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Review

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Modification Strategies with Inorganic Acids for Efficient Photocatalysts by Promoting the Adsorption of O_2

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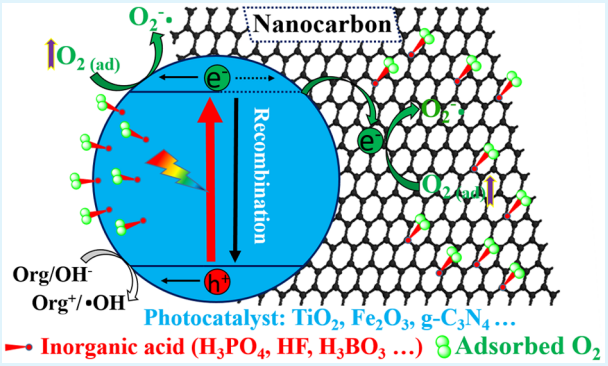
ABSTRACT: Efficient photocatalysis for degrading environmental organic pollutants on semiconductors requires photogenerated charge carrier separation to drive the photochemical processes. To ensure charge separation, it is indispensable to make charges captured effectively. Generally, the step for capturing the photogenerated electrons by the surface adsorbed O_2 is relatively slow as compared to that for capturing holes by the surface adsorbed hydroxyl groups so that it is taken as the rate-determining step. However, it is frequently neglected. Thus, it is greatly desired to develop feasible strategies to promote the adsorption of O_2 for efficient photocatalysts. In this paper, we have mainly discussed surface modification with inorganic acids, such as H_3PO_4, HF, and H_3BO_3, to enhance photogenerated charge carrier separation based on oxygen adsorption promotion for photocatalytic degradation of environmental pollutants. Among these acids, the function and mechanism of H_3PO_4 are highlighted because of its good performance and universality. Several important photocatalyst systems, mainly including TiO_2, α-Fe_2O_3, and g-C_3N_4, along with the nanostructured carbons as electron acceptors in nanocomposites, are addressed to improve the ability to adsorb O_2. A key consideration in this review is the development of a strategy for the promotion of adsorbed O_2 for efficient photocatalysts, along with the process mechanisms by revealing the relationships among the adsorbed O_2, photogenerated charge carrier separation, and photocatalytic performance. Interestingly, it is suggested that the enrichment in surface acidity be favorable for promotion of O_2 adsorption, leading to the improved charge carrier separation and then to the enhanced photoactivities of various semiconductor photocatalysts. Moreover, several outlooks are put forward.



KEYWORDS: *surface modification, inorganic acid, adsorbed O_2, photogenerated charge separation, photocatalyst*

1. INTRODUCTION

With industrialization and population development, various toxic organic pollutants are occurring in the environment that are harmful to both humans and animals. Traditional biological and physical methods have been employed as the primary techniques for the removal of these organic pollutants from the environment.[1−3] However, the biological treatment methods are time-consuming and often produce some highly toxic species during the degradation process, and these produced toxic species easily remain in the wastewater and ambient atmosphere. In physical methods like adsorption, the pollutants only move from one system to another simultaneously with a large amount of solid wastes produced, which generally need additional treatment and further cost, and are harmful to an ecosystem over the long-term. As for those issues, there is an increasing demand for economic and environmentally benign treatment techniques to decompose chemically organic contaminants effectively into nontoxic substances. In recent decades, many reports have shown that numerous organic pollutants, such as chlorinated compounds, alkenes, alkanes, aromatics, dyes, and so forth, could be decomposed into nontoxic oxidation products (CO_2, water, and other inorganic species) in a semiconductor photocatalysis process at the aid of the renewable and abundant sunlight as the supply energy and the economic, safe, and clean molecular O_2 as the oxidant.[4−6] Obviously, it is widely accepted that semiconductor photocatalysis is one of the "green" and potential techniques for degradation of environmental pollutants, especially for the low-concentration ones.

The essential principles of photocatalysis over semiconductors mainly depend on the formation of photogenerated electron−hole pairs that is involved with subsequent reactions of oxidizing and reducing of the appropriate species concurrently, which is simplified in Scheme 1.[7,8] First, the semiconductor absorbs photon energy ($h\nu$) greater or equal to its band gap energy (Eg), resulting in the production of negative electrons (e_{cb}^-) in its conduction-band (CB) and positive holes in its valence-band (VB), respectively, as described by eq 1.[9] After that, a part of holes could reach the surface for oxidation processes with two different mecha-

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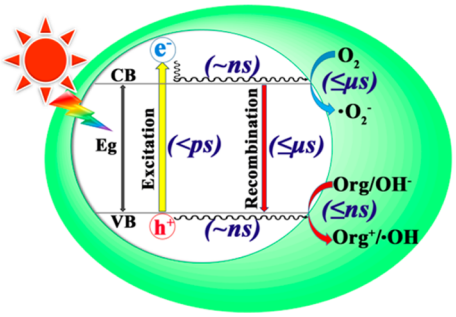
Scheme 1. Schematic Illustration for the Basic Principles of Photocatalysis over Semiconductors with the Associated Reaction Time Scales



nisms:[10] first, induce the oxidation process by transferring to the adsorbed pollutant (eq 2); second, transferring to the adsorbed hydroxyl groups forming hydroxyl radicals, ·OH (eq 3). The formed ·OH group would easily induce a series of oxidation of organic pollutants. Meanwhile, some negative electrons can reduce the molecular oxygen adsorbed on the surface of photocatalyst forming superoxide anion ($O_2^{-\bullet}$). This superoxide anion can further produce ·OH radicals via the formation of HOO· radicals and H_2O_2 (eqs 4–8).[10,11] These formed highly reactive radicals or intermediate substances mentioned above, such as h^+, ·OH, $O_2^{-\bullet}$, HOO·, and H_2O_2, would act concomitantly to oxidize various organic compounds. It is accepted that the ·OH attack mechanism is applicable in the most photocatalytic processes to degrade organic pollutants.

$$M + h\nu \rightarrow M(e_{cb}^- + h_{vb}^+) \quad (1)$$

$$h_{vb}^+ + \text{pollutant} \rightarrow \cdot\text{pollutant} \quad (2)$$

$$h_{vb}^+ + OH^- \rightarrow \cdot OH \quad (3)$$

$$O_2 + e_{cb}^- \rightarrow O_2^{-\cdot} \quad (4)$$

$$O_2^{-\cdot} + H^+ \rightarrow HOO\cdot \quad (5)$$

$$2HOO\cdot \rightarrow H_2O_2 + O_2 \quad (6)$$

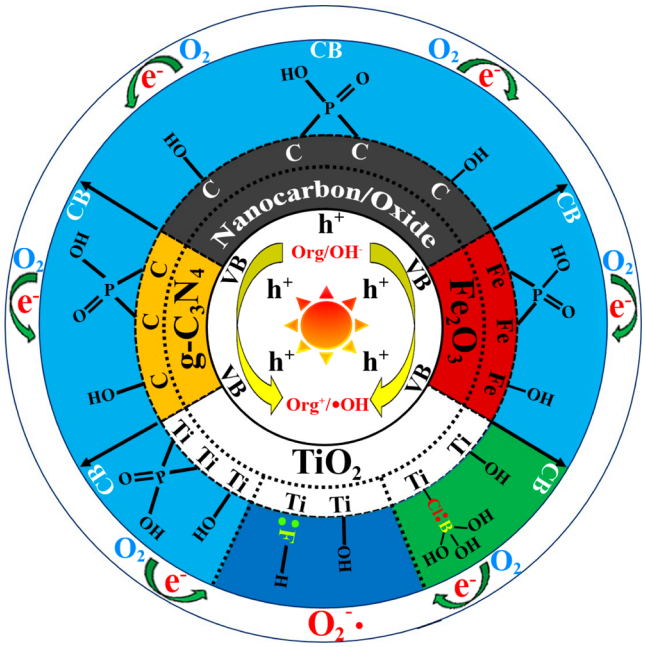
$$HOO\cdot + e_{cb}^- + H^+ \rightarrow H_2O_2 \quad (7)$$

