Heterojunctions

Structure Modification Function of g-C₃N₄ for Al₂O₃ in the In Situ Hydrothermal Process for Enhanced Photocatalytic Activity**

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Abstract: Heterojunctions of $g-C_3N_4/Al_2O_3$ ($g-C_3N_4$ = graphitic carbon nitride) are constructed by an in situ one-pot hydrothermal route based on the development of photoactive γ - Al_2O_3 semiconductor with a mesoporous structure and a high surface area (188 m²g⁻¹) acting as electron acceptor. A structure modification function of $g-C_3N_4$ for Al_2O_3 in the hydrothermal process is found, which can be attributed to the coordination between unoccupied orbitals of the Al ions and lone-pair electrons of the N atoms. The as-synthesized heterojunctions exhibit much higher photocatalytic activity

Introduction

Ever since Wang et al.^[1] reported its hydrogen production ability in 2009, graphitic carbon nitride (g-C₃N₄) has received increasing attention in the fields of photocatalysis, electrochemistry, and photoelectrochemistry due to its fascinating two-dimensional (2D) structure and notable characters, such as low cost, earth-abundant elements, non-toxicity, thermal and chemical stability, and narrow band gap of about 2.70 eV.^[2] Nevertheless, the recombination rate of photoinduced electron-hole pairs of g-C₃N₄ is still fast, which needs to be further slowed down for an enhancement of the guantum efficiency.^[3] Thus, some methods have been exploited, such as ion doping,^[4] noble-metal nanoparticle deposition,^[5] morphology or pore structure design,^[6] acid or alkali treatment,^[7] dye sensitization,^[8] conjugated polymer coupling,^[9] and heterojunction fabrication.^[3,10] In particular, the construction of hybrids by combining $g{-}C_{3}N_{4}$ with other semiconductors is an effective strategy. The basic design thought for composites is based on the fact that the photo-induced electrons on the lowest unoccupied molecular orbital (LUMO) of q-C₃N₄ can migrate to the

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[**] g-C₃N₄ = graphitic carbon nitride. than pure g-C₃N₄. The hydrogen generation rate and the reaction rate constant for the degradation of methyl orange over 50% g-C₃N₄/Al₂O₃ under visible-light irradiation ($\lambda >$ 420 nm) are 2.5 and 7.3 times, respectively, higher than those over pristine g-C₃N₄. The enhanced activity of the heterojunctions is attributed to their large specific surface areas, their close contact, and the high interfacial areas between the components as well as their excellent adsorption performance, and efficient charge transfer ability.

conduction bands (CBs) of the coupled semiconductors, which cannot only enhance the separation efficiency of photo-generated charge carriers, but also endow the composites new unexpected properties due to synergistic effect.^[10g]

On the other hand, searching for appropriate earth-abundant, inexpensive, and nontoxic semiconductors is indispensable for practical large-scale application in industry.^[11] Al₂O₃ can meet the requirements based on its ultraviolet-light-response ability and its active role as electron acceptor.^[12] In constructing q-C₃N₄/Al₂O₃ hybrids, most recently, our group found that α -Al₂O₃-containing amorphous matter obtained through hightemperature combustion is poor of hydroxyl group on its surface and thus cannot form effective heterojunction with g- $C_3N_{4\!\scriptscriptstyle .}{}^{[13]}$ After treating $g\text{-}C_3N_4$ with aqueous ammonia solution to graft hydroxyl groups, the effective $g-C_3N_4/\alpha-Al_2O_3$ composites can be obtained by an ultrasonic dispersion route.^[13] In addition, compared to α -Al₂O₃, the γ phase of Al₂O₃ has a more disorder porous structure and a higher specific surface area and the $g-C_3N_4/\gamma-AI_2O_3$ composite has also been prepared by using ultrasonic dispersion.^[14] However, the simple combination of q-C₃N₄ and Al₂O₃ through ultrasonic dispersion results in limited contact areas between the two components. Hence, more effective g-C₃N₄/Al₂O₃ should be further developed.

In situ fabrication of heterojunctions is a potential technique, which can supply more contact sites and interactions between/among components. g-C₃N₄-based heterojunctions constructed through an in situ route, such as ZnFe₂O₄/g-C₃N₄^(10h) and g-C₃N₄/(BiO)₂CO₃,^[15] have exhibited their superiority in enhancing the photocatalytic performance. In this work, we employ a hydrothermal route to develop a mesoporous photoactive γ -Al₂O₃ phase with a high specific surface area

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 (S_{BET}) and then construct $g-C_3N_4/Al_2O_3$ heterojunctions through an in situ hydrothermal synthesis for the first time. The defect site on Al₂O₃ is designed to trap electrons from g-C₃N₄ to improve the separation efficiency of charge carriers of g-C₃N₄. Interestingly, a structure modification role of g-C₃N₄ for Al₂O₃ in the hydrothermal process is found and the resultant hybrid with an appropriate $g-C_3N_4$ ratio possesses a nearly equal S_{BET} value to pure $g-C_3N_4$ in spite of the low S_{BET} value of $g-C_3N_4$. Compared with bare g-C₃N₄, the composite exhibits much higher photocatalytic ability for hydrogen generation and degradation of methyl orange (MO) under visible light. In addition, compared to pristine g-C₃N₄, the hybrids show weaker photoluminescence intensity, which is different from other g-C₃N₄based composites. This research not only offers a new method for developing inexpensive photoactive mesoporous Al₂O₃ and finds a structure adjustment effect of q-C₃N₄ in designing heterojunctions through a hydrothermal process, but also provides a new insight into defect chemistry concerning the photoluminescence behavior of heterojunctions composed of g-C₃N₄ and semiconductors with ample defect sites.

