Nanoscale

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ARTICLE

Ag/g-C₃N₄ catalyst with superior catalytic performance for the degradation of dyes: a borohydride-generated superoxide radicals approach

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A straightforward approach is developed for fabrication of a visible-light-driven Ag/g-C₃N₄ catalyst. Morphology observation shows that the g-C₃N₄ sheets are decorated with highly dispersed Ag nanoparticles having an average size of 5.6 nm. The photocatalytic activity measurements demonstrate that the photocatalytic degradation rates of methyl orange (MO), methylene blue (MB), and neutral dark yellow GL (NDY-GL) over Ag/g-C₃N₄-4 can reach up to 98.2, 99.3 and 99.6% in the presence of borohydride ions (BH₄⁻) only for 8, 45, and 16 min visible light irradiation, respectively. The significant enhancement in photoactivity of the catalyst is mainly attributed to the high dispersity and smaller size of Ag nanoparticles, the strong surface plasmon resonance (SPR) effect of metallic Ag nanoparticles, the efficient separation of photogenerated charge carriers, the additional superoxide radicals (O₂•⁻) generated from the reduction of dissolved oxygen in the presence of BH₄⁻ and the synergistic effect of Ag nanoparticles and g-C₃N₄.

Introduction

As the largest available carbon-neutral energy source, solar energy can not only offer huge energy resources, but also save large amounts of fossil fuels and therefore protect environment. Semiconductor-based photocatalysis has attracted increasing attention as a potential environmental technology for removing pollutants under sunlight irradiation.[1-4] It has been recognized that the UV region occupies only around 4% of the entire solar spectrum, while the visible light accounts for 45% of the total energy. Accordingly, visible light utilization through semiconductor-based photocatalysis is crucial for solar chemical conversion processes and many visible-light-driven photocatalysts have been successfully developed.[5-8]

Recently, graphene-based visible light photocatalysts have received wide interest due to their good electron conductivity, large specific surface area and high adsorption capacity.[1,4,9-13] However, two dimensional (2D) graphene itself is not a semiconductor whereas 2D graphitic carbon nitride (g-C₃N₄) is.[14-16] The polymeric g-C₃N₄ material is considered as the most stable allotrope among various carbon nitrides under ambient conditions based on its thermal stability up to 600 ℃ in air and perfect acid-alkali-resistance. The g-C₃N₄ is characterized in the form of 2D sheets consisting of tri-s-triazine subunits connected through planar tertiary amino groups in a layer. Importantly, g-C₃N₄ possesses a bandgap of ca. 2.7 eV, which enables it to be

a visible-light-active photocatalyst for photochemical reactions and solar energy conversion.[17,18] Thus g-C₃N₄ has been used as a promising green metal-free photocatalyst for applications in photo-splitting water, photodecomposition of organic contaminants, and photosynthesis under visible light irradiation.[14-20] Similar to many single-component photocatalysts, g-C₃N₄ alone suffers from a high recombination rate of photoexcited charge carriers resulting in low photocatalytic performance.[15,20,21] To break through this bottleneck, many strategies have been used improve the photocatalytic performance of g-C₃N₄ such as metal deposition,[22-24] non-metal doping,[25,26] fabrication of nano/mesoporous structure,[27,28] and combination with another semiconductor.[29-31] Among these approaches, metal deposition demonstrates a great potential to enhance the visible light photocatalytic performance of g-C₃N₄, as the presence of metal nanoparticles is favorable for achieving efficient separation of the photogenerated charge carriers. In fact, nitrogen atoms of g-C₃N₄ play an essential role in changing the nucleation and growth behavior of deposited nanoparticles, thus resulting in great improvement of the catalytic performance. It has been reported that Ag nanoparticles (∼10 nm) supported on g-C₃N₄ showed enhanced photocatalytic activity for the degradation of methyl orange (MO) under visible-light irradiation (100 mL MO solution with the initial concentration of 10 mg L⁻¹ over

100 mg catalyst).[23] Despite these progresses, it is still a challenge to further enhance the catalytic performance and improve the utilization efficiency of catalyst.

It is well known that in the semiconductor photocatalytic process, the reduction of dissolved oxygen by the conduction band electrons and the oxidation of H_2O molecules by photogenerated holes can generate superoxide ($O_2^{\bullet-}$) and hydroxyl ($\bullet OH$) radicals, which can rapidly and nonselectively oxidize a broad range of organic pollutants into carbon dioxide and water. Hence the degradation rate of organic pollutant can be significantly enhanced by the increasing concentration of $O_2^{\bullet-}$ and $\bullet OH$. The DFT (density functional theory) calculation results indicate that the bottom of the conduction band (CB) of g-C_3N_4 is located at about -1.3 V (vs. NHE), which is much more negative than the standard redox potential of $O_2/O_2^{\bullet-}$ (-0.046 V vs. NHE), so that the CB electrons enable the reduction of dissolved O_2 molecules to generate $O_2^{\bullet-}$ radicals. Whereas the top of the valence band (VB) of g-C_3N_4 ($\sim$1.4 V vs. NHE) is lower than the standard redox potential of $OH^-/\bullet OH$ ($\sim$1.99 V vs. NHE), thus limiting the oxidation ability of the VB holes to generate $\bullet OH$ radicals.[18,23] Although hydrogen peroxide (H_2O_2) has long been used to produce $\bullet OH$ radicals,[32] which availably assist in degradation of organic molecules, relatively little attention has been paid so far to the effect of increasing $O_2^{\bullet-}$ radicals.

On the basis of the above-mentioned, it is therefore of great interest to use g-C_3N_4 to support much smaller sized Ag nanoparticles and introduce additional $O_2^{\bullet-}$ radicals for degradation reactions of organic pollutants. If that can be accomplished, then it may be feasible to achieve highly effective photocatalysis. Herein, we demonstrate a one-step facile route to fabricate g-C_3N_4 supported Ag nanoparticles ($\sim$

5.6 nm) with different Ag/g-C_3N_4 ratio. Their catalytic activities were evaluated by the degradation of methylorange (MO), methylene blue (MB), and neutral dark yellow GL (NDY-GL) under visible light irradiation. It is interesting that the degradation reactions of dyes can be accelerated significantly by adding BH_4^-, due to the assistance of the additional $O_2^{\bullet-}$ radicals generated from the reduction of dissolved oxygen during the oxidation of BH_4^-.