$$H_2O_2 + e_{cb}^- \rightarrow \cdot OH + OH^- \quad (8)$$

In fact, only a small part of photogenerated electron–hole pairs would arrive at the surfaces to be captured so as to induce redox reactions at the effective utilization of light energy because most part (~90%) would recombine and then dissipate the related energy as heat.[12] In this case, it is highly desired to promote the surface adsorption of electron acceptors like O_2 molecules and electron donors like hydroxyl groups on solid semiconductors in advance. The acceptance and donation of electrons directly influence the photogenerated charge separation and photocatalytic efficiency of semiconductor photocatalysts. It is postulated that the adsorbed oxygen performs the function as the electron acceptor. Surprisingly, it is often neglected. In this review, we have tried to develop feasible strategies in recent years to enhance the adsorption of O_2 for efficient photocatalysts to degrade environmental pollutants. Fortunately, we have successfully developed the strategies on the surface modification with inorganic acids. Obviously, it is important to clarify the crucial factors on semiconductor photocatalysis and to give reasonable guides to design high-activity photocatalysts for environmental purification. This greatly spurs us to complete the review on the promoted O_2 adsorption for efficient photocatalysts by inorganic acids (i.e, phosphoric acid, fluoride acid, and boric acid) modification, to degrade environmental organic pollutants. Although there are several photocatalysis-related reviews published, including ours,[13] they are mainly involved with the controlled synthesis of nanostructured photocatalysts.

In this paper, we try to present the recent advances on the surface modification strategies for efficient photocatalysts to degrade organic pollutants, as depicted in Scheme 2, using

Scheme 2. Schematic Illustration of the Arrangement Structure on the Surface Modification Strategies in This Review



different inorganic acids, particularly phosphoric acid, to modify different photocatalysts. Thus, the review is composed of 4 sections, including the Introduction, Role of Adsorbed O2, Strategies for Promoting O2 Adsorption, and Conclusions and Perspectives. In the Introduction, a widely accepted mechanism on semiconductor photocatalytic degradation of pollutants is described. It is emphasized for the vital role of adsorbed O_2 in the photocatalytic processes in section 2. The newly developed strategies on surface modification with inorganic acids to promote O_2 adsorption on the single-component and two-component photocatalyst systems are discussed in details in section 3. Lastly, on the basis of the developed strategy for O_2 adsorption, prospective outlooks about efficient photocatalysts are presented in section 4.

2. VITAL ROLE OF ADSORBED O_2

According to the basic principle of semiconductor photocatalysis, it is expected that the photocatalytic efficiency primarily relies on the competition between photogenerated charge carrier separation and recombination process. As one of two half-reactions in photocatalysis, the adsorbed O_2 would capture the photogenerated electrons. For the O_2 molecule, it exhibits a triplet ground-state with two spin-parallel electrons.

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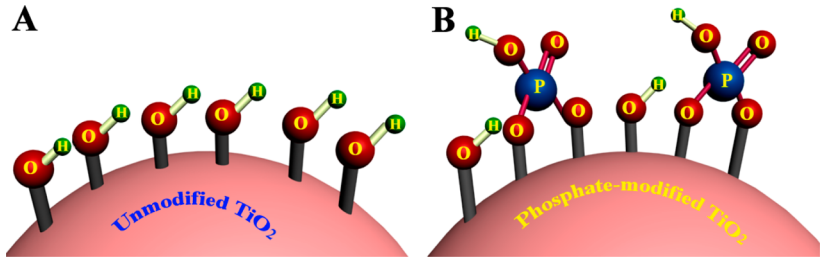
Scheme 3. Schematic of the Surface Structure of TiO_2 Unmodified (A) and Modified with Phosphate Groups (B)



This indicates that between the two electrons, one would be spin reversed during the half-reaction. However, the reverse spinning of the electron is thermodynamically and kinetically forbidden. In addition, its one-electron reduction to $O_2^{-\bullet}$ exhibits a rather low reduction potential (−0.16 V vs NHE at pH = 0), compared with the multielectron ones (+0.695 V for O_2/H_2O_2 and +1.229 V for O_2/H_2O).[14] As a result, it is difficult for the adsorbed O_2 to get the first electron to produce $O_2^{-\bullet}$ radicals. This agrees with the slow processes of capturing photogenerated electrons by the adsorbed O_2 (~μs), compared to that of capturing photoinduced holes by the adsorbed organic substances (~ns).[15,16] Therefore, the adsorbed O_2 molecule would play vital roles in semiconductor photocatalysis, especially in reactions related to environmental cleanup applications.

Some studies have demonstrated that the molecular oxygen adsorbed on photocatalysts can greatly inhibit the charge carrier recombination by capturing the photoinduced electrons. Durrant et al. proposed their work on the photochemical reduction of adsorbed oxygen on nanoporous TiO_2 film by means of transient absorption spectra (TAS). They demonstrated that the electron-related TAS signal probed at 900 nm decayed with a half-life of about 25 μs in a nitrogen atmosphere, whereas the signal exhibited the decay process with a half-life of about 12 μs in air.[17] Yamakata et al. studied the water and oxygen induced decay-kinetics of free electrons in Degussa P25 TiO_2 by means of time-resolved infrared absorption spectra, indicating that O_2 from the gas phase trapped the electrons and speed up the decay rate at a delay time of 10−100 μs.[18] Berger et al. found that the molecular oxygen could improve the photogenerated charge separation in semiconductor photocatalysis since more holes could be trapped within the particles in the presence of O_2.[19] Xu et al. have investigated the O_2 adsorption on semiconductor nanoparticles, and revealed that the anatase phase could be much more active than rutile one for photocatalytic degradation of organic pollutants, which is closely related to the distinction in their adsorption capability toward O_2 in water.[20] Obviously, the oxygen adsorption is a key step for photocatalytic-reactions taking place on the semiconductor photocatalysts surfaces for efficient degradation of pollutants.

Lowering the energy barrier between photoelectrons and O_2 molecules and promoting O_2 adsorption are the two feasible strategies to facilitate the separation of photogenerated charge carriers. It is widely accepted that the O_2 adsorption at semiconductor photocatalysts can be enhanced by nanosized noble metal deposition. Malwadkar et al. have revealed by the temperature-programmed desorption measurements that the highly dispersed gold on TiO_2 would be taken as distinct low-energy sites for the direct adsorption and activation of O_2 molecules, which has a vital role in the overall photocatalytic processes.[21] Li et al. have investigated that in $Pt/TiO_{2-x}N_x$ photocatalyst, O_2 could adsorb on Pt nanoparticles to give surface O_{ad} atoms, which capture the photogenerated electrons from the Pt particles, and hence responsible for the enhanced visible-light activity for photocatalytic degradation system toward VOCs.[22] Notably, it is a feasible route for the promotion of O_2 adsorption on photocatalysts to deposit the noble metal within the nanoscale, consequently leading to the improved photocatalytic activities. However, it is expensive to use noble metals, and usually noble metal deposition is a complicated process. Thus, it is impractical for efficient photocatalysis to be applied in wide fields. In this case, it is greatly desired to explore new strategies to promote the adsorption of O_2 for efficient photocatalysts.