Results and Discussion

XRD analysis

Figure 1 shows the X-ray diffraction (XRD) patterns of the asprepared pure $g-C_3N_4$, pure Al_2O_3 , and the $g-C_3N_4/Al_2O_3$ composites with different mass ratios. It can be seen from the pattern of Al_2O_3 that there are two peaks at 45.7 and 67.1°, corresponding to the (400) and (440) diffraction planes of cubic γ - Al_2O_3 , respectively (JCPDS card No. 10-0425); meanwhile, the broad peak shape implies its low crystallinity, which also indicates the existence of defect. Furthermore, the raw material of $Al(NO_3)_3$ or other intermediate crystal products cannot be detected, indicating the transformation of $Al(NO_3)_3$ to Al_2O_3 through the hydrothermal and calcination processes is complete. As for the pure $g-C_3N_4$ sample obtained through pyrolysis of melamine without the hydrothermal process, a distinct diffraction peak located at 27.4° and an obscure peak at 13.1° are indexed as (002) and (100) planes of $g-C_3N_4$, respectively





(JCPDS card No. 87-1526). The XRD pattern of g-C₃N₄ treated hydrothermal in the absence of Al(NO₃)₃ is also presented in Figure 1. It is obvious that there is no change for the peak positions in comparison with the untreated g-C₃N₄. However, for the g-C₃N₄/Al₂O₃ hybrids, there are two changes compared to pure g-C₃N₄. Firstly, the peaks at 13.1 and 27.4° of pure g-C₃N₄ shift to 14.2 and 27.6°, respectively, in the g-C₃N₄/Al₂O₃ hybrids, demonstrating that the corresponding interlamellar spacings become narrower in the presence of Al ions. It is speculated that the unoccupied 3p or 3d orbitals of the Al ions can coordinate with the lone-pair electrons on the N atoms.^[16] Scheme 1 shows the graphic representation of g-C₃N₄ with Al for shorting the (100) spacing. Secondly, the intensity of the



Scheme 1. Graphic representation of g-C₃N₄ in the presence of Al.

peak at 14.2° for the hybrids is much stronger than that of pure g-C₃N₄. This result indicates that the Al element benefits the growth of (100) planes, which is also attributed to the coordination effect. In addition, it can be seen from the patterns of the g-C₃N₄/Al₂O₃ composites with high g-C₃N₄ contents, that the two peaks of the Al₂O₃ phase cannot be observed due to its weak crystallinity. On the other hand, there are two very weak peaks at 37.6 and 49.4° emerging in the 60 and 70% g-C₃N₄/Al₂O₃ composites. The former peak corresponds to the (311) planes of Al₂O₃ and the latter is to be further investigated, which shows that g-C₃N₄ can change the growth of the Al₂O₃ planes.

Morphology, surface areas, and microstructures

To compare the morphology and to verify the defect, transmission electron microscopy (TEM) and high-resolution (HR) TEM images of the commercial γ -Al₂O₃ and the as-prepared Al₂O₃ are shown in Figure 2. It can be seen from Figures 2a and b that the commercial γ -Al₂O₃ shows a regular particle aggregation, whereas the as-prepared Al₂O₃ exhibits a short rod-like structure. It is clear that there is lattice fringe in the HRTEM image of commercial γ -Al₂O₃ shown in Figure 2c, and the interplanar spacing is about 0.46 nm, corresponding to the (111) plane of γ -Al₂O₃. For comparison, it is hard to find obvious lattice fringe in the image of the as-prepared Al₂O₃ sample, verify-







Figure 2. TEM images of a) commercial γ -Al₂O₃ and b) as-prepared Al₂O₃, and HRTEM images of c) commercial γ -Al₂O₃ and d) as-prepared Al₂O₃. Scale bars = 50 nm for **2a**, **2b**, and 10 nm for **2c**, **2d**.

ing its low-crystallinity or amorphous-similar structure, which is the base of abundant defects.