Results and discussion

Structure and morphology

Figure 1(a) shows XRD patterns of the pure g-C_3N_4 and as-prepared Ag/g-C_3N_4 catalysts with different Ag content. The diffraction pattern of g-C_3N_4 can be assigned to the hexagonal phase of g-C_3N_4 (JCPDS 87-1526).[24,33] There are two diffraction peaks at 2θ of 13.0° and 27.5° which can be indexed to the (100) crystal plane arising from in-planar ordering of tri-s-triazine units with a distance of 0.675 nm and (002) crystal plane of the stacking of the conjugated aromatic system with an interplanar distance of 0.326 nm, respectively. For the Ag/g-C_3N_4 catalysts, the intensity of diffraction peaks of g-C_3N_4 become weaker with increasing Ag content. However, no obvious diffraction peaks of Ag were observed for most samples due to the relatively low Ag content. Only for Ag/g-C_3N_4-8, there are two observable peaks at 2θ of 38.1° and 44.3° which can be assigned to the (111) and (200) crystal plane of the face-centered cubic structure of Ag, respectively (JCPDS 04-0783).[34] This result suggests the coexistence of Ag and g-C_3N_4 in the catalyst.
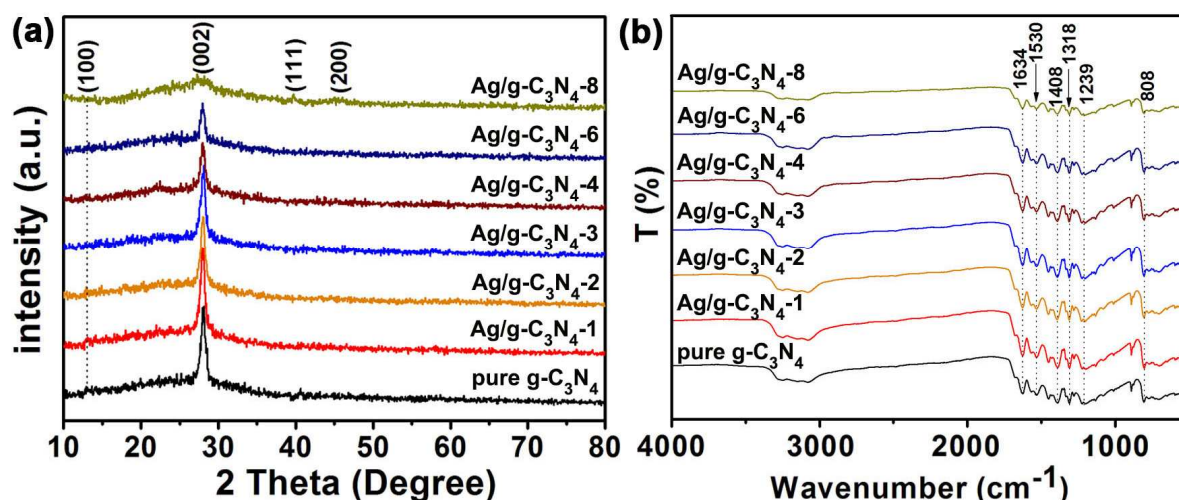

Figure 1. (a) XRD diffraction patterns and (b) FT-IR spectra of g-C_3N_4 and Ag/g-C_3N_4 catalysts with different Ag content.

The FTIR spectra of g-C_3N_4 and Ag/g-C_3N_4 catalysts with different Ag content are presented in Figure 1(b). It is obviously seen that all the absorption peaks of Ag/g-C_3N_4 catalysts with different Ag content are almost the same as those

of g-C_3N_4. The broad absorption peaks in the range of 3000-3500 cm^{-1} are attributed to the stretching vibration of N−H and that of O−H of the physically adsorbed water, respectively. The absorption peaks at about 1634, 1530, 1408, 1318 and 1239

cm^{-1} can be ascribed to the typical stretching modes of CN heterocycles. [33,35,36] In addition, the sharp absorption peak at 808 cm^{-1} is assigned to the characteristic breathing mode of triazine units.[33,35,36] Figure 1S shows the Raman spectra of g-C_3N_4 and Ag/g-C_3N_4-4, it can be clearly seen that the Raman signals of g-C_3N_4 in Ag/g-C_3N_4-4 are greatly enhanced, which is attributed to surface-enhanced Raman scattering (SERS) effect from the supported silver nanoparticles.

The surface elemental composition and the valence states of the elements in g-C_3N_4 and Ag/g-C_3N_4 catalysts were investigated using XPS. Figure 2 shows the survey spectrum and high-resolution XPS spectra of various elements. As shown in Figure 2(a), there are C and N signals of g-C_3N_4 in the survey spectrum, while the peaks of C, N and Ag elements appear in the spectra of Ag/g-C_3N_4-1 and Ag/g-C_3N_4-4. From the high-resolution XPS spectrum of C1s shown in Figure 2(b),

the peaks centered at 284.6 eV and 288.0 eV can be ascribed to C=C and N=C=N species, respectively. Figure 2(c) presents the high-resolution XPS spectrum of N1s, which can be fitted into three components: the main peak at 398.5 eV is attributed to C-N=C coordination which originates from the sp^2-bonded N in triazine rings, whereas the other two weak peaks at higher binding energies (around 399.6 and 401.1 eV) can be assigned to N-$(C)_3$ and C-N-H species, respectively.[37,38] As shown Figure 2(d), the two peaks are located at 368.1 and 374.1 eV, corresponding to metallic Ag3d5/2 and 3d3/2 binding energy, respectively.[39,40] Based on the results of ICP-AES analysis, the weight percentages of Ag in Ag/g-C_3N_4-1, Ag/g-C_3N_4-2, Ag/g-C_3N_4-3, Ag/g-C_3N_4-4, Ag/g-C_3N_4-6 and Ag/g-C_3N_4-8 were measured to be 0.73, 1.41, 1.98, 2.43, 3.95, and 4.62 wt%, respectively.

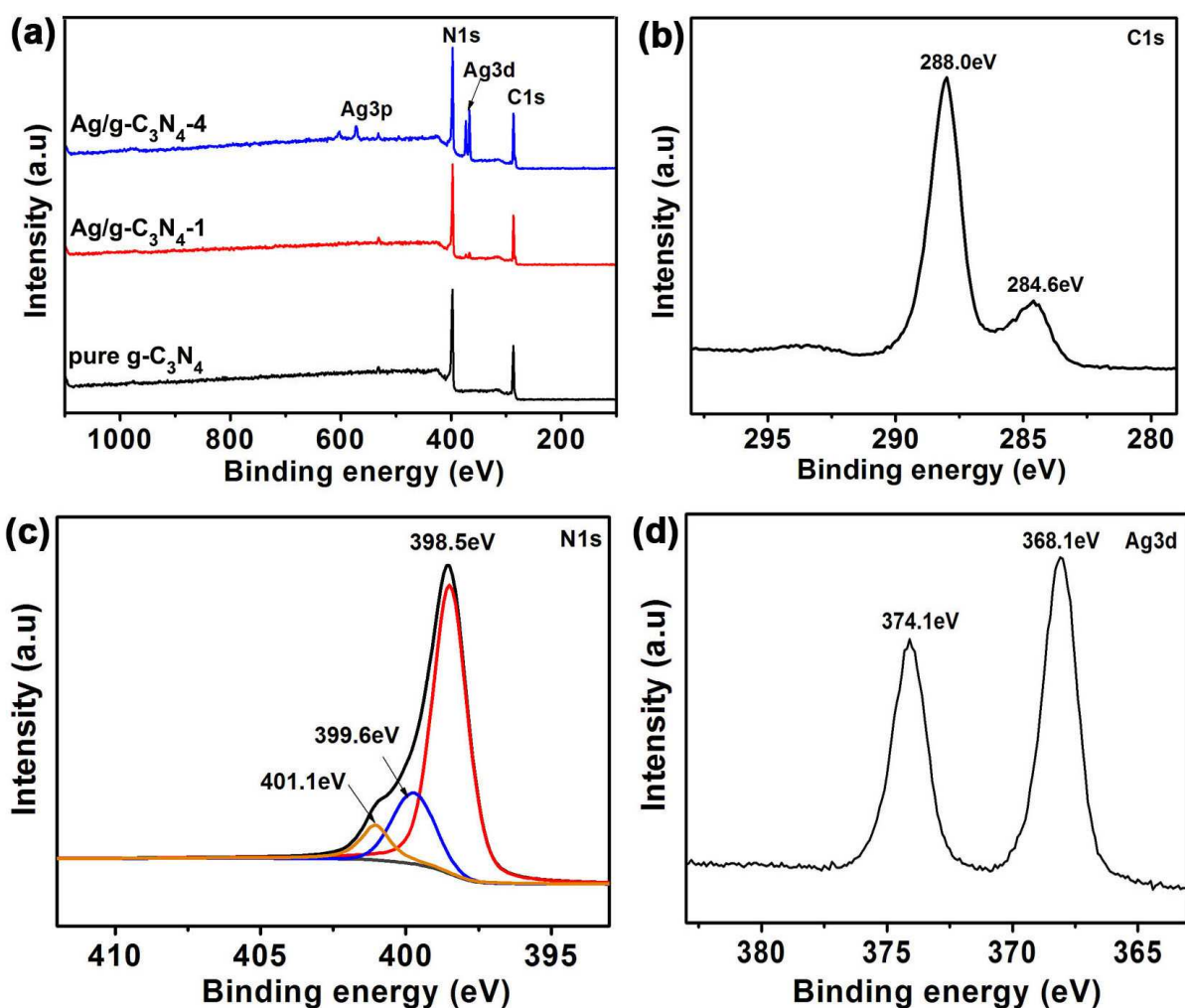Figure 2. XPS survey spectra of g-C_3N_4, Ag/g-C_3N_4-1 and Ag/g-C_3N_4-4 (a); High resolution C1s (b) and N1s (c) and Ag3d (d) spectra of Ag/g-C_3N_4-4.

