Supplementary Information

Ag/g-C_3N_4 catalyst with superior catalytic performance for the degradation of dyes: a borohydride-generated superoxide radicals approach

Yongsheng Fu, Tinghuang, Lili Zhang and Xin Wang

Table 1S. MO photodegradation performances in the presence of Ag/g-C_3N_4 or Ag/g-C_3N_4/TiO_2 nanocomposites.

Samples	catalyst amount (mg)	MO volume (mL)	initial MO concentration (mg L^{-1})	particle size of the Ag (nm)	MO degradation rate after 120 min (%)	reference
Ag/g-C_3N_4	150	50	10	10-20	79	1S
Ag/g-C_3N_4	100	100	10	10	98	2S
Ag/g-C_3N_4-4	10	50	10	5.6	86	This work

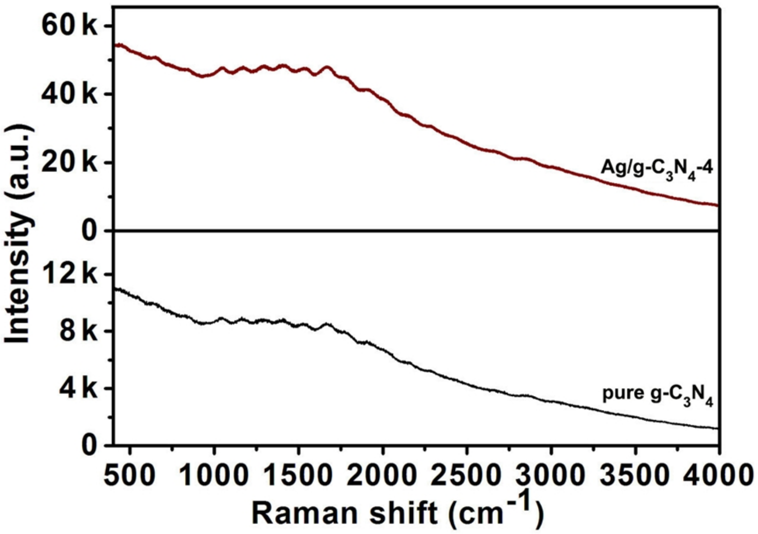

Figure 1S. Raman spectra of pure g-C_3N_4 and ACN-4 samples.

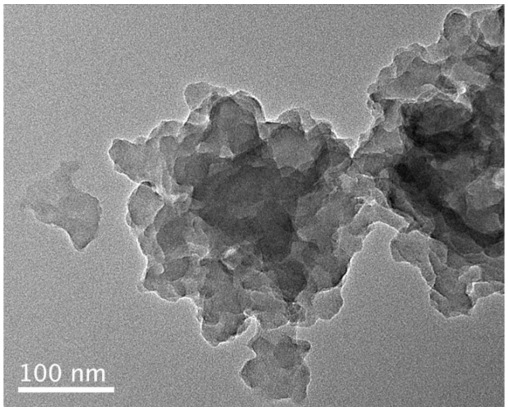

Figure 2S. TEM image of pure g-C_3N_4 catalyst.

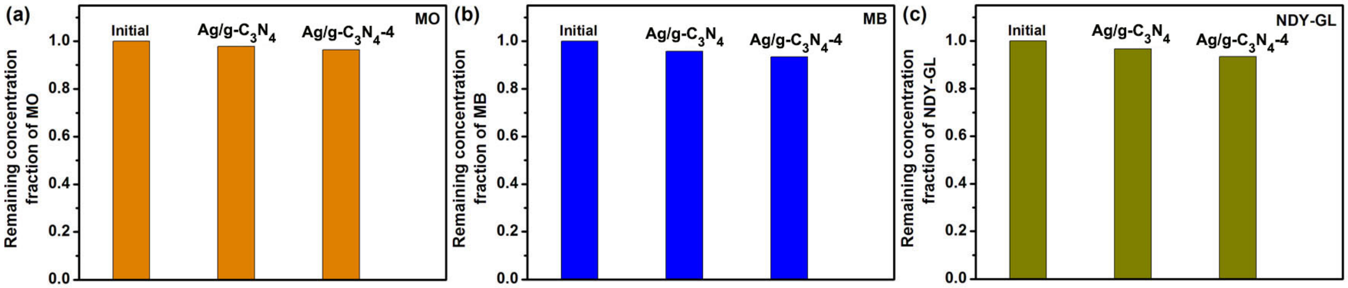

Figure 3S. Bar plot showing the remaining MO, MB and NDY-GL in solution after reaching the adsorption-desorption equilibrium in the dark for 60 min with stirring.