The scanning electron microscopy (SEM) image of the as-prepared Al₂O₃ is displayed in Figure 3 a. It is obvious that Al₂O₃ exhibits a cotton-like morphology, implying its amorphous-similar structure and high specific surface area. Compared with bare Al_2O_3 , the sheet-like g-C₃N₄ can be observed in the 50% g-C₃N₄/ Al_2O_3 composite (Figure 3 b). It is evident that $g\text{-}C_3N_4$ is not coated on the surface of ${\sf Al}_2{\sf O}_3$ simply, but embodied in the cotton-like Al₂O₃. In addition, the EDS pattern shown in Figure 3 c and the corresponding elemental mapping images show that the elements C, N, O, and Al can be found in the sample, providing the direct solid evidence for the combination of g- C_3N_4 and Al_2O_3 . From the TEM image of the 50% g- C_3N_4/Al_2O_3 hybrid (Figure 3 d), it is seen that the strips of $g-C_3N_4$ are combined with Al₂O₃. Figure 3 e shows the HRTEM image of the composite. By measuring the lattice fringe, the interplanar spacing is about 0.198 nm, corresponding to the (400) plane of γ - Al_2O_3 . However, the main field is composed of a cloud without lattice fringe, which is consistent with Figure 2d.

The TEM images of Pt-50% g-C₃N₄/Al₂O₃ after Pt particle deposition through in situ light irradiation, are exhibited in Figure 4. The dark dots are Pt metal particles, which prefer depositing on Al₂O₃ rather than doing on striped g-C₃N₄.

Figure 5 exhibits the N₂ adsorption/desorption isotherms and the corresponding pore size distribution curves (inset) of the as-prepared Al₂O₃ and g-C₃N₄/Al₂O₃ samples. The isotherms belong to the IV Brunauer type^[17] with a H3 hysteresis loop, indicating the existence of mesopores (2–50 nm). All the data of the obtained specific surface areas (S_{BET}), the average pore diameters, and the total pore volumes are summarized in Table 1. The pure Al₂O₃ has a high S_{BET} value of 188.6 m²g⁻¹ and the S_{BET} value of pure g-C₃N₄ is only 14.0 m²g⁻¹. However,



Figure 3. SEM images of a) pure Al_2O_3 and b) the 50% g-C₃N₄/Al₂O₃ sample. c) EDS spectrum and corresponding elemental mapping images of 50% g-C₃N₄/Al₂O₃. d) TEM and e) HRTEM images of 50% g-C₃N₄/Al₂O₃.

after introduction of $g-C_3N_4$, the decrease in the S_{BET} value is not proportionate to the $g-C_3N_4$ mass ratio in the hybrids. For example, there is a very slightly reduction for the 30% $g-C_3N_4/$ Al_2O_3 sample from 188.6 to 185.0 m²g⁻¹. Furthermore, the average pore diameter and the pore volume become larger. These results indicate that the addition of $g-C_3N_4$ can induce a change in the growth and structure of Al_2O_3 , which can also be proven by the pore size distribution shown in the inset of Figure 5, suggesting that the hybrid has a broader pore size



Figure 4. TEM images of 50 % g-C₃N₄/Al₂O₃ after Pt metal particle deposition.



Figure 5. N₂ adsorption/desorption isotherms and pore size distribution curves (inset) of a) the as-synthesized Al₂O₃, b) 30%g-C₃N₄/Al₂O₃, c) 40%g-C₃N₄/Al₂O₃, d) 50%g-C₃N₄/Al₂O₃, e) 60%g-C₃N₄/Al₂O₃, and f) 70%g-C₃N₄/Al₂O₃ composites.

than pure Al₂O₃. This result indicates that $g-C_3N_4$ has a structure adjustment role for Al₂O₃ in the hydrothermal process, which is related to the coordination between the Al ions and the N atoms. To the best of our knowledge, there is no report on $g-C_3N_4$ acting as structure-directing agent and there are few re-

composite exhibits two C1s peaks and there is also a shift from 288.10 to 287.58 eV, showing the existence of graphitic carbon nitride and the effect of Al_2O_3 on $g-C_3N_4$. From the XPS results, it can be concluded that a strong chemical interaction exists between the components Al_2O_3 and $g-C_3N_4$.

ports on bulk g-C₃N₄-based hybrids with a high surface area over 100 m²g⁻¹. In this research, such high S_{BET} values of these composites supply a firm foundation for enhanced adsorption capacity and photocatalytic activity.

Figure 6a depicts the X-ray photoelectron spectroscopy (XPS) survey spectra of bare Al_2O_3 and 50% g-C₃N₄/Al₂O₃. The C1s peak in the Al_2O_3 is due to the adventitious elemental carbon. Compared to the survey spectrum of Al_2O_3 , the 50% g-C₃N₄/Al₂O₃ sample exhibits a stronger C1s peak and the new N1s peak appears owning to the introduction of g-C₃N₄. At the same time, the peak intensities of the O1s, Al2s, and Al2p orbitals decrease because of the reduction of the Al₂O₃ mass ratio.