3. O_2 ADSORPTION-PROMOTED STRATEGIES

In general, surface modification of semiconductors might exhibit obvious effects on the photocatalytic processes by changing the charge transfer pathways taking place at the photocatalysts surfaces.[13,23] It has been demonstrated that the surface modification with inorganic nonmetals and redox inert anions, such as F^-, $[PO_4]^{3-}$, and $[SO_4]^{2-}$, attracted great attention due to the capacities to improve the photocatalytic activities of oxides for degradation of organic pollutants under UV-irradiation.[24−27] It is well-known that phosphate anions could greatly alter the interfacial and surface chemistry of TiO_2 by substituting the surface adsorbed hydroxyl groups of TiO_2. A general operating system for phosphate modification put forward by Zhao et al.,[28] also applicable to some inert anions, suggested that the formed negative electric field on the surface layers is favorable to the separation of photoinduced charges by trapping holes. However, it is difficult to accept the suggested mechanism according to the following two points: First, the step in which the photoinduced holes are captured by the surface adsorbed organic compounds is quite fast so as not to be taken as the rate-determining step. Second, the surface modification could also promote the photocatalytic performance of oxides for degradation of VOC pollutants in air, in which the negative electrostatic field on the surface of photocatalysts are not formed, because the surface-modified H_3PO_4 groups would not be ionized in air atmosphere. Naturally, it is expected that the reasonable mechanisms on surface modification is related to the promotion of O_2 adsorption. Interestingly, we have successfully developed the strategies on surface modification with inorganic acids to promote the adsorption of O_2 in recent years, which have clarified the above expectations, for efficient photocatalytic degradation of pollutants on the single-component and two-component photocatalysts.

3.1. For the Single-Component Photocatalysts. Herein, the photocatalyst only consists of a single component, mainly involved with currently popular ones, such as TiO_2, α-Fe_2O_3, and g-C_3N_4. Thus, the separation of photogenerated charge carriers would take place on the surfaces of the same component.

3.1.1. Modification with H_3PO_4. 3.1.1.1. Anatase TiO_2. The formation of the $[PO_4]^{3-}$ anion group is widely used as a ligand in many organic/inorganic systems due to its strong cooperating ability.[29] It is naturally expected that the phosphate groups could easily be modified on oxide nanoparticles owing to hydroxyl groups.[30] Generally

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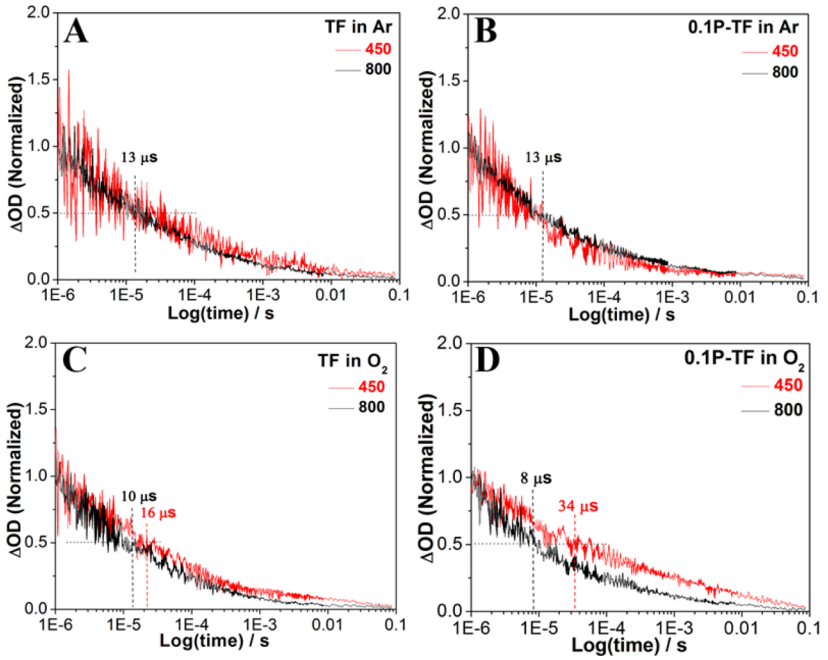

Figure 1. Temporal profiles of the transient absorption spectroscopy (TAS) of TF (A) and 0.1P-TF (B) in argon. Reprinted with permission from ref 33. Copyright 2012, Royal Society of Chemistry. Temporal profiles of transient absorption spectroscopy of TF (C) and 0.1P-TF (D) in O_2. Reprinted with permission from ref 34. Copyright 2012, Royal Society of Chemistry. In the TAS figures, 450 and 800 always represent the photogenerated holes and electrons, respectively (TF, unmodified nc-TiO_2 film; 0.1P-TF, phosphate-modified nc-TiO_2 film).

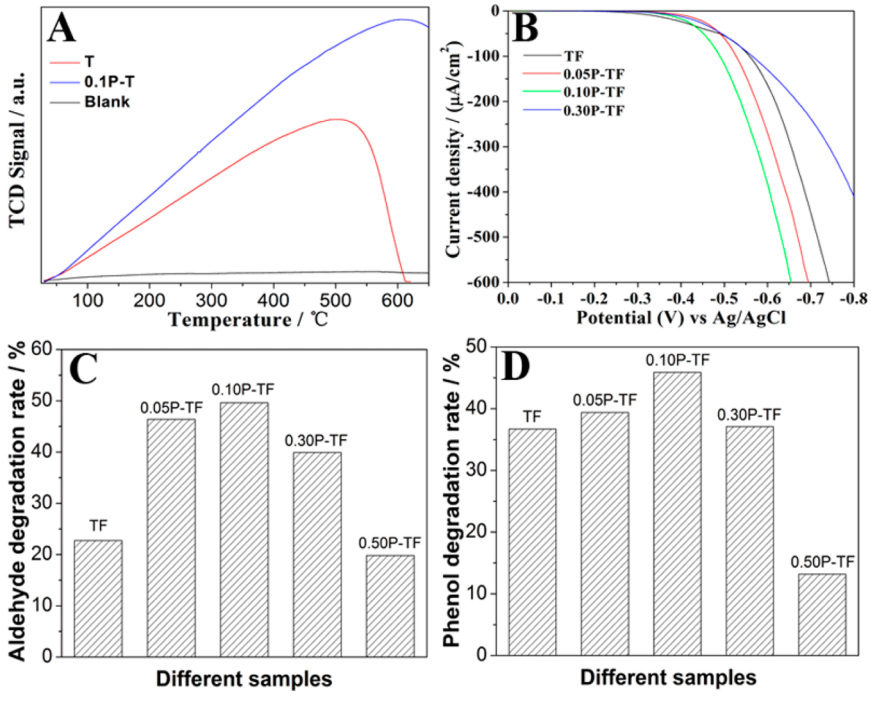

Figure 2. Curves of O_2 temperature-programmed desorption (A). Reprinted with permission from ref 36. Copyright 2012, Royal Society of Chemistry. Electrochemical reduction of O_2 on different phosphate-modified nc-TiO_2 films (B); photocatalytic degradation of gas-phase acetaldehyde (C) and liquid-phase phenol (D) on different phosphate-modified nc-TiO_2 in the presence of O_2 (T, nc-TiO_2; 0.1P-T, phosphate-modified nc-TiO_2; TF, unmodified nc-TiO_2 film; xP-TF, different phosphate-modified nc-TiO_2 films). Reprinted with permission from ref 34. Copyright 2012, Royal Society of Chemistry.

speaking, anatase TiO_2 is one of the most popular oxide semiconductor photocatalysts. On the basis of the FT-IR spectra and XPS, it was confirmed that the phosphate groups were anchored on the nanocrystalline anatase TiO_2 (nc-TiO_2) via −Ti−O−P−OH forms, as shown in Scheme 3. Although the phosphate modification does not alter the phase composition, crystallite morphology and UV−vis absorption properties of nc-TiO_2, but greatly influences the photogenerated charge carrier properties based on the measurement of atmosphere-controlled surface photovoltage spectroscopy (SPS) responses, which have well been used to explore the photoinduced charge carrier properties in semiconducting solid materials.[31,32]