TEM and FE-SEM were used to characterize the morphology and size distribution of the Ag nanoparticles on the g-C_3N_4 sheets. It can be clearly seen from Figure 2S that g-C_3N_4 has a

porous framework comprising a two-dimensional layered structure. While for the Ag/g-C_3N_4-4 catalyst, the g-C_3N_4 sheets are decorated with highly dispersed Ag nanoparticles having an

average diameter of 5.6 nm with a narrow particle size distribution (Figure 3(a) and 3(b)). As shown in the inset of Figure 3(a), the lattice spacing of d= 0.23 nm can be ascribed to

the (111) planes of the face-centered cubic structure of the Ag nanoparticle, which is consistent with the XRD results.
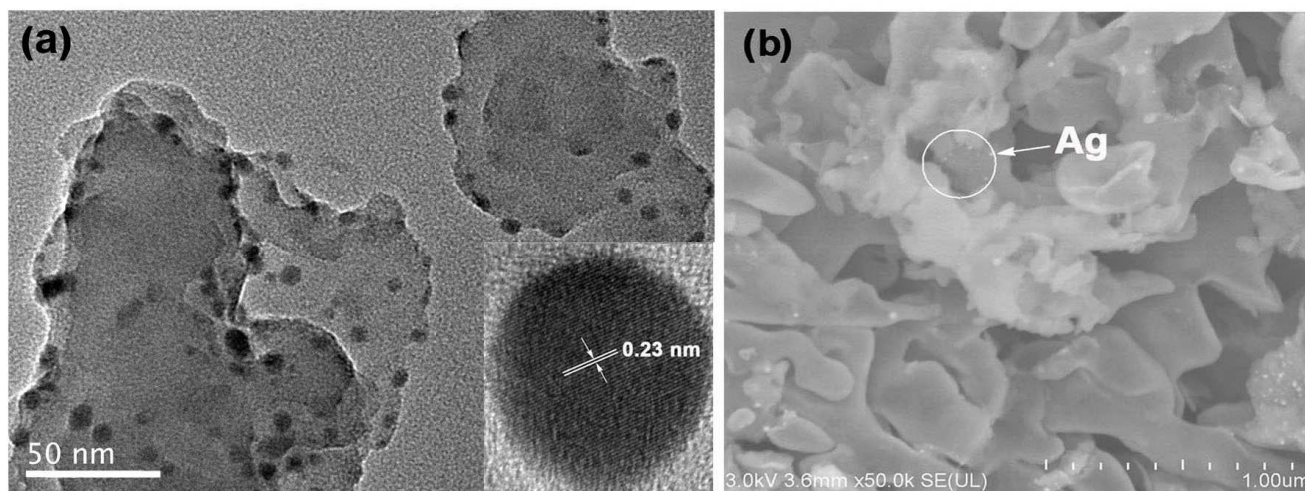

Figure 3. TEM image (a) and (b) FESEM image of Ag/g-C$_3$N$_4$-4 catalyst. The inset is the high-resolution TEM image of an Ag nanoparticle anchored on the g-C$_3$N$_4$ sheet.

Photocatalytic activity of the catalysts under visible light irradiation

The photocatalytic activities of the g-C$_3$N$_4$ and Ag/g-C$_3$N$_4$ catalysts were evaluated by the degradation of MO, MB and NDY-GL under visible light irradiation. Before the photocatalytic reaction test, the batch mode adsorption studies for the dyes were carried out by agitating catalyst (10 mg) in dye solution (10 mg L^{-1}, 50 mL) in the dark at 25 ℃. As shown in Figure 3S, it is obvious that the remaining dye concentrations were still relatively high after reaching the adsorption-desorption equilibrium due to the low catalyst dosage.

Figure 4(a), (d) and (g) show the absorbance versus wavelength plots at various times for the photodegradation of MO, MB and NDY-G over Ag/g-C$_3$N$_4$-4, respectively. The blank experiment result indicates that the degradation of MO, MB and NDY-GL can be neglected in the absence of catalysts (Figure 4(b), (e) and (h)). While the photocatalytic activity of anyone of the Ag/g-C$_3$N$_4$ catalysts is higher than that of g-C$_3$N$_4$ alone. Among the catalysts with different Ag content, the Ag/g-C$_3$N$_4$-4 catalyst exhibited the best photocatalytic activity (Figure 4(b), (e) and (h)): the degradation rates of MO, MB and NDY-GL over the Ag/g-C$_3$N$_4$-4 catalyst were 86, 57, and 78 % after 120 min, respectively. The reaction processes of MO, MB and NDY-GL photocatalytic degradation over g-C$_3$N$_4$ and Ag/g-C$_3$N$_4$ catalysts with different Ag content were successfully fitted with the pseudo-first-order kinetic model and the Ag/g-C$_3$N$_4$-4 catalyst exhibited the highest rate constant of 0.01425 min^{-1}, 0.00605 min^{-1} and 0.01305 min^{-1} for MO, MB and NDY-GL, respectively (Figure 4(c), (f) and (i) and Table 1).

A comparative survey of recent results on the photocatalytic degradation of MO over the binary Ag/g-C$_3$N$_4$ catalysts is summarized in Table 1S,[23,40] which shows that the degradation rate of MO over our Ag/g-C$_3$N$_4$-4 catalyst can reach up to 86% under visible light irradiation for 120 min when the catalyst dosage was as

low as 10 mg in 50 mL MO solution with an initial concentration of 10 mg L^{-1}. Obviously, the smaller-sized Ag nanoparticles can enhance the catalytic performance and achieve better utilization of the catalysts.[41-42]

Table 1 The rate constants of the pseudo-first-order kinetics of MO, MB and NDY-GL photocatalytic degradation over different catalysts.

Samples	The rate constant of pseudo-first-order kinetics (k, min^{-1})		
	MO	MB	NDY-GL
no catalyst	0.00011	0.00025	0.00021
g-C$_3$N$_4$	0.00201	0.00160	0.00262
Ag/g-C$_3$N$_4$-1	0.00373	0.00247	0.00467
Ag/g-C$_3$N$_4$-2	0.00549	0.00316	0.00559
Ag/g-C$_3$N$_4$-3	0.00864	0.00454	0.00861
Ag/g-C$_3$N$_4$-4	0.01425	0.00605	0.01305
Ag/g-C$_3$N$_4$-6	0.01159	0.00538	0.01015
Ag/g-C$_3$N$_4$-8	0.01025	0.00481	0.00898

On the basis of the previous work and the above experimental results, a possible mechanism for the photocatalytic degradation dyes is proposed as follows: the electron-hole pairs can be quickly generated in the g-C$_3$N$_4$ upon visible-light excitation (Eq. (1)) due to the SPR effect of metallic Ag nanoparticles, followed by instant transfer of photogenerated electrons from CB of g-C$_3$N$_4$ to the Ag nanoparticles at the interface of the Ag/g-C$_3$N$_4$ catalyst (Eq. (2)), which shifts the Fermi level to more negative potential than the standard redox potential of O$_2$/O$_2$$^{•-}$ (-0.046 V vs. NHE), thereby the dissolved oxygen can be readily reduced by

negatively charged Ag nanoparticles to produce $O_2^{\cdot-}$ radicals (Eq. (3)) [15,23,43,44]. Finally, the dye molecules can be oxidized by $O_2^{\cdot-}$ radicals.