Figures 6b-e show the high-resolution XPS spectra of the Al2p, O1s, N1s, and C1s orbitals of related samples, respectively. The Al2p peak at 73.88 eV can be seen for pristine Al₂O₃, which is close to the references values (73.85^[18] and 73.90 eV^[19]). After combination with g-C₃N₄, this peak shifts toward a higher binding energy of 74.48 eV (Figure 6b); meanwhile, the binding energy of O1s at 530.78 eV in pure Al₂O₃ also shifts to a higher value of 531.38 eV (Figure 6 c). The two shifts towards higher binding energies of Al₂O₃ indicate that g-C₃N₄ is closely covered on the surface of Al₂O₃ and there is a chemical interaction between them. Furthermore, the peak at 398.85 eV in pure g-C₃N₄, typically a characteristic peak of g-C₃N₄ that can be attributed to sp²-hybridized N atoms (C=N-C),^[20] moves to a lower binding energy of 398.23 eV in the 50% g-C₃N₄/Al₂O₃ hybrid. For C1s spectra, only one peak located at 284.68 eV is observed for the pure Al₂O₃ sample, whereas there are two peaks at 288.10 and 284.60 eV observed for the g-C₃N₄ sample. The peak at around 284.6 eV is derived from contaminated carbon,^[21] whereas the peak at 288.10 eV is identified as sp²-bonded C atoms (N-C=N) involved in C₃N₄ triazine cycles.^[21,22] The $g-C_3N_4/AI_2O_3$



Table 1. S_{BET} values and pore parameters of the samples and their photocatalytic performances f	for MO	remov
al.		

Sample	S_{BET} [m ² g ⁻¹]	Average pore diameter [nm]	Pore volume [cm ³ g ⁻¹]	Fitted equation	<i>k</i> [h ⁻¹]	Correlation coefficient (R)
g-C ₃ N ₄	14.0	7.8	0.04	y=0.0623x+0.0121	0.0623	0.9981
Al ₂ O ₃	188.6	6.8	0.32	-	-	-
30% g-C ₃ N ₄ /Al ₂ O ₃	185.0	9.3	0.43	y=0.0984x+0.0715	0.0984	0.9996
40% g-C ₃ N ₄ /Al ₂ O ₃	160.3	8.5	0.34	y=0.1348x+0.0619	0.1348	0.9995
50% g-C ₃ N ₄ /Al ₂ O ₃	147.8	9.4	0.35	y=0.4550x+0.0471	0.4550	0.9982
60% g-C ₃ N ₄ /Al ₂ O ₃	147.0	10.1	0.37	y=0.3219x+0.0492	0.3219	0.9974
70% g-C ₃ N ₄ /Al ₂ O ₃	113.0	11.4	0.32	y=0.2028x+0.0481	0.2028	0.9978
$g-C_3N_4/AI_2O_3 (2:1)^{[a]}$	60.2	5.6	0.20	y=0.2456x+0.0377	0.2456	0.9937
[a] For reference.						



Figure 6. a) XPS survey spectra of bare Al_2O_3 and the 50% g- C_3N_4/Al_2O_3 composite, and high-resolution XPS spectra of b) Al2p, c) O1s, d) N1s, and e) C1s of the different samples.

Optical absorption and photocatalytic hydrogen generation performances

The optical absorption of pristine AI_2O_3 , $g-C_3N_4$, and the $g-C_3N_4/AI_2O_3$ composites with different $g-C_3N_4$ contents was mea-

All the hybrids display higher photocatalytic activity than pure g-C₃N₄. The 50% g-C₃N₄/Al₂O₃ sample reaches the highest hydrogen evolution with a rate of 52.10 μ mol h⁻¹, which is 2.5 times higher than that of pristine g-C₃N₄.

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sured by UV/Vis diffuse reflectance spectroscopy (DRS). It can be seen from Figure 7 that the commercial y-Al₂O₃ does not any absorbance in the show of $\lambda = 200 - 800 \text{ nm}.$ range whereas the as-prepared Al₂O₃ can respond to the ultraviolet light, which can be attributed to its disorder amorphous fraction.^[12a] The result also indicates the photoactive function of the as-synthesized γ -Al₂O₃ through a hydrothermal process. Compared to pure g-C₃N₄, the absorption band edges of the hybrids are slightly blue shifted due to the existence of Al₂O₃. However, in the UV region below $\lambda = 400$ nm, some composites display stronger optical absorption than the pure g-C₃N₄ although the absorption of the component Al₂O₃ is still the weakest. This phenomenon is consistent with a previous report on g-C₃N₄/TiO₂,^[23] indicating that there should be a synergistic effect between g-C₃N₄ and Al₂O₃ to enhance the photoabsorption.

Figure 8a shows the photocatalytic H₂ production over the as-prepared photocatalysts under visible-light illumination $(\lambda > 420 \text{ nm})$. No hydrogen could be detected without either photocatalyst or light irradiation. All the in situ Pt-deposited samples exhibit photocatalytic activity for hydrogen generation. The H₂ evolution amount is nonlinearly increased with the irradiation time, especially in the initial three hours, because the mass of deposited Pt is gradually becoming more and more under the light illumination, thus leading to an enhanced electrons transfer ability step by step. The average photocatalytic hydrogen production rates in 6 h of the samples are shown in Figure 8b.







Figure 7. UV/Vis DRS results of the as-prepared Al_2O_3 , commercial γ - Al_2O_3 , g- C_3N_4 , and the g- C_3N_4/Al_2O_3 hybrids.



Figure 8. a) Photocatalytic H_2 production amount versus time and b) average H_2 evolution rate in 6 h over the photocatalysts.