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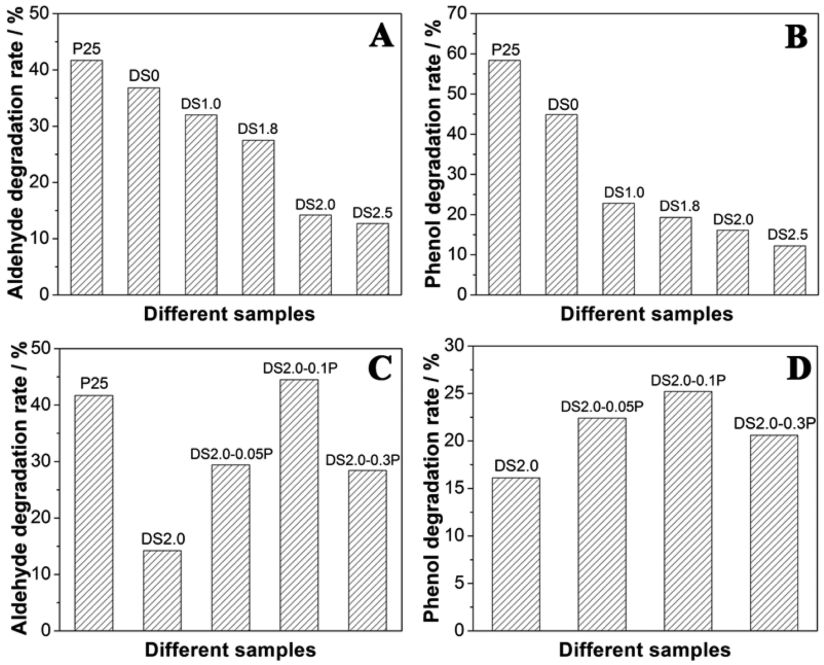

Figure 3. Photocatalytic degradation rates detected for gas-phase acetaldehyde (A, C) and liquid-phase phenol (B, D) on various unmodified and phosphate-decorated rutile TiO_2 nanorods (DSX: DS means direct synthesis, and X stands for molar concentration of aqueous HCl solution used). Reprinted with permission from ref 43. Copyright 2012, American Chemical Society.

According to the principles of SPS, the SPS response of nc-TiO_2 should primarily derive from the photoinduced charge carrier separation via diffusion process. When nc-TiO_2 is exposed to the O_2-containing atmosphere, the oxygen molecules could adsorb on the surfaces of nc-TiO_2 so as to trap the photogenerated electrons. Hence, it is concluded that the photoinduced positive holes could preferentially immigrate to the testing electrode surfaces. The unmodified and phosphate-modified nc-TiO_2 exhibit the same SPS attributes, and their SPS responses mainly depend on the concentration of O_2. However, the surface modification of nc-TiO_2 with an appropriate amount of phosphate groups could markedly enhance its SPS responses. This means that the photoinduced charge carrier separation of nc-TiO_2 could be significantly improved. This is experimentally proved by the time-resolved transient absorption spectroscopy (TAS).

TAS method is often employed to explore the decay dynamics of photoinduced charge carriers, along with the carrier lifetime.[33−35] As for nc-TiO_2, the probed TAS response signals at 450 and 800 nm are attributed to the photogenerated holes and electrons, respectively. It is found from Figure 1A,B that the decay processes of photogenerated holes and electrons are the same in argon atmosphere either in TF or in 0.1P-TF, demonstrating that the phosphate groups modification does not alter the dynamic processes of photoinduced charge carriers of nc-TiO_2 in argon. However, it is observed from Figure 1C,D that the decay processes of photogenerated electrons are greatly accelerated in O_2, especially for the 0.1P-TF. This indicates that the presence of O_2 is beneficial to capture the photoinduced electrons, and it is beneficial for the modified phosphate groups to adsorb O_2 in order to improve further the separation of charge carriers. On the basis of the curves of O_2 temperature-programmed desorption (O_2-TPD) shown in Figure 2A, it is demonstrated that the phosphate modification remarkably increases the amount of adsorbed O_2 on the nc-TiO_2 surfaces, particularly for the chemically adsorbed one.[36−38]

Obviously, it is deduced that the large amount of chemically adsorbed O_2 is extremely useful for capturing the photoinduced electrons after phosphate modification, which is responsible for the results of SPS, TAS, and the electrochemical reduction of O_2 (Figure 2B). Moreover, it is confirmed that modification with a proper amount of phosphate groups enhances the electrochemical reduction currents of nc-TiO_2.

According to the above analysis, it is deduced that modification with an appropriate amount of phosphate groups could facilitate O_2 adsorption on nc-TiO_2 so as to favor the photoinduced electrons captured, further resulting into significantly improved photoinduced charge carrier separation. As a result, photocatalytic activities of nc-TiO_2 for the degradation of model pollutants gas-phase acetaldehyde and liquid-phase phenol could be greatly improved after modification with phosphate groups, as shown in Figure 2C,D, which shows much better performance than commercially available P25 TiO_2.[33,35−38] Therefore, the improved photoactivities of nc-TiO_2 for pollutants degradation is mainly attributed to the promoted O_2 adsorption after phosphate modification. What leads to the increase in amount of adsorbed O_2 on nc-TiO_2 surfaces? It is ascribed to the formed surface end (−Ti−O−P−OH) after phosphate modification (Scheme 3), which is different from surface hydroxyl (−Ti−OH) on unmodified nc-TiO_2.

Moreover, it is suggested that the "−Ti−O−P−OH" is probably much useful for O_2 adsorption as compared to "−Ti−OH", because the attributed surface H^+ is altered by increasing the surface acidity. This is proved by the acidity measurements through TPD curves of NH_3 and FT-IR spectra of adsorbed pyridine, indicating that the surface acidity of nc-TiO_2 is improved after phosphate modification. It is worthy of noting that the two designed experiments further support the above consideration. One is to substitute the H from the "−Ti−O−P−OH" group with potassium ions, and the other is to use different sodium orthophosphate to modify TiO_2. For the two experiments, it is understandable that the surface acidity of TiO_2 would be small compared to that of TiO_2 modified with phosphoric acid. As expected, the decrease in the surface acidity is unfavorable for O_2 adsorption, leading to the low separation of photoinduced charge carrier and then to the weak photocatalytic activities. Very recently, Fabien Dufour et al. have shown that the most efficient photocatalyst among the fabricated different-morphology anatase TiO_2 nanoparticles is found to be the morphology with the stronger acidic surface sites by means of FT-IR spectroscopy with pyridine as a surface probe and the EPR analysis of photogenerated radicals.[39] However, in some works,[40,41] it was demonstrated that the phosphoric acid modification (or sulfated) induces a detrimental effect on the photocatalytic

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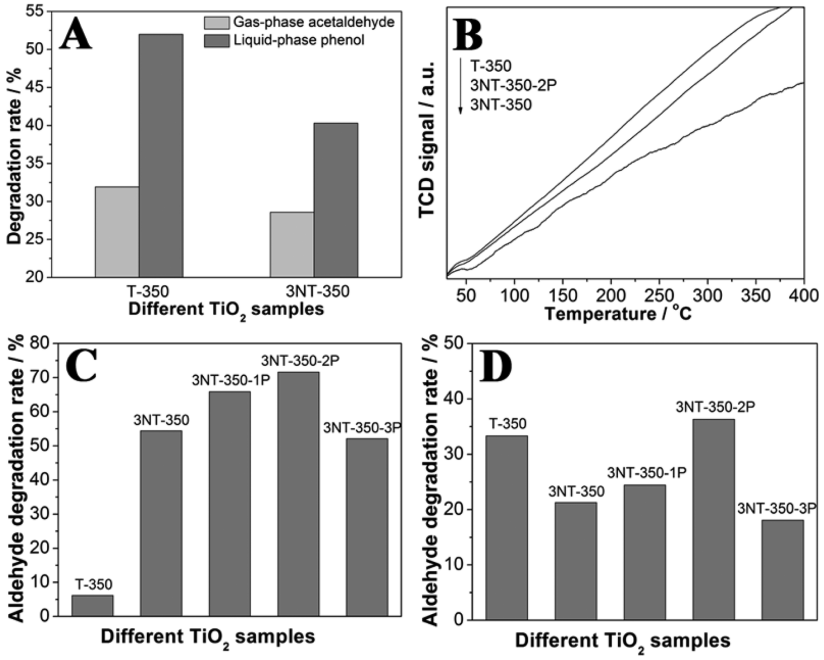

