Supplementary materials

Photocatalytic Performance and Degradation Pathway of Rhodamine B with TS-1/C₃N₄ Composite under Visible Light

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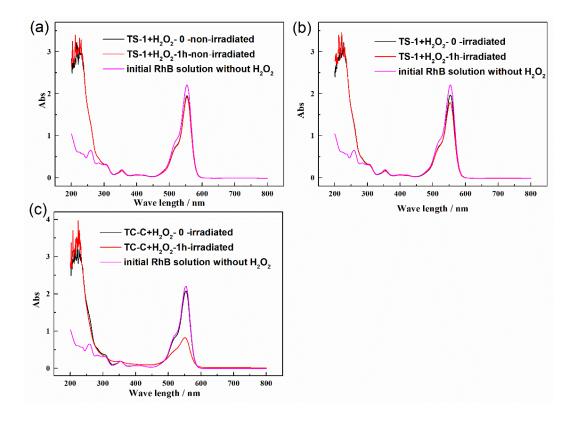


Figure S1. UV–vis adsorption spectral changes for the RhB solution in different conditions (**a**) TS-1+H₂O₂-unirradiate; (**b**) TS-1+H₂O₂-irradiate; (**c**) TC-C+H₂O₂-unirradiate.

In order to further study the effect of H_2O_2 on the reaction process during reaction, the concentration of H_2O_2 was detected by UV-Vis spectra and the results are shown in Figure S1. The absorption peak of is around 220 nm. It is discovered that the concentration of H_2O_2 does not decrease before and after reactions irradiated or non-irradiated over TS-1 and H_2O_2 . But a little bit of an increase was observed over TC-C composite and H_2O_2 under irradiation.

The possible reasons for this phenomenon are proposed as below. C_3N_4 can generated eand h⁺ under visible light, however the h⁺ on valence band (VB) of C_3N_4 is too weak to oxide OH⁻ to OH. A series of reactions between the H₂O₂ and other oxidant species are listed as below ^[1–3].

$$H_2O_2 + h\nu \rightarrow OH \tag{1}$$

$$H_2O_2 + Ti-OH \rightarrow Ti-O + OH + H_2O$$
⁽²⁾

$$H_2O_2 + e^- \rightarrow OH + OH^-$$
 (3)

$$O_2 + e^- \rightarrow O_2^- \tag{4}$$

$$OH + OH \rightarrow H_2O_2$$
 (5)

$$\mathrm{H}^{*} + \mathrm{O}_{2}^{*} \to \mathrm{HO}_{2}^{*} \tag{6}$$

$$HO_2 + H^+ + e^- \rightarrow H_2O_2 \tag{7}$$

The H₂O₂ can be activated by visible light or e⁻ to decompose to OH (reaction 1 and 3), and can react with Ti-OH to produce OH (reaction 2). Dissolved O₂ in solution is reduced by e⁻ to form O₂⁻ (reaction 4). Highly reactive hydroxyl radicals OH can combine with each other to yield H₂O₂ (reaction 5). And H₂O₂ are also produced by reaction (6) and (7). In consequence, H₂O₂ is consumed in reactions (1) (2) (3) while supplemented by reactions (5) (6) (7). Visible light and active species (h⁺ or O₂⁻ or OH) can promote RhB degradation to some extent independently. The specific reactions take place in different cases are listed in Table S1.

Table S1 A list of reactions that take place in different cases.

case	reaction
TS-1+H2O2 non-irradiated	(2)(5)
TS-1+ H ₂ O ₂ irradiated	(1)(2)(5)
TC-C+ H ₂ O ₂ irradiated	(1)(2)(3)(4)(5)(6)(7)

For the first case, H_2O_2 can be activated by Ti-OH in TS-1 to produce OH. Some of OH combined with each other to form H_2O_2 , and the others react with RhB. From the results of photocatalysis (Figure 7), it is inferred that there is a very small amount of OH to react with RhB, so the concentration of H_2O_2 changed little during dark reaction for one hour (Figure S1(a)). It is consistent with curves I and II in Figure 7(a). The presence or absence of H_2O_2 does not affect the degree of RhB concentration reduction (about 20%).

For the second case, TS-1 is not able to generate photo-electrons under visible light, so the circumstance is similar to the first one. It is concluded from Figure S1(b) that the decomposition rate of H₂O₂ is little (reaction (1)) under visible light. Compared curve II and IV (Figure7a), the more decreased concentration in curve IV than of curve II Figure 7a is contributed to the photolysis of visible light.

For the third case, the concentration of H_2O_2 has a little bit of an increase after irradiation for one hour (shown in Figure S1(c)). Although the large number of H_2O_2 involved in the reaction resulting in its consumption, it was supplemented by reactions (4), (5), (6). The phenomenon is consisted with the reference reported ^[2-3].

References:

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