$$g\text{-}C_3N_4 \quad + \quad hv \longrightarrow g\text{-}C_3N_4 \ (h+e) \qquad (1)$$

$$g\text{-}C_3N_4 \ (e) \ + Ag \longrightarrow g\text{-}C_3N_4 \ + \ Ag \ (e) \qquad (2)$$

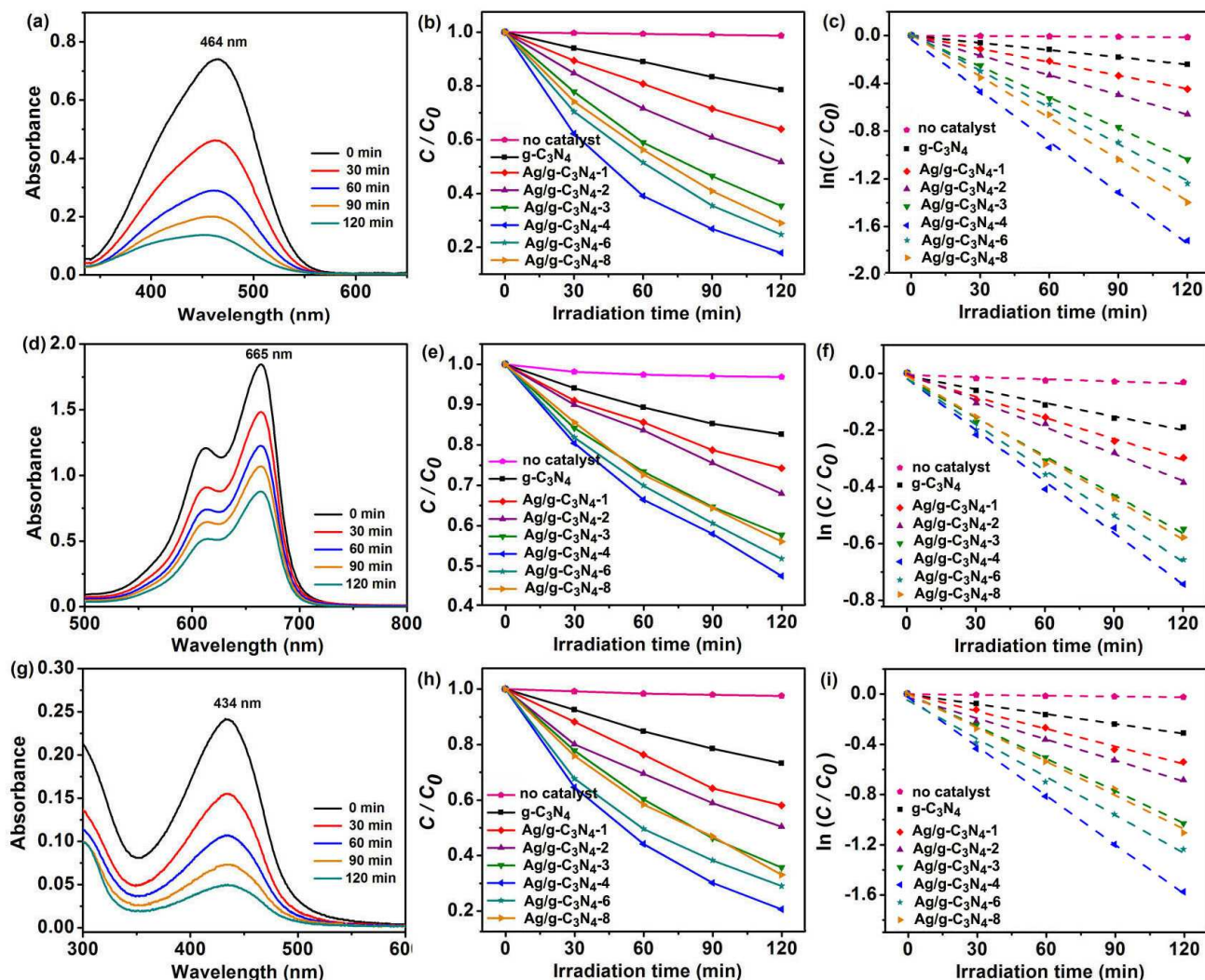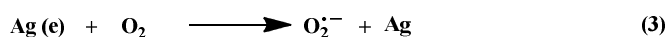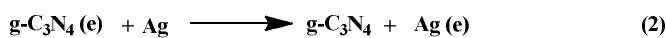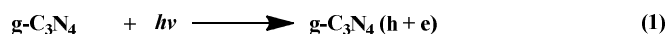$$Ag \ (e) \ + \ O_2 \longrightarrow O_2^{\cdot-} \ + \ Ag \qquad (3)$$

Figure 4. (a), (d) and (g) Time-dependent UV-vis absorption spectra for the degradation of MO, MB and NDY-GL over the Ag/g-C$_3$N$_4$-4 catalyst; (b), (e) and (h) Photocatalytic degradation of MO, MB and NDY-GL dyes over different catalysts; (c), (f) and (i) Plot of ln(c/c_0) against reaction time for photocatalytic degradation of MO, MB and NDY-GL with different catalysts.

Borohydride-assisted photocatalysis for dyes degradation

As shown in Figure 5(a-c), it is interesting that MO can be catalytically degraded over g-C$_3$N$_4$ and Ag/g-C$_3$N$_4$ catalysts in the presence of BH$_4^-$ even in the dark at 25 °C. It should be noted that there is little change in absorbance of MO solution without catalyst before and after adding BH$_4^-$ for 20 min, suggesting that the MO cannot be reduced by BH$_4^-$ in aqueous solution. While the degradation rate of 15.3 % for MO over g-C$_3$N$_4$ for 20 min was observed. Furthermore, introducing a certain amount of Ag into g-C$_3$N$_4$ results in dramatical changes of catalytic activity. Among various Ag/g-C$_3$N$_4$ catalysts investigated, the Ag/g-C$_3$N$_4$-4 catalyst gave the highest MO degradation rate up to 95.5 % within 20 min in

the presence of BH$_4^-$ in the dark (Figure 5(b)). In addition, catalytic degradation process of the MO over Ag/g-C$_3$N$_4$ catalysts in the presence of BH$_4^-$ followed the pseudo-first-order kinetics in the dark, and the Ag/g-C$_3$N$_4$-4 catalyst exhibited the highest rate constant of 0.1589 min^{-1}(Figure 5(c) and Table 2).