Figure 4. Photocatalytic degradation rates (A) of gas-phase acetaldehyde and liquid-phase phenol on the T-350 (undoped) and 3NT-350 (N-doped TiO_2) under UV irradiation and curves of O_2 temperature-programmed desorption (B) of unmodified and 3NT-350-xP (different phosphate-modified N-doped TiO_2); photocatalytic degradation rates of gas-phase acetaldehyde on the 3NT-350-xP under visible-light (C) and UV irradiation (D). Reprinted with permission from ref 48. Copyright 2014, Wiley-VCH.

reaction. This is mainly because too much acid is used, which is unfavorable for charge transportation and separation. In addition, the phosphate modification can easily induce surface polymeric species. In that case, it is unfavorable for O_2 adsorption. Therefore, it is well demonstrated that the improved surface acidity of TiO_2 is crucial for O_2 adsorption promotion and the surface modification with an appropriate amount of phosphoric acid is a feasible strategy for efficient TiO_2 photocatalysts to degrade colorless pollutants.

3.1.1.2. Rutile TiO_2. For TiO_2, there are two main polymorphs: anatase and rutile. It is well-known that anatase-phase displays superior photoactivities than the rutile one; therefore, rutile is rarely investigated in the field of photocatalysis.[42] However, rutile phase has abundant features over anatase, such as high refractive index, chemical stability, narrow energy band gap, and high hardness. In fact, compared with the anatase or even with P25 TiO_2, the rutile TiO_2 synthesized at low temperature could exhibit much higher photocatalytic activity for degrading colored dyes, such as methylene green, rhodamine B and methyl orange, selected as model pollutants. It is acceptable that the high photocatalytic activity of the resulting rutile TiO_2 for colored dyes degradation is mainly ascribed to the promoted self-oxidation degradation process, other than the photocatalytic degradation dependent on the charge separation of rutile, since the large surface area and the residual chloride species are favorable for dye molecule adsorption.[43] However, the activity of above-mentioned rutile is often low in the photocatalytic degradation of colorless organic pollutants, such as benzene, phenol and 4-nitro-phenol.[44]

For the colorless pollutants, it is not feasible to be degraded through the self-oxidation process. Thus, it is anticipated that the low photocatalytic activity is attributed to the poor capturing of the photoinduced electrons by the adsorbed O_2. As for this, the rutile TiO_2 nanorods are synthesized by the HCl-introduced sol-thermal process at the relatively low temperature, and then modified with phosphoric acids.[43] As assumed, it is found from Figure 3A,B that the as-prepared rutile exhibits low photoactivities for gas-phase acetaldehyde and liquid-phase phenol degradation as compared to anatase TiO_2. Interestingly, its photoactivities are markedly improved after phosphate modification, even higher than that of anatase one (Figure 3C,D). This could be attributed to the increase in the amount of adsorbed O_2 on the rutile TiO_2 and hence to enhance the photoinduced charge carrier separation primarily according to the O_2-TPD measurements and the SPS responses in air. Similar to anatase TiO_2, the phosphate modification for promoting the adsorption of O_2 is also applicable to rutile one.

3.1.1.3. N-Doped TiO_2. Anatase TiO_2 is the most widely investigated photocatalysts, owing to its nontoxicity, chemical stability and low cost. However, this wonderful material has a wide energy band gap (3.2 eV) that can absorb only ~5% of solar spectrum, which limits its photochemical applications. A great number of attempts have been made to extend its optical absorption to the visible portion of the spectrum.[45,46] Among those methods, doping with nonmetallic ions, particularly with nitrogen, is considered an effective strategy. In general, N-doping creates the localized surface states above the valence band, consequently resulting into the visible-light extension that further leads to the enhanced visible-light photocatalytic activity of anatase TiO_2. However, the photocatalytic activity of the N-doped TiO_2 under UV irradiation is commonly low as compared to the undoped one.[47] Actually, it is difficult to recognize the key point that the widely accepted levels of the produced localized states possess enough energy for photoinduced holes to induce oxidation reactions. Therefore, it is expected that this phenomenon is related to the adsorbed O_2 since it is the key step for efficient separation of photoinduced charge carriers during photocatalytic degradation process of various pollutants.[48] Obviously, it is important to verify the above assumptions from a scientific and engineering point of view.

Thus, a simple hydrolysis−solvothermal method in the presence of ammonia is developed to synthesize N-doped TiO_2 nanocrystals. The results demonstrate that the as-synthesized N-doped TiO_2 displays relatively high visible-light photocatalytic activities for colorless pollutants degradation as compared to the undoped one, while its UV photoactivity is decreased (Figure 4A). As assumed above, it is confirmed from the O_2-TPD curves (Figure 4B) that the N-doped TiO_2 displays a small amount of adsorbed O_2 compared with the undoped one, leading to the poor photocatalytic activity under UV irradiation.

As expected, the adsorption of O_2 on N-doped TiO_2 could be promoted after modification with a proper amount of phosphoric acid. This makes the photogenerated electrons much effectively captured. Consequently, the photocatalytic activities for gas-phase acetaldehyde

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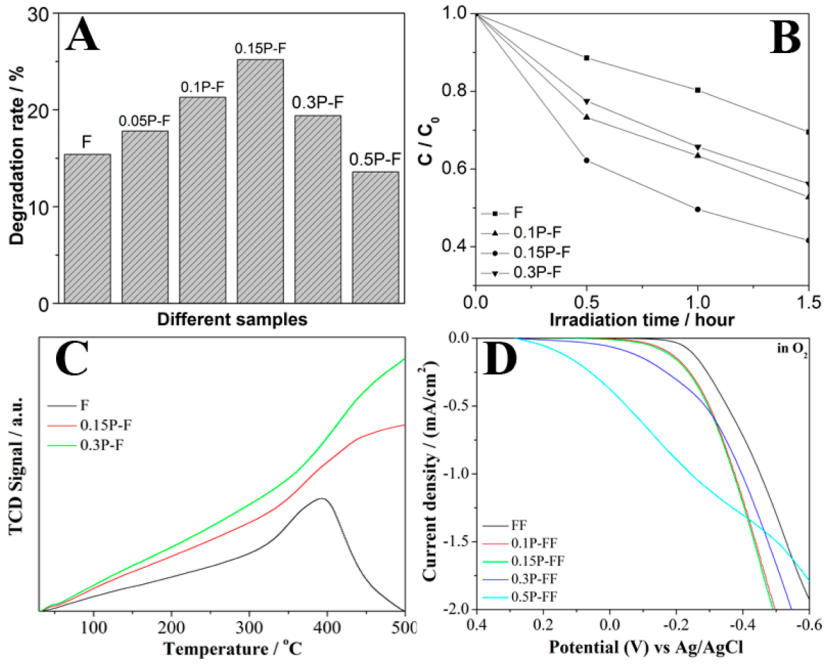

Figure 5. Photocatalytic degradation rates of liquid-phase phenol (A) and gas-phase acetaldehyde (B) on xP-F (different phosphate-modified α-Fe_2O_3 samples) under light irradiation. Curves of O_2 temperature-programmed desorption (C) and electrochemical reduction of O_2 (D) on xP-F. Reprinted with permission from ref 50. Copyright 2013, American Chemical Society.

