2/\cdot\text{O}_2^-$  (-0.33 eV vs. NHE), the electrons can reduce the  $\text{O}_2$  to generate  $\cdot\text{O}_2^-$ , which is a common oxidizing species in the photocatalytic process. Thus, combined with holes itself, the reactive species involved in the degradation of RhB are holes,  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  radicals. Similar experiments were also conducted  $\text{S}_2$  as the photocatalyst, as illustrated in Figure S2 (b). In the presence

of the EDTA-Na<sub>2</sub>, or *p*-benzquinone, the elimination of RhB is decelerated, suggesting the holes and ·O<sub>2</sub><sup>-</sup> radicals all might contribute to the oxidation of RhB. However, when TBA is added, the removal rate is not obviously decreased. Based on this experimental result, it can be proposed that the ·OH radical is not the oxidizing species. It could be attributed to the fact that the holes in the VB of C<sub>3</sub>N<sub>4</sub> can directly oxidize the RhB, but cannot oxidize the OH<sup>-</sup> to generate ·OH radicals due to the negative potential of VB of C<sub>3</sub>N<sub>4</sub> to the standard redox potential of ·OH/OH<sup>-</sup>.