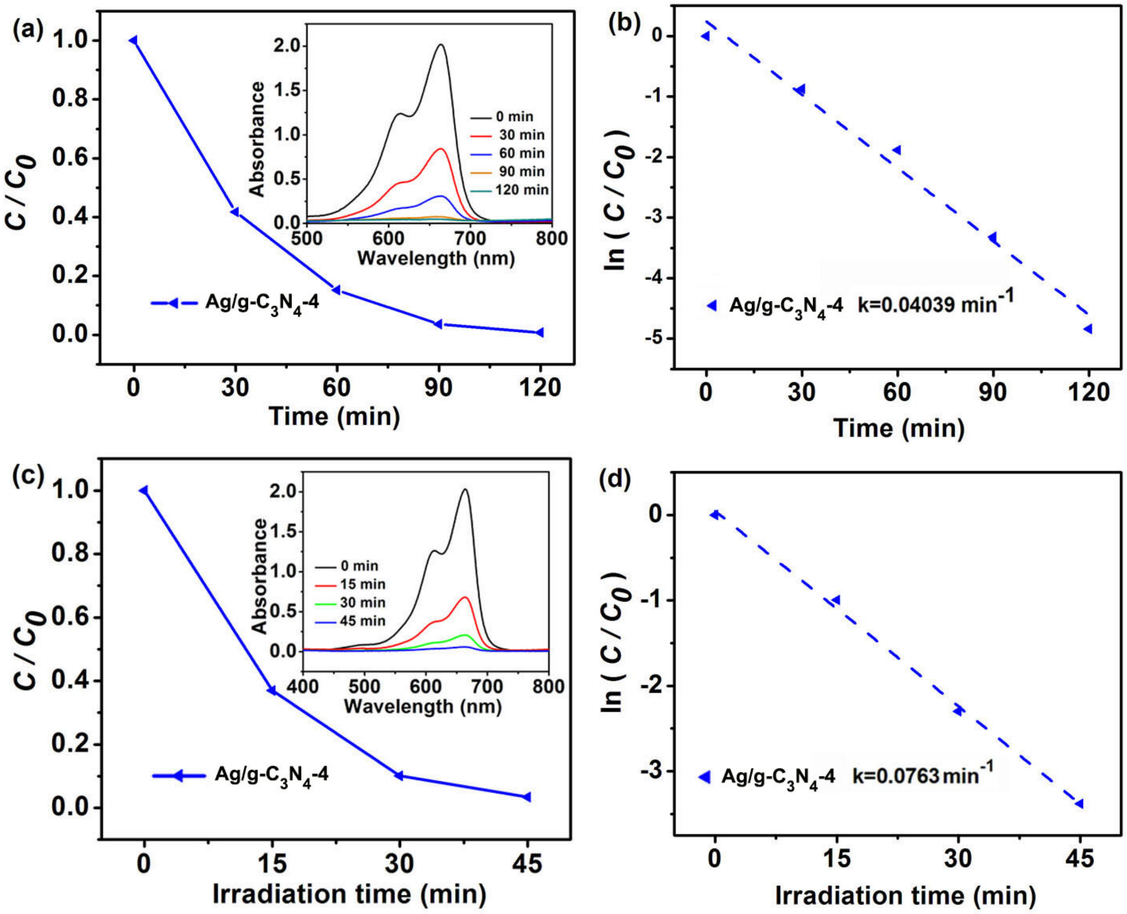

Figure 4S. Catalytic degradation of MB over Ag/g-C_3N_4-4 catalyst in the presence of BH_4^- in the dark (a) and under visible light irradiation (c); Plot of ln(c/c_0) against reaction time for Catalytic degradation of MB over Ag/g-C_3N_4-4 catalyst in the presence of BH_4^- in the dark (b) and under visible light irradiation (d). The insets are time-dependent UV-vis absorption spectra for the catalytic degradation of MB over the Ag/g-C_3N_4-4 catalyst in the presence of BH_4^- in the dark (a) and under visible light irradiation (c).