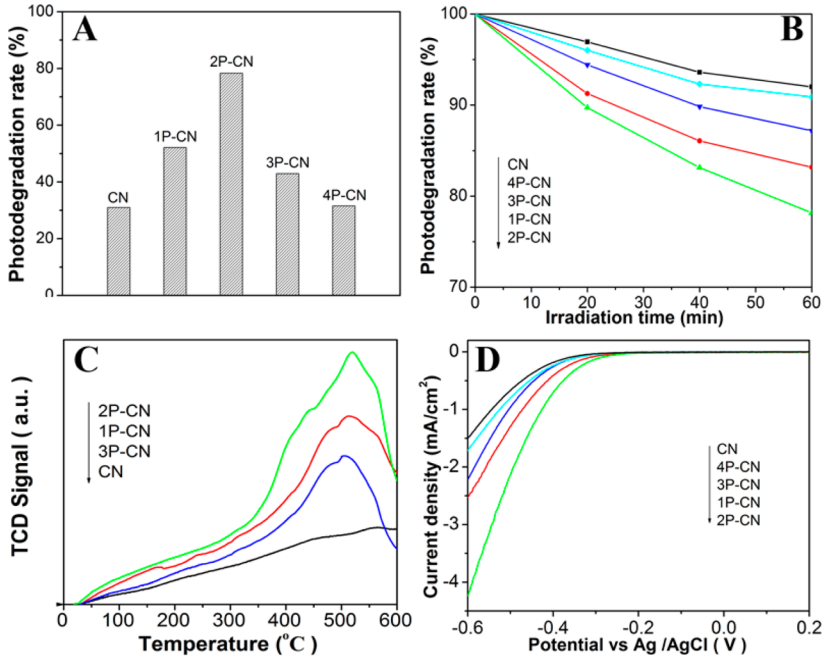

Figure 6. Photocatalytic degradation rates of liquid-phase phenol (A) and gas-phase acetaldehyde (B); curves of O_2 temperature-programmed desorption (C) and electrochemical reduction of O_2 (D) on CN (C_3N_4) and xP-CN (different phosphate-modified g-C_3N_4 samples). Reprinted with permission from ref 56. Copyright 2014, Royal Society of Chemistry.

degradation on N-doped TiO_2 could be improved after phosphate modification under visible-light (Figure 4C) and UV irradiation (Figure 4D). Therefore, it is a practicable strategy to improve the visible-light photoactivities of nonmetallic ion-doped oxides with wide band-gap energy by phosphate modification.

3.1.1.4. α-Fe_2O_3. Hematite (α-Fe_2O_3) is characterized by various advantages, owing to its low cost, fine corrosion resistance, and remarkable environmental compatibility. Therefore, intensive research has been focused on its wide potential applications in numerous fields including gas sensors, catalysis pigments, and lithium ion battery electrodes.[49] In particular, as an *n*-type semiconductor, α-Fe_2O_3 has a narrow band gap (2.0−2.2 eV) that absorbs a substantial amount of visible-light of solar spectrum, and therefore has attracted much attention owing to its potential applications in the field of photocatalysis for degrading organic pollutants.[50] Numerous studies have been made to enhance further the visible-light photocatalytic activity of α-Fe_2O_3.

Interestingly, a newly developed strategy on phosphate modification has been expanded to α-Fe_2O_3. As shown in Figure 5, the visible-light photoactivity of nanosized α-Fe_2O_3 for liquid-phase phenol degrada-

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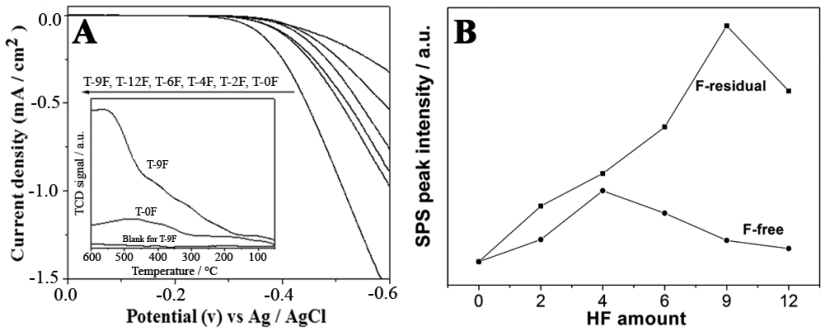

Figure 7. Electrochemical reduction of O_2 on different TiO_2 electrodes, and curves of O_2 temperature-programmed desorption of T-0F (F-free TiO_2) and T-9F (F-residual TiO_2) and the blank curve of T-9F as an inset (A); intensities of SPS response peak at 350 nm of resulting F-residual TiO_2 and its corresponding F-free ones (B). Reprinted with permission from ref 61. Copyright 2013, American Chemical Society.

tion (Figure 5A) and gas-phase acetaldehyde degradation (Figure 5B) is significantly improved by modification with a proper amount of phosphate groups. On the basis of the atmosphere-controlled SPS responses and the photoelectrochemical measurements, it is suggested that the increased photoactivity is ascribed to the enhanced separation of charge carrier by promoting photoinduced electrons captured by the surface adsorbed O_2. Moreover, it is confirmed from the O_2-TPD curves (Figure 5C) and electrochemical O_2 reduction ones (Figure 5D) that the promotion effect is mainly due to the increased amount of O_2 adsorbed on the surface of α-Fe_2O_3 through the partial substitution of −Fe−OH with −Fe−O−P−OH on the surface ends. It is expected that the developed strategy could also be applicable to other visible-responsive semiconductor nanophotocatalysts.

3.1.1.5. g-C_3N_4. Graphitic carbon nitride (g-C_3N_4) has been regarded as an efficient photocatalyst due to its high chemical and thermal stability, versatile optical, electronic, tribological and catalytic properties, proper conduction band (CB) and valence band (VB) potentials, which are centered at −1.3 and 1.4 eV respectively, versus NHE.[51,52] In general, it is taken as metal-free novel polymeric photocatalyst with enormous potential for water splitting to evolve H_2, carbon dioxide reduction and degradation of various pollutants.[53−55] From the point of practical application, it is of great significance to improve the photocatalytic efficiency of g-C_3N_4. Consequently, numerous methods have been reported to improve its photocatalytic performance with certain success, such as copolymerization, elemental doping and coupling with metals or other semiconductors. As for the developed strategy on phosphate modification for promoting the adsorption of O_2, is it feasible for g-C_3N_4 to be an efficient photocatalyst? As expected, it is successful. In our previous work,[56] g-C_3N_4 was prepared simply by heating melamine in an alumina crucible at 500 °C for 4 h under continuous flow of argon gas, and then decorated by an immersion process by taking different content of phosphoric acid solution, followed by calcining at 450 °C for 1 h. It is observed that phosphate modification does not change the phase composition, optical absorption, crystallinity, and morphology of the resulting g-C_3N_4. The phosphate modification does not alter the SPS attribute of g-C_3N_4 in N_2 and air atmosphere, meaning that it still requires the presence of adsorbed O_2 to enhance significantly the separation of photoinduced charge carriers of g-C_3N_4 in air atmosphere.

This is responsible for the improved photocatalytic activities of g-C_3N_4 for degrading phenol (Figure 6A) and acetaldehyde (Figure 6B) after phosphate modification. As expected, one can see from the O_2-TPD curves (Figure 6C) that the amount of adsorbed O_2 on g-C_3N_4 could be improved significantly after decoration with an appropriate amount of phosphate, and the largest amount is observed for 2% phosphate-modified sample. This agrees with the electrochemical O_2 reduction curves (Figure 6D). Interestingly, similar results have been reported for the modifications with sulfuric acid and hydrofluoric acid. However, the phosphate modification has much positive effects on the photocatalyst performance as compared with the sulfuric acid or hydrofluoric acid modification. This can be attributed to the three −OH groups of phosphoric acid. Therefore, it is authentic that the acidity increase after modification with inorganic acids is a feasible approach to improve significantly the photoactivities of g-C_3N_4.