When above reactions were carried out under visible light irradiation, the degradation rate of MO over Ag/g-C$_3$N$_4$-4 catalyst reached to 98.2 % only for 8 min (Figure 5(d-e)). As shown in Figure 5(f), the degradation rates followed first-order kinetics and the Ag/g-C$_3$N$_4$-4 catalyst exhibited the highest kinetics rate constant of 0.3870 min^{-1} (Table 2), which is 2.44 and 27.16 times that of in the presence of BH$_4^-$ in the dark and in the absence of BH$_4^-$ under visible light irradiation, respectively.
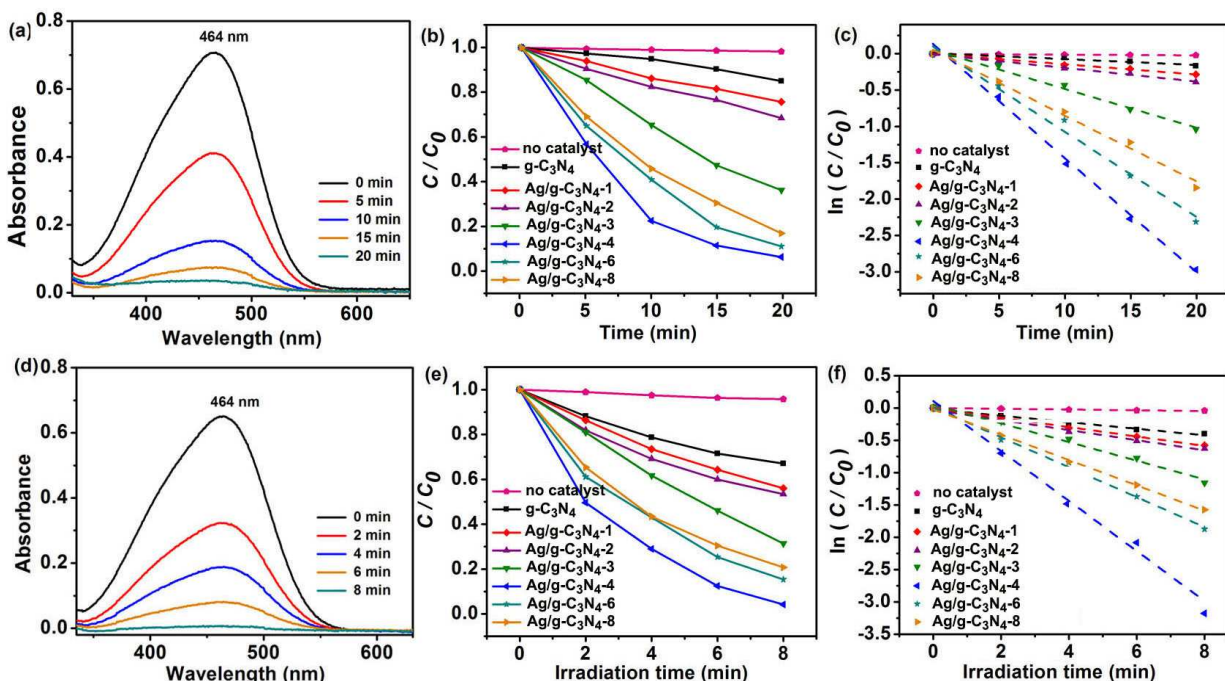
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Figure 5. Time-dependent UV-vis absorption spectra for the catalytic degradation of MO over the Ag/g-C$_3$N$_4$-4 catalyst in the presence of BH$_4^-$ in the dark (a) and under visible light irradiation (d); catalytic degradation of MO over different catalysts in the presence of BH$_4^-$ in the dark (b) and under visible light irradiation (e); plot of ln(c/c_0) against reaction time for catalytic degradation of MO with different catalysts in the presence of BH$_4^-$ in the dark (c) and under visible light irradiation (f).

Table 2 The rate constants of the pseudo-first-order kinetics of MO catalytic degradation over different catalysts in the presence of BH$_4^-$ in the dark and under visible light irradiation.

Samples	The rate constant of pseudo-first-order kinetics (k, min^{-1})	
	In the dark	Under visible light irradiation
no catalyst	0.00009	0.0057
g-C$_3$N$_4$	0.00811	0.0505
Ag/g-C$_3$N$_4$-1	0.01416	0.0726
Ag/g-C$_3$N$_4$-2	0.01878	0.0782
Ag/g-C$_3$N$_4$-3	0.05348	0.1445
Ag/g-C$_3$N$_4$-4	0.15888	0.3870
Ag/g-C$_3$N$_4$-6	0.11714	0.2315
Ag/g-C$_3$N$_4$-8	0.09050	0.1957

Similar results were obtained for the degradation of MB and NDY-GL in the presence of BH$_4^-$ in the dark and under visible light irradiation, respectively (Figure 4-5S). It can be seen that the degradation rates of MB on Ag/g-C$_3$N$_4$-4 catalyst were 96.0 and 99.3 % in the dark for 120 min and under visible light irradiation for 45 min, respectively. The degradation rates of NDY-GL reached to 93.8 and 99.6 % in the dark for 28 min and under visible light irradiation for 16 min, respectively.

The Ag/g-C$_3$N$_4$-4 catalyst can be used repeatedly for the degradation of dyes. Figure 6 shows that the degradation rate of MO still reached over 95 % after 6 cycles in the presence of BH$_4^-$ under visible light irradiation, indicating that the catalyst is stable and effective for the degradation of organic pollutants in water.
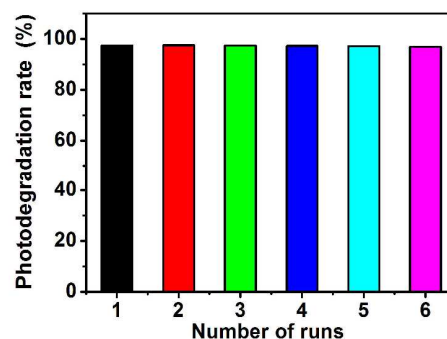

Figure 6. Bar plot showing the photodegradation rate of MO in solution for 6 cycles using Ag/g-C$_3$N$_4$-4 catalyst in the presence of BH$_4^-$ under visible light irradiation.

Mechanism of borohydride-assisted photocatalysis

The above results indicate that the Ag/g-C$_3$N$_4$ catalysts not only possess the excellent visible-light-photocatalytic activity for degradation of dyes, but also have the strong ability to degrade organic molecules in the presence of BH$_4^-$ even in the dark, and therefore they can exhibit the extremely superior excellent catalytic performance in the presence of BH$_4^-$ under visible light irradiation. As will be seen later in this section, the high performance of the catalyst is mainly attributed to the high dispersity and smaller size of Ag nanoparticles, the synergistic effect of the combination of Ag nanoparticles and g-C$_3$N$_4$, the strong surface plasmon resonance (SPR) effect of metallic Ag nanoparticles, the efficient separation of photogenerated electron-hole pairs and the additional O$_2^{\bullet-}$ radicals generated from the reduction of dissolved oxygen in the presence of BH$_4^-$.