The transient photocurrent is widely considered as the direct evidence for demonstrating the electron and hole separation in heterostructured photocatalysts.^[23,24] Figure 9 shows the transient photocurrent versus time curves of the 50% g- C_3N_4/Al_2O_3 sample and pure g- C_3N_4 electrodes under visible-light illumination ($\lambda > 420$ nm) in an on-and-off cycle mode. It is obvious that the photocurrent response exhibits a good reproducibility for both samples through five intermittent irradiation on-off cycles, indicating that the electrodes are stable. The photocurrent value of the 50% g- C_3N_4/Al_2O_3 electrode is about 2.3 times higher than that of the pristine g- C_3N_4 electrode. This indicates an enhanced separation efficiency of photo-induced



Figure 9. Transient photocurrent responses of $g-C_3N_4$ and a $g-C_3N_4/Al_2O_3$ hybrid electrodes with light on-and-off cycles.

electrons and holes in the hybrids, which can be ascribed to the match of energy level between $g-C_3N_4$ and Al_2O_3 .

To further understand the charge carrier transfer behavior, the PL measurement was conducted with an excitation wavelength of $\lambda = 290$ nm. There are three abnormal PL phenomena observed from Figure 10a. Firstly, the intensity order of the pure g-C₃N₄ and the heterojunctions are contrary to their photocatalytic hydrogen activities. That is, the photocatalytic activity increases with the PL intensity, which conflicts with the previous papers on g-C₃N₄-based hybrids.^[3,10] The reason is that the PL intensity is determined by two factors. Generally, The PL signal is derived from the radioactive recombination of photoinduced electrons and holes; hence, a high PL emission intensity indicates a high recombination rate of electron-hole pair,^[25] thus a low quantum efficiency. On the other hand, photo-generated electrons can be bound by the defects of the photocatalysts to form free or binding excitons so that the PL signal can easily occur, and the greater the number of defects, the stronger the PL peak intensity, the higher is the photocatalytic activity.^[26] For the investigated g-C₃N₄/Al₂O₃ hybrids, defects play a dominant role for the PL signal and the sample with stronger PL intensity exhibits the higher photocatalytic ability due to the existence of abundant defect sites in γ -Al₂O₃. As for the reported g-C₃N₄-based composites, because the employed semiconductors are crystals without or with little defects, their PL behavior is determined by the separation of the charge carriers and the sample with the stronger PL intensity exhibits the lower photocatalytic ability.

Secondly, the main emission wavelength of pure g-C₃N₄ at $\lambda = 460$ nm is blue shifted to $\lambda = 440$ nm for the composites. To investigate the reason, the PL test of hydrothermal-treated g-C₃N₄ was carried out. It is seen that its main wavelength is still at $\lambda = 460$ nm and its intensity is lower than that of original g-C₃N₄, demonstrating that hydrothermal process cannot change the emission wavelength but can improve the crystallinity of g-C₃N₄ and thus decrease the PL intensity. Therefore, the shift of the emission wavelength for the composites is due to the interaction between Al₂O₃ and g-C₃N₄.

Thirdly, under the excitation wavelength of $\lambda = 290$ nm, pure Al₂O₃ exhibits a broad emission peak from $\lambda = 325$ to 375 nm. However, this peak is not detected completely in the g-C₃N₄/



Figure 10. a) Photoluminescence spectra of various samples (excitation wavelength: $\lambda = 290$ nm) and schematic diagram for PL occurrence of b) pure Al₂O₃ and g-C₃N₄, and c) g-C₃N₄/Al₂O₃ heterojunctions.

Al₂O₃ hybrids. Based on the PL signals, the recombination processes of photo-induced electrons and holes are proposed as Figures 10 b and c for pure Al₂O₃, pure $g-C_3N_4$, and $g-C_3N_4$ /Al₂O₃ hybrids. Accepting the photo energy, the electrons on the valence band (VB) of Al₂O₃ or the highest occupied molecular orbital (HOMO) of $g-C_3N_4$ can be excited to the CB or LUMO of them, and then some of the electrons migrate back to the VB directly or through the lower defect energy levels. For the $g-C_3N_4$ /Al₂O₃ composites, the electrons on the LUMO of $g-C_3N_4$ would combine with holes, or transfer to the CB of Al₂O₃. The electrons on Al₂O₃ excited from the VB or transferred from $g-C_3N_4$ would move to other sites or to the HOMO of $g-C_3N_4$, but not to the VB of Al₂O₃.

To further investigate the existence of defects, electron paramagnetic resonance (EPR) measurements were performed. It is clear that the as-prepared γ -Al₂O₃ shows obvious triplet *g* value signals (*g*=1.987, 2.004, and 2.024) (Figure 11), whereas the commercial γ -Al₂O₃ does not. This triplet *g* value signals



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Figure 11. EPR signals of the as-prepared and commercial γ -Al₂O₃.

can confirm the presence of solid-state defect,^[27] which can act as acceptors for photo-generated electrons from $g-C_3N_4$.