3.1.2. 001-Facet Exposed TiO_2 Modified with HF. In general, the photocatalytic activity of TiO_2 strongly depends on its crystal-phase, crystallinity, particle size, and surface area. In addition, the exposed high energy facets are beneficial for the efficient photocatalytic reactions. On the basis of the theoretical studies, the (001) surface of anatase TiO_2 is more active than the (101) one. In general, it is exposed with the (101) facet, which is thermodynamically stable because of its low surface energy (0.44 J·m^{-2}), whereas the (001) facet exhibits high surface energy (0.90 J·m^{-2}) and is difficult to be exposed.[57] The synthesis of anatase TiO_2 with exposed (001) facet was first obtained by using hydrofluoric acid (HF) during the reaction as a structure-directing agent. Afterward, much attention has been focused toward the high-energy (001) facet in order to achieve efficient photocatalysis based on anatase TiO_2. Some researchers have reported that the large percentage of (001) facet anatase TiO_2 displays superior photocatalytic performance, due to the exposure of (001) facet.[58] In contrast, some researchers suggested that the exposure of the (001) facet in a high percentage is not beneficial for the enhancement of photocatalytic activity.[59,60] Surprisingly, the roles of the residual fluoride and the adsorbed O_2 are usually neglected. Obviously, there are some disagreements in the reported literatures. To clarify the crucial and efficient photocatalytic reactions of TiO_2 for the exposed high energy (001) facet and the residual chloride, it is essential to explore their effects on the surface adsorbed O_2 and photogenerated charge separation.

As for the above consideration, various percentages of the exposed high energy (001) facet anatase TiO_2 are fabricated by a HF-modified hydrothermal process, for exploring the effects of the high energy facet exposure and the residual fluoride in the TiO_2 photocatalysis.[61] On the basis of the experimental results, it is confirmed that higher the percentage of 001 facet exposure, the larger will be the residual fluoride amount. And also, the proper amount of exposed facet or residual fluoride corresponds to the high current of electrochemical reduction of O_2, resulting from the promoted adsorption of O_2 (Figure 7A). This is responsible for the enhanced separation of photoinduced charge carriers based on the SPS response intensity as shown in Figure 7B, consequently resulting into the greatly enhanced photocatalytic activities for degradation of colorless gas-phase acetaldehyde and liquid-phase phenol (Figure 8), compared with the nonexposed TiO_2. However, if the residual chloride is removed by washing with NaOH solution, the charge separation becomes weak. (Figure 7B). These results are consistent with the decreased photocatalytic activities, as shown in Figure 8. Thus, it is deduced by comparison that the residual fluoride is vital for the charge carrier separation and in the photocatalytic degradation process than the exposed high-energy facet.

It is expected that the essential role of residual fluoride is closely related to the adsorbed O_2. However, it is unclear that which kind of fluoride is much better for O_2. Interestingly, it is confirmed by the following several points that hydrogen fluoride (HF) is the best

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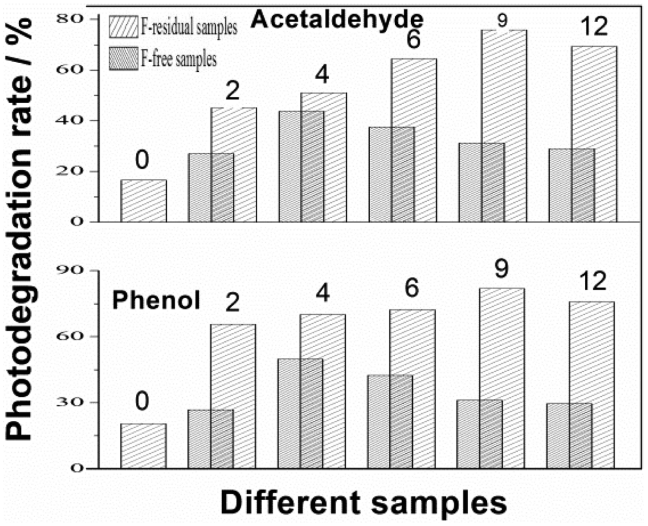

Figure 8. Photocatalytic degradation rates of gas-phase acetaldehyde and liquid-phase phenol on the resulting F-free and F-residual TiO_2. The number indicates the volume of used HF solution during the preparation of TiO_2. Reprinted with permission from ref 61. Copyright 2013, American Chemical Society.

residual fluoride. First, the role of residual fluoride of high energy facet exposed TiO_2 is similar to that of HF modified on nonexposed TiO_2. Second, the coordination bonds between H−F and Ti^{4+} is easily produced on the acidic conditions. Third, it could result into the widely accepted isoelectric point (IEP) value lower than pH 7, because the HF molecule (pK_a = 3.15) is a typical kind of weak acid. This is also in agreement with the surface-carried negative charges under neutral conditions. If it is generally accepted −Ti−F, the IEP value should be higher than pH 7. Fourthly, the molecular form of HF rather than F^- is crucial for formation of exposed high energy (001) facets of anatase TiO_2. Fifthly, the HF molecules were examined in the desorbed substances according to the TPD−mass curve. Lastly, the most important point in the presence of HF results into the markedly increased amounts of adsorbed O_2 based on the theoretical calculation results. The theoretical results show that the adsorption-energy of O_2 with H in "-Ti:F−H" is −3.25 eV, much greater than that in "−Ti−O−H" (−0.53 eV) and that of O_2 with F in "−Ti:F" (−0.19 eV), suggesting that the "−Ti:F−H" form is much favorable for O_2 adsorption in comparison to the "−Ti−O−H" and "−Ti:F" ones. This is in good agreement with our previous work about phosphate modification (−Ti−O−P−OH or −Fe−O−P−OH) in which the attribute of surface H^+ is altered by the increased acidity.[30−33,48] As highlighted in Chemical & Engineering News, it is hydrogen fluoride's unexpected role in photocatalysis.[62] Therefore, it is understandable that the modified HF on TiO_2 is more favorable for the adsorption of O_2 thereby promoting the capturing of photoinduced electrons, leading to the enhanced charge carrier separation and then to the increased photocatalytic activities for degrading pollutants.

3.1.3. Cl-Residual Rutile TiO_2 Modified with H_3BO_3. Among the well-known inorganic acids, boric acid (H_3BO_3) has seldom been used to decorate semiconductor photocatalysts owing to its low solubility and hence low dispersion on the oxide photocatalysts.[44] Interestingly, it is demonstrated that the H_3BO_3 molecules could be successfully modified on the Cl-residual rutile TiO_2 nanorods surfaces via the coordination-bond connections (−Ti−Cl:B−OH) between B with vacancy atomic orbit in H_3BO_3 and Cl with lone-pair electrons in residual chloride. On the basis of the O_2−TPD curves (Figure 9A) and the fluorescence spectra of the produced hydroxyl radicals (·OH) (Figure 9B) as important active species during the photocatalytic degradation of pollutants, it is confirmed that the modified H_3BO_3 is favorable to increase the amount of adsorbed O_2, which is much effective to capture the photoinduced electrons and hence promote the separation of charge carrier. This results into the improved photocatalytic activities of Cl^- residual rutile TiO_2 for colorless gas-phase acetaldehyde and liquid-phase phenol degradation after modification with H_3BO_3, as shown in Figure 9C. Therefore, the H_3BO_3 modification is also a feasible route to promote the adsorption of O_2 for efficient photocatalytic degradation of pollutants, similar to H_3PO_4 and HF ones.

3.2. For the Two-Component Photocatalysts. In general, to improve the separation of photoinduced charge carriers, nanostructured crystalline carbons, like carbon nanotubes (CNT) and graphene (GC), are frequently used to couple with an oxide semiconductor, in which they would be taken as the electron acceptors to favor charge transfer and separation.[63−65] In this case, the process that the adsorbed O_2 captures the photogenerated electrons in photocatalysis would happen on the surfaces of coupled carbons, other than on the oxides. Thus, it is a feasible strategy to promote the adsorption of O_2 on the used electron acceptors by modification with phosphoric acids in advance for efficient photocatalysis on the fabricated two-component photocatalysts, like CNT/TiO_2 and GC/Fe_2O_3.