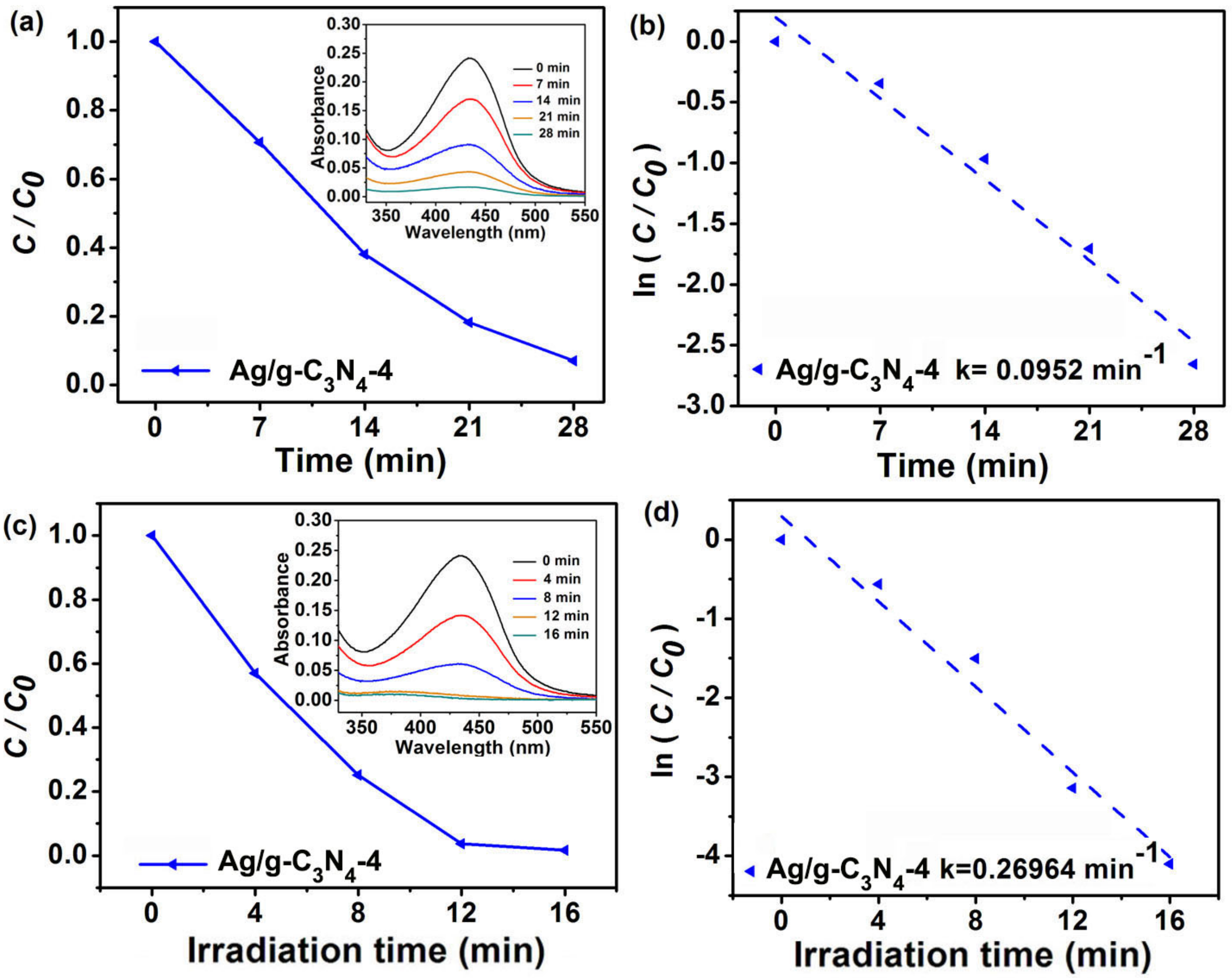

Figure 5S. Catalytic degradation of NDY-GL over Ag/g-C_3N_4-4 catalyst in the presence of BH_4^- in the dark (a) and under visible light irradiation (c); Plot of ln(c/c_0) against reaction time for Catalytic degradation of NDY-GL over Ag/g-C_3N_4-4 catalyst in the presence of BH_4^- in the dark (b) and under visible light irradiation (d). The insets are time-dependent UV-vis absorption spectra for the catalytic degradation of NDY-GL over the Ag/g-C_3N_4-4 catalyst in the presence of BH_4^- in the dark (a) and under visible light irradiation (c).