Photocatalytic performance for the degradation of methyl orange

Figure 12a shows the photocatalytic decomposition of solutions of the refractory organic dye MO. It can be seen that only 0.3% MO is removed in 2 h in the absence of photocatalysts, demonstrating that MO is a relative stable dye and the self-photolysis of MO can be neglected under visible-light illumination. With pure $g-C_3N_4$, the degradation efficiency is 12.9. Compare value below 47.9% in 2 h over 50% g-C₃N₄/Al₂O₃, exhibiting its poor photocatalytic ability. Over hydrothermaltreated $g-C_3N_4$, the removal yield of MO is decreased to 9.4% (not shown in Figure 12a), indicating that the high-temperature hydrothermal process decreases the photocatalytic activity of g-C₃N₄. When the heterojunctions are employed, the adsorption capacity for MO is increased from 1.2% (bare $q-C_3N_4$) to 4.7-6.9% and then the photocatalytic degradation efficiency is greatly enhanced. To quantitatively reveal the photocatalytic activities of these samples, the following pseudo-first-order equation [Eq. (1)] is employed, ^[12a] in which k is the reaction rate constant, C₀ represents the initial concentration of MO (10 mg L^{-1}), C_1 is the concentration after 30 min adsorption, and C is the MO concentration at time t.

$$\ln C_0/C = kt + \ln C_0/C_1 \tag{1}$$

The time-course variation of $\ln(C_0/C)$ of all samples is illustrated in Figure 12b. The results of the calculated rate constants (*ks*) and the correlation coefficients (*Rs*) are listed in Table 1. From Figures 12a and b as well as Table 1, it is clear that the pure g-C₃N₄ has a low rate constant of only 0.0623 h⁻¹ and that the g-C₃N₄/Al₂O₃ hybrids show much higher photocatalytic performances. Especially for 50% g-C₃N₄/Al₂O₃, the reaction rate constant (0.4550 h⁻¹) is 7.3 times that of pure g-C₃N₄/ For comparison, the photocatalytic activity of a 2:1 g-C₃N₄/ Al₂O₃ heterojunction obtained through ultrasonic dispersion^[14] is 3.9 times that of pure g-C₃N₄. This indicates that the one-pot fabrication of the heterojuncions through a hydrothermal process is a more efficient route, which can be ascribed to the



Figure 12. Time-course variation of a) C/C_0 and b) ln (C_0/C) of the degradation of MO, and c) photocatalytic degradation of 4-chlorophenol (4-CP) over various samples under visible-light illumination.

close contact of g-C₃N₄ and Al₂O₃ through the in-situ process and the higher surface areas.

The stability and re-usability of the 50% g-C₃N₄/Al₂O₃ composite were evaluated by a cycling degradation experiment and the results are shown in Figure 13a. It can be seen that the sample does not display an obvious loss in its photocatalytic degradation activity after four runs, demonstrating that the g-C₃N₄/Al₂O₃ hybrids are stable and the interaction between g-C₃N₄ and Al₂O₃ is strong due to their in situ formation process. As shown in Figure 13b, compared with unused g- C_3N_4/Al_2O_3 , the used photocatalyst exhibits a weaker $g-C_3N_4$ peak intensity, whereas the Al₂O₃ almost remains the same. This result demonstrates that there is slight g-C₃N₄ loss in the photocatalytic process; meanwhile, there is also loss of fine g- C_3N_4/Al_2O_3 nanoparticles in the recycling process. As a result, the activity is decreased after four cycle runs.



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 2θ (degree) **Figure 13.** a) Cycle runs of the 50% $g-C_3N_4/Al_2O_3$ heterojunction for the photocatalytic degradation of MO under visible-light irradiation ($\lambda\!>\!420$ nm). b) XRD patterns of 50 % g-C_3N_4/Al_2O_3 before and after use.

50 60 70 80

10 20 30

To investigate the reactive species accounting for the MO degradation, scavenger experiments were conducted in the presence of ammonium oxalate monohydrate (AO, 2 mм, h⁺ scavenger), 1,4-benzoquinone (BQ, 1 mм, O2⁻⁻ scavenger), or isopropanol (*i*PrOH, 10 mм, OH' scavenger).^[28] As shown in Figure 14a, it is obvious that the addition of only 1 mм BQ most acutely depressed the photodegradation of MO, which demonstrates that O_2^{-} is the dominant species responsible for the MO degradation. Meanwhile, AO and *i*PrOH can also lower the degradation efficiency of MO, indicating that h⁺ and OH[•] are the active species at the same time. Because the HOMO potential of g-C₃N₄ is 1.4 eV versus a normal hydrogen electrode (NHE),^[29] which is less than the potentials of $OH^{*}/H_{2}O$ $(2.27 \text{ eV})^{[30]}$ and OH⁺/OH⁻ (1.99 eV),^[31] this implies that the holes on g-C₃N₄ cannot oxidize H₂O or OH⁻ to form OH⁻ radicals. Therefore, the OH radicals involved in the photocatalytic reaction are derived from $\mathsf{O}_2^{{\boldsymbol{\cdot}}^-}$ based on the fact that the LUMO potential of $g-C_3N_4$ at $-1.3 eV^{[29]}$ is more negative than that of $E^{\circ}(O_2/O_2^{\bullet-})$ (-0.28 eV vs. NHE).^[30]