It is known that the optical response of hybrid metal-semiconductor system is regarded as the controlling factor for its photocatalytic activity. The optical absorption properties of g-C$_3$N$_4$ and Ag/g-C$_3$N$_4$ catalysts with different Ag content were investigated by UV−vis DRS. As shown in Figure 7(a), an obvious absorption edge of g-C$_3$N$_4$ appears at about 460 nm corresponding to the band gap of 2.7 eV, implying its visible-light-induced photocatalytic activity.[23,45,46] While for the Ag/g-C$_3$N$_4$ catalysts, their the absorption within the visible light range (450-650 nm) is significantly extented, especially, a new absorption peak appears at around 530 nm and the intensity increases along with the Ag content. The strong and broad absorption band in the visible light region for the Ag/g-C$_3$N$_4$ catalysts can be attributed to the localized SPR effect of metallic Ag nanoparticles, which shows efficient plasmon resonance in the visible region.[15,47] Such an enhanced light absorption of the catalysts facilitates to yield more electron-hole pairs, which subsequently results in a higher photocatalytic activity. Moreover, the SPR effect of metallic Ag nanoparticles causes enhancement of the local electromagnetic fields, which speeds up the generation rate of photogenerated electron-hole pairs in the near-surface region of g-C$_3$N$_4$.[43,44,48,49] The photogenerated electrons can be instantly scavenged by Ag nanoparticles at the interface of the Ag/g-C$_3$N$_4$ catalyst, creating a Schottky barrier that effectively reduces the probability of the recombination of photogenerated electron-hole pairs.[15,43,44] This deduction is further evidenced by PL emission spectroscopy. In general, a weaker PL intensity represents a lower recombination probability of photogenerated carriers, resulting in a higher photocatalytic activity. Figure 7(b) shows the PL emission spectra of the g-C$_3$N$_4$, Ag/g-C$_3$N$_4$-4 and Ag/g-C$_3$N$_4$-4 (with BH$_4^-$) under the excitation wavelength of 325 nm. The strong emission peak of g-C$_3$N$_4$ centered at 455 nm suggests a high recombination probability of photogenerated electron-hole pairs. While for Ag/g-C$_3$N$_4$-4, the significant quenching of the PL is observed in comparison with g-C$_3$N$_4$ due to the SPR effect of metallic Ag nanoparticles, indicating the strongly inhibited recombination of photoexcited carriers.[48,49] It is worth noting that the PL intensity of Ag/g-C$_3$N$_4$-4 can be further quenched when adding BH$_4^-$, this is one of reasons why adding BH$_4^-$ may further enhance the catalytic activity, which will be discussed in detail later.
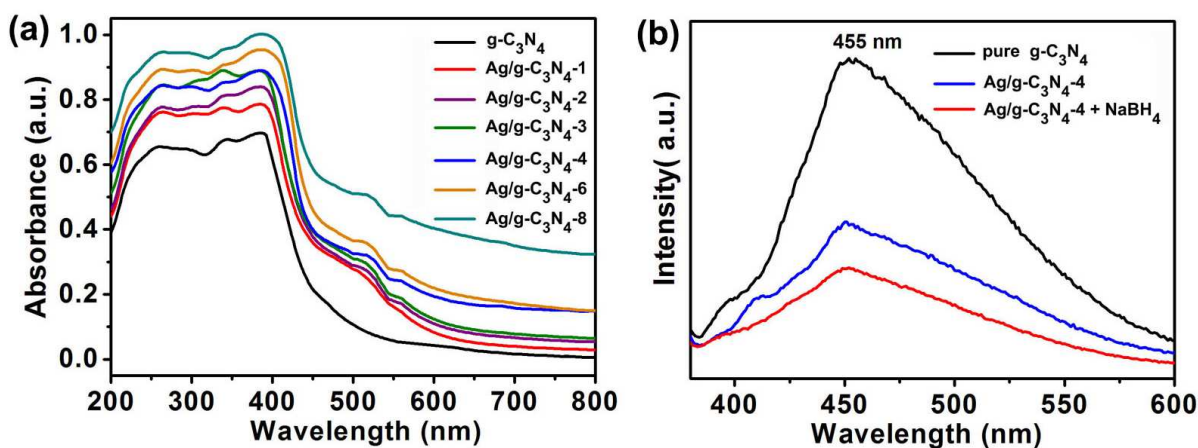

Figure 7. (a) UV−vis DRS of g-C$_3$N$_4$ and Ag/g-C$_3$N$_4$ catalysts with different Ag content; (b) Room-temperature PL emission spectra of g-C$_3$N$_4$, Ag/g-C$_3$N$_4$-4 and Ag/g-C$_3$N$_4$-4 in the presence of BH$_4^-$ (λ_{ex} = 325 nm).

The transient photocurrent response is also one of the most sensitive and powerful techniques to qualitatively estimate the separation efficiency of photogenerated carriers during the photoreactions. The transient photocurrent responses of the g-C$_3$N$_4$ and Ag/g-C$_3$N$_4$-4 electrodes were recorded for several on-off cycles of visible light irradiation in 0.5 M Na$_2$SO$_4$ aqueous solution. As shown in Figure 8, a fast and stable photocurrent response with entire reversibility is observed for each switch-on and switch-off on both electrodes. The photocurrent response of the Ag/g-C$_3$N$_4$-4 electrode (0.25 μA) is about 5 times as high as that of g-C$_3$N$_4$ electrode (0.05 μA) due to the synergistic effect between Ag nanoparticles and g-C$_3$N$_4$. Another interesting phenomenon is that adding BH$_4^-$ to the above electrolyte may further enhance the transient photocurrent responses of g-C$_3$N$_4$ and Ag/g-C$_3$N$_4$-4 electrodes. The photocurrent responses of g-C$_3$N$_4$ (0.75 μA) and Ag/g-C$_3$N$_4$-4 (0.98 μA) with BH$_4^-$ (150 μL

of 0.1 g mL^{-1} NaBH$_4$ aqueous solution with 0.5 M NaOH) are much higher than that of g-C$_3$N$_4$ (0.05 μA) and Ag/g-C$_3$N$_4$-4 (0.25 μA) without BH$_4^-$ measured in 0.5 M Na$_2$SO$_4$ aqueous solution, respectively.

Figure 8. Photocurrent transient responses of g-C$_3$N$_4$ and Ag/g-C$_3$N$_4$-4 electrodes in 0.5 M Na$_2$SO$_4$ aqueous solution with BH$_4^-$ and without BH$_4^-$.

It has been reported that the oxidation reaction of BH$_4^-$ on electrode materials (such as Au, Ag, Pt, Pd, etc) is in parallel with its hydrolysis proceeds, which can be described as the following equetion[50-53]:
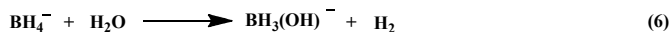
$$BH_4^- + xOH^- \longrightarrow B(OH)_4^- + (x-4)H_2O + (4-x/2)H_2 + xe^- \quad (4)$$

Because both the bottom of the CB of g-C$_3$N$_4$ and the aligned Fermi energy level of Ag are located at more negative values than the standard redox potential of complete eight-electron oxidation process (-1.24 V vs. SHE), it is entirely possible that the complete oxidation of BH$_4^-$ becomes the predominant reaction[51,53]:
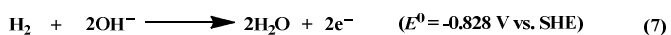
$$BH_4^- + 8OH^- \longrightarrow B(OH)_4^- + 4H_2O + 8e^- \quad (5)$$

On the basis of above analyses, we can conclude that the BH$_4^-$ ions in aqueous alkaline medium can be directly oxidized on the surface of g-C$_3$N$_4$ or Ag/g-C$_3$N$_4$-4 and the released electrons are quickly transferred to the ITO electrode, resulting in the current responses.

It is found that even in the dark, g-C$_3$N$_4$ and Ag/g-C$_3$N$_4$-4 with BH$_4^-$ also exhibited considerable current responses of 0.34 μA and 0.48 μA, respectively. In this case, the hydrolysis reaction of BH$_4^-$ may be represented as:

$$BH_4^- + H_2O \longrightarrow BH_3(OH)^- + H_2 \quad (6)$$

The resulting H$_2$ on the electrode surface can also be oxidized by hydroxyl ions with the release of two electrons:[50]

$$H_2 + 2OH^- \longrightarrow 2H_2O + 2e^- \quad (E^0 = -0.828 \text{ V vs. SHE}) \quad (7)$$

As a result, the chemically generated electrons can be instantly transferred to the ITO electrode, leading to the current responses.