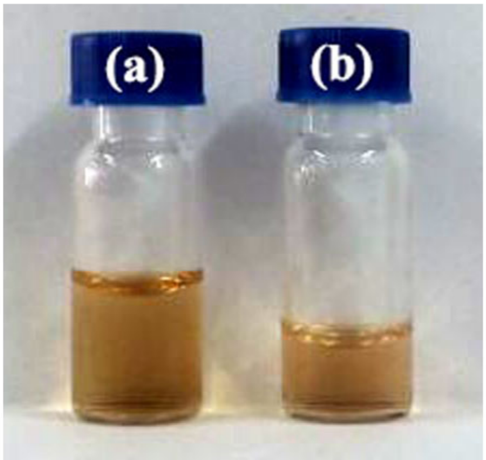

Figure 6S. (a) $[FeNO]^{2+}$ standard solution and (b) The last step reaction solution of color reaction.

A typical experiment for the color reaction between the ferrous irons (Fe^{2+}) and nitric oxide (NO) is as follows: 2 mg of the as-obtained Ag/g-C_3N_4-4 catalyst was added into 5.0 mL of 0.1 g mL^{-1} $NaBH_4$ aqueous solution with 0.5 M NaOH and stirred for 10 min. Then 0.5 mL of phosphate buffer solution (PBS, pH = 7.8) and 2.0 mL of hydroxylamine hydrochloride aqueous solution (10 M) were added to 3.0 mL of above supernatant with stirring for 10 min at the room temperature. After that, 1 mL of above reaction solution was added to the 2 mL of Ag_2SO_4 aqueous solution (0.02 M), then the resulting mixture was stirred for 2 min and centrifuged to remove the precipitation. Finally, a small amount of $FeSO_4$ was added into the above supernatant and allowed to dissolve, then 0.5 mL HAc (2 M) was introduced.

The mechanisms of color reaction between the ferrous irons (Fe^{2+}) and nitric oxide (NO) are as the following steps:

$$\mathbf{BH_4^- + \mathit{x}OH^- \longrightarrow B(OH)_4^- + (\mathit{x}\text{-}4)H_2O + (4\text{-}\mathit{x}/2)\,H_2 + \mathit{x}e^-} \quad (1)$$

$$\mathbf{e^- + O_2 \longrightarrow O_2^{\cdot -}} \quad (2)$$

$$\mathbf{O_2^{\cdot -} + NH_2OH + H^+ \longrightarrow NO_2^- + H_2O_2 + H_2O} \quad (3)$$

$$\mathbf{NO_2^- + Fe^{2+} + HAc \longrightarrow Fe^{3+} + NO\,(g) + Ac^-} \quad (4)$$

$$\mathbf{Fe^{2+} + NO \longrightarrow \left|FeNO\right|^{2+}} \quad (5)$$

In aqueous alkaline medium, BH_4^- can be oxidized directly on the surface of Ag/g-C_3N_4-4 catalyst with electrons being released (Eq. (2)), then electrons can quickly activate the adsorbed oxygen to produce $O_2^{\bullet -}$ radicals (Eq. (2)). As a strong oxidant, $O_2^{\bullet -}$ radicals could oxidize hydroxylamine (NH_2OH) to NO_2^- (Eq.

(3)), which can be reduced to generate NO (Eq. (4)). Finally, the Fe^{2+} and NO react readily to produce $[FeNO]^{2+}$ complexion (Eq. (5)). It can be clearly seen that the color of reaction solution (Eq. (5)) appears brown (Fig 6S(b)), which is almost the same as that of $[FeNO]^{2+}$ standard solution (Fig 6S(a)). Therefore, we can conclude that Ag/g-C_3N_4 catalyst can catalyze oxidation of BH_4^- to release electrons which can activate the adsorbed oxygen to $O_2^{\bullet -}$ radicals.

References

1S. L. Ge, C. Han, J. Liu and Y. Li, *Appl. Catal. A: Gen.*, 2011, **409-410**, 215-222.

2S. Y. Yang, Y. Guo, F. Liu, X. Yuan, Y. Guo, S. Zhang, W. Guo and M. Huo, *Appl. Catal. B: Environ.*, 2013, **142-143**, 828-837.