To further observe the existence of OH[•] and O₂^{•–} radicals directly, the 2-hydroxyterephthalic acid fluorescence and nitroblue tetrazolium techniques were used based on the facts that OH' radicals can react with terephthalic acid (TA) to form the high-fluorescent compound TAOH,^[32] and NBT has a maximum absorption peak at $\lambda = 259$ nm whereas the product of O_2^{-1} and NBT does not.^[33] To perform TAOH and NBT tests, TA was dissolved in 2.0 mm NaOH to obtain a 0.5 mm solution and NBT was dissolved in water to receive a 2.5×10^{-5} M solution. Then, 0.1 g of the photocatalyst were added to 100 mL of the solutions, and the mixtures were irradiated under visible light. The fluorescence and ultraviolet-visible absorption intensities

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Figure 14. a) C/C_0 variation of the MO degradation over various samples in the presence of scavengers, time-course variation of b) the 2-hydroxyterephthalic acid fluorescence (TAOH) intensity, and c) transformation percentage of nitroblue tetrazolium (NBT) over the 50% g- C_3N_4/Al_2O_3 hybrid.

of the aqueous solutions were measured on a Hitachi F-4600 fluorescence spectrophotometer (excitation wavelength: λ = 315 nm) and Evolution 220 UV/Vis spectrophotometer, respectively. The TAOH experiment results shown in Figure 14b illustrate that the peak intensity of TAOH over 50% g-C₃N₄/Al₂O₃ is increased with the irradiation time, demonstrating the existence of OH[•] radicals. Meanwhile, the NBT concentration is dramatically decreased with the time as shown in Figure 14c, implying that there are abundant O₂⁻⁻ radicals reacting with NBT, which is consistent with the scavenger result.

On the basis of the photocatalytic H₂ generation and MO degradation data and tests, the potential routes of the photoinduced electron transfer are proposed as shown in Figure 15. Under visible-light illumination, electrons are migrated from the HOMO of $g-C_3N_4$ to its LUMO; afterwards, some electrons move to the defect sites of amorphous Al₂O₃ due to the sink effect. This leads to an enhanced separation efficiency of the



Figure 15. Proposed mechanism for a) the photocatalytic H₂ generation and b) the MO degradation over g-C₃N₄/Al₂O₃ heterojunctions under visible-light irradiation. TEOA = triethanolamine.

electron-hole pairs and improved the photocatalytic activity. Then the electrons on the LUMO of $g-C_3N_4$ or the defect sites of Al_2O_3 reduce H^+ to produce H_2 . As for the MO degradation, electrons on the two positions can reduce O_2 adsorbed on the surface of the photocatalysts to generate $O_2^{\star-}$. The $O_2^{\star-}$ radicals then react with H_2O to produce OH radicals. Finally, MO can be degraded by the left h^+ , $O_2^{\star-}$, and OH radicals.

To observe the universality of the as-prepared heterojunctions, colorless 4-chlorophenol was selected to evaluate the photocatalytic activity. Figure 12 c displays the decrease of the 4-CP concentration with the reaction time. After 4 h of irradiation, the 4-CP removal is 51.3 and 36.5% over $g-C_3N_4$ and 50% $g-C_3N_4/Al_2O_3$, respectively. The corresponding calculated first-order reaction rate constants are 0.1704 and 0.1052 h^{-1} (not shown), respectively, which means that the photocatalytic activity of 50% $g-C_3N_4/Al_2O_3$ is 1.62 times that of pure $g-C_3N_4$ in the degradation of the colorless organic pollutant 4-CP.

Conclusion

We have successfully synthesized photoactive γ -Al₂O₃ and fabricated mesoporous g-C₃N₄/Al₂O₃ heterojunctions through an in situ one-pot hydrothermal route and a following calcination treatment. A structure adjustment role of g-C3N4 for Al₂O₃ in the hydrothermal process is found, which is beneficial to keep



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the high specific surface area of the composites. The photoluminescence behavior of pure g-C₃N₄ and the g-C₃N₄/Al₂O₃ composites are also investigated, which is different with other g-C₃N₄-based heterojunctions, showing that defects play an important role. The defect site of the as-synthesized γ -Al₂O₃ is confirmed by EPR technique. This work not only prepares a defect photoactive Al₂O₃ with a high surface area through a hydrothermal method, but also presents the structure modification function of g-C₃N₄ for Al₂O₃ in the hydrothermal process for the first time and thus provides new insight into fabricating high efficient heterojunctions.