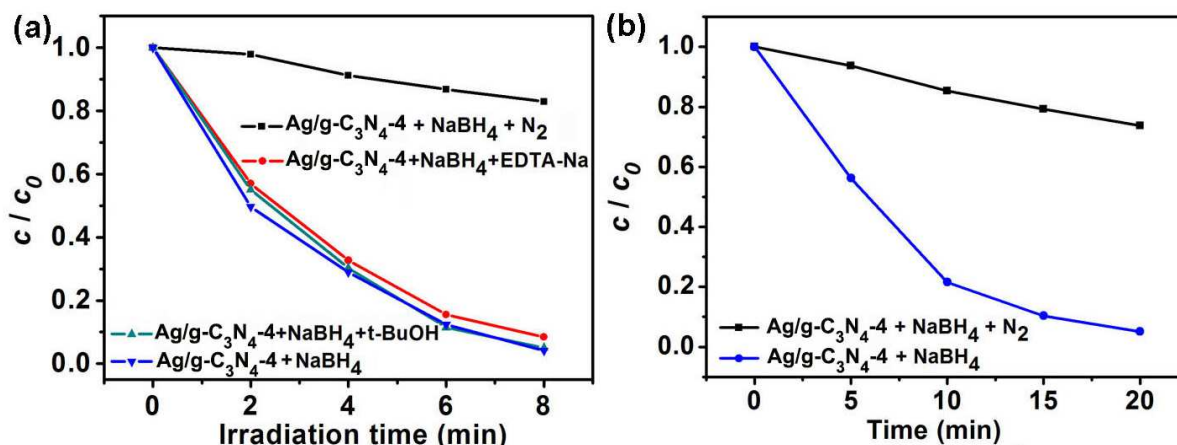Figure 9 Influence of various trapping agents on the MO catalytic degradation in the presence of Ag/g-C$_3$N$_4$-4 catalyst and BH$_4^-$ under visible-light irradiation (a) and in the dark (b).

As widely accepted, the active species (such as •OH, O$_2^{•-}$ and the photogenerated holes) play important roles in degrading organic pollutants. For better understanding the photocatalytic mechanism of the MO degradation over Ag/g-C$_3$N$_4$ in the presence of BH$_4^-$, the active species were measured through trapping by tert-butyl alcohol (t-BuOH, 1 mmol L^{-1}) as a hydroxyl radical scavenger and disodium ethylenediamine tetraacetate dehydrate (EDTA-2Na,1 mmol L^{-1}) as a hole scavenger, respectively.[54] As can be seen Figure 9(a), the change of the photodegradation rate of MO was unnoticeable when adding t-BuOH, suggesting that there were few •OH radicals in the photocatalytic system. This may be ascribed to
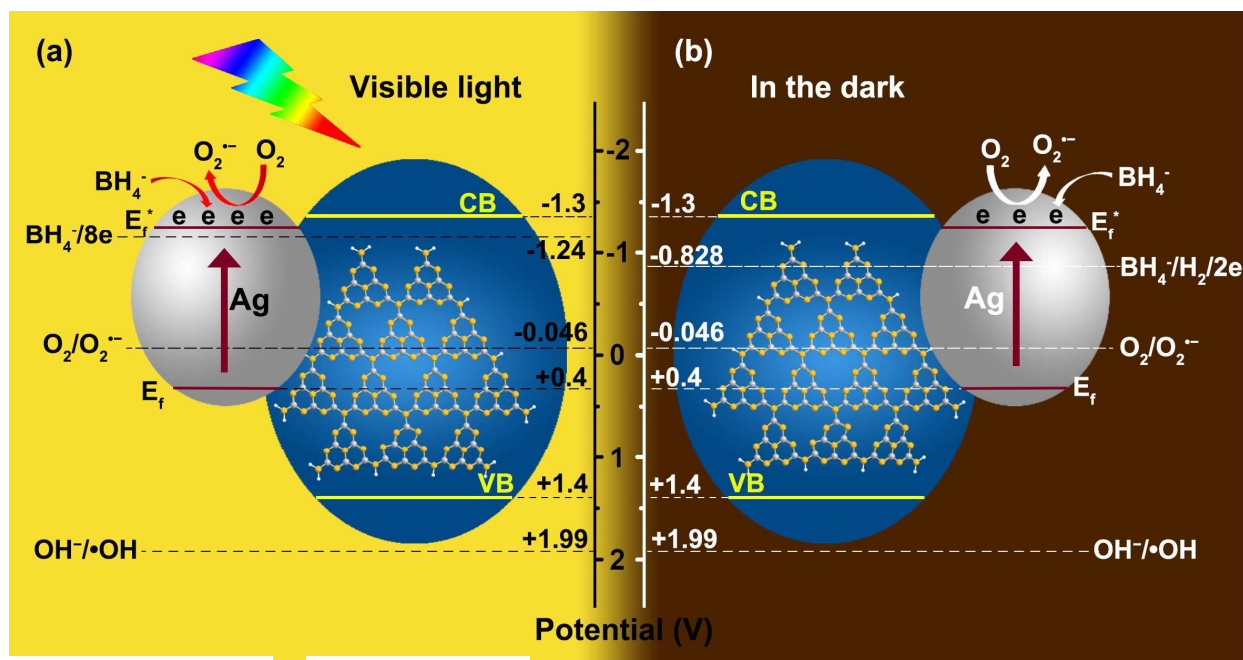
that the top of the valence band (VB) of g-C$_3$N$_4$ is lower than the standard redox potential of OH$^-$/•OH, and therefore the photogenerated holes on VB cannot oxidize OH$^-$ to give •OH radicals (Scheme 1).[23] Similarly, the change of the photodegradation rate of MO was not obvious when adding EDTA–2Na, implying that the photogenerated holes were not the main active species in the photocatalytic process. However, whether under visible light irradiation or in the dark, the photodegradation of MO in the presence of BH$_4^-$ was greatly reduced when the reaction system was purged with pure N$_2$ to remove dissolved O$_2$ (Figure 9(a) and (b)). Accordingly, we can conclude that O$_2^{•-}$ radicals are the main active species for the

catalytic degradation process of MO over Ag/g-C_3N_4-4 in the presence of BH_4^- under visible light irradiation or in the dark.[55] The generation of $O_2^{\bullet-}$ radicals in the catalytic process was confirmed by a color reaction between the ferrous irons (Fe^{2+}) and nitric oxide (NO), resulting in a brown $[FeNO]^{2+}$ complexion, as shown in Figure 6S.

On the basis of the above result of active species trapping experiments, the $O_2^{\bullet-}$ radicals as the main active species play a key role in the catalytic degradation process of MO over Ag/g-C_3N_4-4 in the presence of BH_4^- under visible light irradiation or in the dark, while the role of photogenerated holes could be negligible. A possible generation mechanism of the $O_2^{\bullet-}$ radicals is proposed as in Scheme 1(a): both the bottom of the CB of g-C_3N_4 and the aligned Fermi energy level of Ag are located at more negative values than the standard redox potential of complete eight-electron oxidation process (-1.24 V vs. SHE). Therefore, the BH_4^- can be oxidized directly on the aligned Fermi energy level of Ag under visible light irradiation in aqueous alkaline medium to release 8 electrons (Eq. (5)), which can attack the adsorbed oxygen to produce $O_2^{\bullet-}$ radicals

(Eq. (3)). Consequently, the resulting $O_2^{\bullet-}$ radicals helped to significantly speed up the degradation when adding BH_4^- and the photocatalytic degradation rates of MO, MB and NDY-GL reached up to 98.2, 99.3 and 99.6% only for 8, 45, and 16 min visible light irradiation, respectively (Figure 5, Figure 4S and Figure 5S).

As mentioned before, the degradation rates of MO, MB and NDY-GL over Ag/g-C_3N_4-4 reached up to 95.5, 96.0 and 93.8% for 20, 120, 28 min, respectively, in the presence of BH_4^- in the dark. Based on the results of catalytic degradation experiments and transient photocurrent measurements in the dark (Figure 5, Figure 4S and Figure 5S), a possible mechanism for the catalytic activity enhancement in the dark is proposed as shown in Scheme 1(b). The excellent catalytic activity may be contributed to the fact that, as the hydrolysis product of the BH_4^- (Eq. (6)), H_2 can be oxidized to H_2O with the release of 2 electrons (Eq. (7)) on the surface of Ag/g-C_3N_4 and the resulting electrons may transfer to the adsorbed oxygen to generate $O_2^{\bullet-}$ radicals.

Scheme 1 Proposed mechanism of the $O_2^{\bullet-}$ radicals generation.

Conclusions

In summary, a visible-light-driven Ag/g-C_3N_4 catalyst with different Ag content has been successfully prepared via a facile one-step route. Morphology observation indicates that g-C_3N_4 sheets were evenly decorated with Ag nanoparticles having an average diameter of 5.6 nm and narrow particle size distribution. The photocatalytic activity measurements demonstrate that the photocatalytic degradation rates of MO, MB and NDY-GL over Ag/g-C_3N_4-4 reached up to 98.2, 99.3 and 99.6% in the presence of BH_4^- only for 8, 45, and 16 min visible light irradiation, respectively. The significant enhancement in photoactivity of the catalyst can be ascribed to

the high dispersity and smaller size of Ag nanoparticles, the strong surface plasmon resonance (SPR) effect of metallic Ag nanoparticles, the efficient separation of photogenerated electron-hole pairs, the additional $O_2^{\bullet-}$ radicals generated by the reduction of dissolved oxygen in the presence of BH_4^- and the synergistic effect of Ag nanoparticles and g-C_3N_4.

Experimental

Preparation of g-C_3N_4 Nanosheets

All chemicals and reagents used in this study were of analytical grade and were used without further purification. The bulk g-C_3N_4 was synthesized according to a procedure reported

previously[23]: 5 g of dicyandiamide was added into a crucible covered loosely with a lid and heated at 2 ℃/min up to 530 ℃ in a muffle furnace for 4 h. After the reaction, the yellow bulk g-C_3N_4 was obtained. The g-C_3N_4 nanosheets were prepared by exfoliating the as-prepared bulk g-C_3N_4 in the ultrapure water. In brief, 50 mg of g-C_3N_4 was dispersed into 100 mL of ultrapure water with sonication for 24 h. The resulting suspension was centrifuged at 3000 rpm to remove the residual unexfoliated g-C_3N_4, followed by centrifugation at 15000 rpm to obtain g-C_3N_4 nanosheets.

Preparation of Ag/g-C_3N_4 Catalysts

Ag/g-C_3N_4 catalysts with different Ag content (1, 2, 3, 4, 5, 6, 8 wt %) were synthesized. Typically, the procedure for the synthesis of Ag/g-C_3N_4 catalyst with 1% Ag content is as follows: 99 mg of the as-obtained g-C_3N_4 nanosheets was added into 50 mL of ultrapure water with sonication for 1 h. Then 20 μL of $AgNO_3$ (1 mg of Ag content) aqueous solution was added to above g-C_3N_4 nanosheets dispersion. The mixture was stirred for 30 min at room temperature, followed by adding the freshly prepared $NaBH_4$ aqueous solution (20 μL, 0.3 g mL^{-1}). The reaction mixture was continuously stirred for 60 min at room temperature. After that, the mixture was centrifuged at 10000 rpm, and the product was washed and dried through freeze drying and labeled as Ag/g-C_3N_4-1.

Characterization

The crystallinity and phase of Ag/g-C_3N_4 catalysts were characterized by X-ray diffraction (XRD) on a Bruker D8 Advanced diffractometer with Cu Kα radiation (λ= 1.5418 Å) and the scanning angle ranged from 10° to 80° of 2θ. The chemical composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS) on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K radiation (h=1253.6 eV). The peak positions were internally referenced to the C 1s peak at 284.6 eV. The Ag content in the Ag/g-C_3N_4 catalysts was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Shimadzu ICP-7510). The morphologies and structure were examined with transmission electron microscopy (TEM; JEOL JEM-2100) and field-emission scanning electron microscopy (FESEM; LEO1550). Fourier transform-infrared (FT-IR) spectra were recorded on a Bruker VECTOR 22 spectrometer using the KBr pellet technique. Raman spectra were acquired on a Renishaw inVia Reflex Raman Microprobe. Ultraviolet-visible (UV-vis) diffuse reflection spectra (DRS) were carried out on a Shimadzu UV-3100 spectrophotometer in the wavelength range of 200-800 nm with $BaSO_4$ as reference. Photoluminescence (PL) spectra were recorded on a Jobin Yvon SPEX Fluorolog-3-P spectroscope and a 450 W Xe lamp was used as the excitation source with excitation wavelength of 325 nm. Photocurrent measurements were carried out on a CHI 660D electrochemical workstation in a standard three-electrode system using the prepared samples as the working electrodes with an active area of ca. 0.5 cm^2. Platinum foil and a saturated calomel electrode (SCE) were used as the counter and reference electrodes,

respectively. Photocurrent measurements were performed in 1 M Na_2SO_4 by using 500W xenon lamp with a 420 nm cutoff filter (the average light intensity was 31.2 mWcm^{-2}) as the source of visible light irradiation.

Catalytic activity measurement

The photocatalytic activity of the as-prepared catalysts was evaluated by the degradation of methylorange (MO), methylene blue (MB), and neutral dark yellow GL (NDY-GL) under visible light irradiation. Photo-irradiation was carried out using a 500 W xenon lamp with UV cut-off filters (JB450) to completely remove any radiation below 420 nm and to ensure illumination by visible-light only. Experiments were conducted at ambient temperature as follows: take MO for instance, 10 mg of catalyst was added to 50 mL of a 10 mg L^{-1} dye aqueous solution. Before starting the illumination, the reaction mixture was stirred for 60 min in the dark to reach the adsorption-desorption equilibrium between the dye and the catalyst. After adding 150 μL of 0.1 g mL^{-1} $NaBH_4$ aqueous solution with 0.5 M NaOH to the above reaction mixture, the lamp was turned on. At a given time interval of irradiation, 5 mL aliquots were withdrawn, and then centrifuged to remove essentially all the catalyst. The concentrations of the remnant dye were spectrophotometrically monitored by measuring the absorbance of solutions at 464 nm during the photodegradation process.

Acknowledgements

Notes and references

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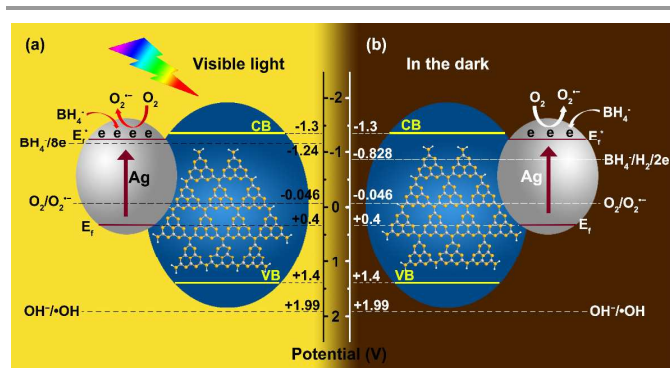
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Electronic Supplementary Information (ESI) available: The typical experiment details for the color reaction between the ferrous irons (Fe^{2+}) and nitric oxide (NO); MO photodegradation performances in the presence of Ag/g-C_3N_4 or Ag/g-C_3N_4/TiO_2 nanocomposites; TEM image of pure g-C_3N_4 catalyst; The remaining MO, MB and NDY-GL in solution after reaching the adsorption-desorption equilibrium in the dark for 60 min with stirring; Catalytic degradation of MB and NDY-GL over Ag/g-C_3N_4-4 catalyst in the presence of BH_4^- in the dark and under visible light irradiation. See DOI: 10.1039/b000000x/

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Table of contents graphic

The Ag/g-C$_3$N$_4$ catalyst exhibits superior catalytic performance for the degradation of dyes by the assistance of the additional O$_2^{\bullet-}$ radicals generated from the reduction of dissolved oxygen during the oxidation of BH$_4^-$.