Experimental Section

Catalysts preparation: All chemicals and commercial y-Al₂O₃ as reference were procured from Aladdin (Shanghai, China) and used as received. g-C₃N₄ was prepared through the thermal condensation of melamine. Melamine (5.0 g) was added in a semicovered crucible and heated to 550°C for 2 h at a rate of 10°C min⁻¹. g- C_3N_4/Al_2O_3 hybrids were synthesized through a hydrothermal route and a following calcination. The designed total weight of the onepot heterojunction was 0.30 g. In a typical procedure for 50% g-C₃N₄/Al₂O₃, Al(NO₃)₃·9H₂O (1.103 g) was dissolved in distilled water (30 mL) and then as-prepared $g-C_3N_4$ (0.150 g) was dispersed in the solution under ultrasonication for 20 min. Afterwards, 1 м NaOH solution was added dropwise to the mixture till the pH reached 8-9. After being magnetically stirred for 2 h, the mixed suspension was transferred into a 50 mL Teflon-lined stainless autoclave and heated at 140 °C for 24 h. Then the obtained product was collected, thoroughly washed with deionized water for three times and air dried at 80 °C for 3 h. Finally, the resultant solid particles were calcined at 400 °C for 2 h to obtain g-C₃N₄/Al₂O₃ composites, which are labeled as x % g-C₃N₄/Al₂O₃ (x = mass fraction of g-C₃N₄ in the hybrids). By using the aforementioned process, pristine Al₂O₃ was synthesized without the addition of $g-C_3N_4$. For comparison, g- C_3N_4/Al_2O_3 (2:1) was prepared through chemisorption according to reference [14], in which Al₂O₃ was obtained by precipitation synthesis.

Catalysts characterization: The XRD patterns of the samples were obtained on a Rigaku D/MAX 2500 X-ray diffractometer. The SEM and element mapping images were acquired from a HITACHI S4800 instrument equipped with energy dispersive X-ray spectrometers (EDS, Bruker Quantax). TEM and HRTEM tests for the morphology observation were recorded on a JEOL JEM-2010 microscope. N₂ adsorption/desorption measurements were carried out on a Micromeritics Tristar II 3020 apparatus. XPS spectra were achieved by using a PHI 1600 ESCA XPS system. The UV/Vis DRS were collected by using a Thermo Scientific Evolution 220 spectrophotometer. EPR measurements were carried out on a Bruker EMX-8/2.7 X-band EPR spectrometer for detecting the oxygen vacancy of samples.

Photoelectrochemical measurements were performed on an electrochemical workstation (CHI-660E, China) by using a conventional three-electrode quartz cells. An aqueous solution containing 0.2 m Na₂S and 0.04 m Na₂SO₃ was employed as the electrolyte. The counter and the reference electrodes were platinum wire and Ag/AgCl (saturated KCl), respectively. The as-obtained photocatalyst film electrodes deposited on cleaned 1.5 cm \times 1.0 cm fluoride-tin oxide (FTO) glass served as the working electrode.

Photocatalytic activity tests: Photocatalytic hydrogen evolution was carried out in a PerfectLight Labsolar-III gas-closed circulation

system by using a 300 W Xe lamp with $\lambda =$ 420 nm cut-off filter as visible-light source. In a typical experiment, powders of the photocatalyst (0.1 g) were dispersed in a mixed solution (100 mL) containing deionized water (70 mL), triethanolamine (25 mL), and an aqueous solution of H₂PtCl₆·6H₂O (5 mL). Herein, TEOA is taken as sacrificial reagent to capture the photo-induced holes. The designed in situ photodeposited Pt metal quality serving as cocatalyst to transfer electrons is 0.001 g, which accounts for 1.0 wt% of the added catalysts. After stirring the suspension for 30 min, the light was turned on to trigger reaction. Hydrogen evolved was analyzed by an on-line gas chromatograph equipped with a thermal conductivity detector (TCD) every 1 h. In the photocatalytic process, the solution temperature was kept at 30 °C by using a thermostatic water bath. There was no hydrogen generated without photocatalyst or light irradiation, demonstrating that hydrogen was produced through a photocatalytic reaction.

The photocatalytic degradation performance towards pollutants was evaluated by the removal of methyl orange (MO), a typical refractory azo dye, and colorless 4-chlorophenol (4-CP). A 350 W Xe lamp with a $\lambda = 420$ nm cutoff filter was employed as the visiblelight source, with a total light intensity of 0.40 $W\,cm^{-2}$ in the range of $\lambda = 420-1064$ nm measured by using a Newport 842-PE optical power/energy meter. In each experiment, an aliquot of the sample (0.10 g) was suspended in aqueous solutions of MO or 4-CP (100 mL, 10 mg L⁻¹). After being stirred for 30 min to achieve the adsorption/desorption equilibrium of MO on the catalyst, the light was turned on to begin the photocatalytic reaction. The MO concentration was analyzed by using a Thermo Scientific Evolution 220 UV/Vis spectrophotometer and the value at the maximal absorbance wavelength was noted to plot the removal efficiency of MO and thus, measure the photodegradation ability of the samples. The concentration of 4-CP was collected by measuring the absorbance at $\lambda = 230$ nm. For the cycle experiments, the nanopowders were separated from the MO solution by centrifugation at 13000 rmin⁻¹ for 5 min and subsequently dried at 110 °C for 2 h for the next photocatalytic reaction cycle.

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