3.2.1. For CNT/TiO_2. For the unique electronic and physical properties of a carbon nanotube (CNT), it has attracted considerable attention in photocatalysis.[66] It is well-known that a CNT is often used to couple with TiO_2 to improve the photoactivity of oxide-based semicouductors.[67,68] Generally, the improved photocatalytic activity is ascribed to the roles of a coupled CNT as effective receptors of photogenerated electrons and hence promote the charge separation. As expected, coupling a proper amount of multiwall CNTs (MWCNTs) could greatly enhance the photocatalytic activity of nanosized TiO_2 for degrading either colored or colorless pollutants. In fact, it is always feasible for the colored pollutant degradation, while the photoactivity is decreased for the colorless pollutants. On the basis

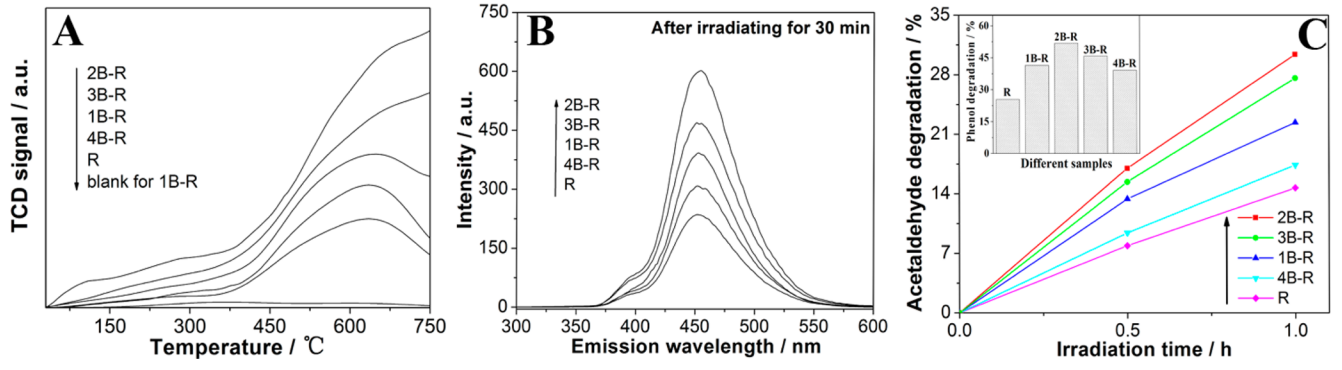

Figure 9. Curves of O_2 temperature-programmed desorption (A) and the fluorescence spectra related to the formed hydroxyl radical amount after irradiation for 30 min (B) of R (unmodified rutile TiO_2) and xB-R (different H_3BO_3-modified rutile TiO_2); photocatalytic degradation rates of gas-phase acetaldehyde and liquid-phase phenol as an inset (C). Reprinted with permission from ref 44. Copyright 2014, Royal Society of Chemistry.

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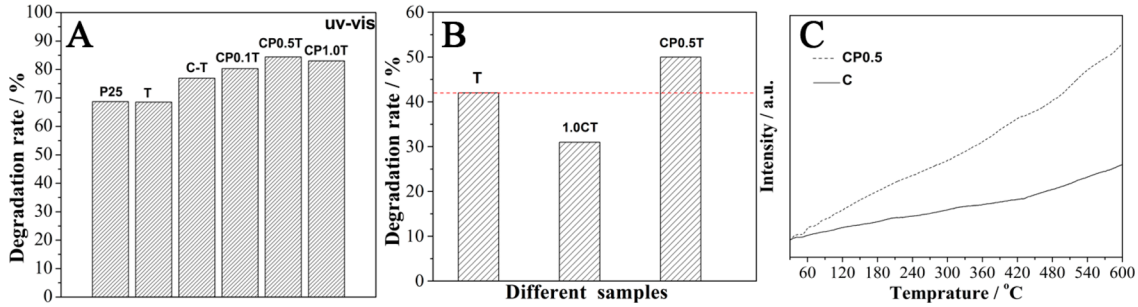

Figure 10. Photocatalytic degradation rates of RhB over P25, T, C-T, CP0.1T, CP0.5T, and CP1.0T (A) and of phenol over T and 1.0CT and CP0.5T samples (B); curves of O_2 temperature-programmed desorption of unmodified and phosphate-modified MWCNT (C), (T is TiO_2, C is MWCNT, and P means modified phosphate group. The number is the atom number ratio percentage of used C to T). Reprinted with permission from ref 63. Copyright 2013, Wiley-VCH.

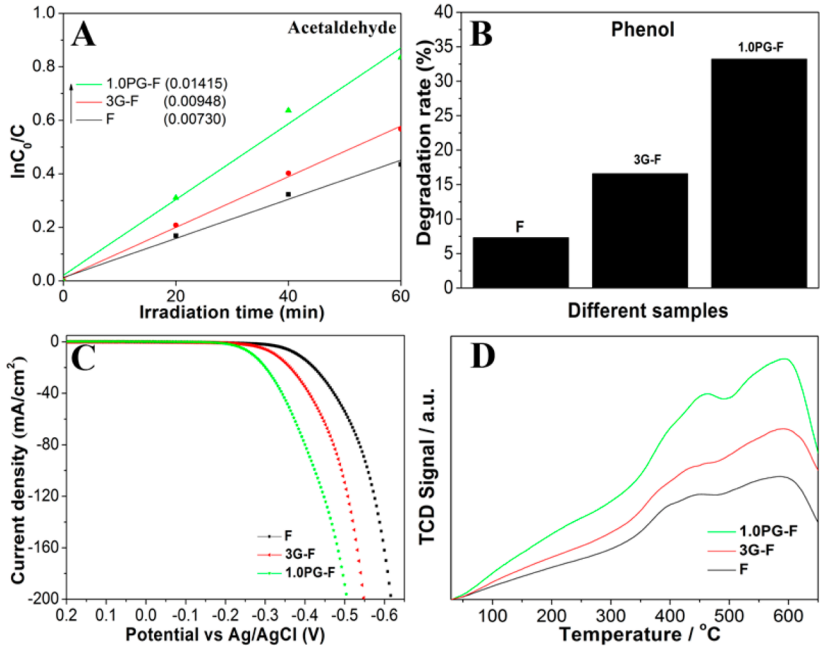

Figure 11. Photocatalytic degradation rates of gas-phase acetaldehyde (A) and liquid-phase phenol (B) on F, 3G-F, and 1.0PG-F. The corresponding degradation rate constant is listed in the parentheses in panel A; curves of O_2 electrochemical reduction in the dark (C) and O_2 temperature-programmed desorption (D) on F, 3G-F, and 1.0PG-F. (F means Fe_2O_3, and in the XG-F, X is the mass content percentage of used graphene, and G means graphene. In the YPG-F, Y is the concentration of used phosphoric acid, and P means modified phosphate). Reprinted with permission from ref 72. Copyright 2013, Royal Society of Chemistry.

of the energy-band levels of CNT and TiO_2, it is possible that the photoinduced electrons of TiO_2 would transfer to the CNT, leading to the enhanced charge separation. In this case, it is expected that it is the adsorbed O_2 on CNT since it is key for efficient photocatalytic processes by holding back the buildup of negative charges. Obviously, it is interesting to reveal the mechanism for enhanced activity by investigating the role of adsorbed O_2 on the coupled CNT.[63]

Thus, an effectively contacted MWCNT−TiO_2 nanocomposite is successfully fabricated by a simple one-pot phase-separated hydrolysis−solvothermal method. It is clearly demonstrated that the as-prepared nanocomposite between TiO_2 and a proper amount of MWCNTs displayed much higher photocatalytic activity for RhB degradation compared to the resulting TiO_2 (Figure 10A), while exhibiting low photocatalytic activities for degrading gas-phase acetaldehyde and liquid-phase phenol. Interestingly, as shown in Figure 10B, the modification of MWCNTs with a proper amount of phosphoric acid prior to the synthesis could significantly enhance the activities for degrading phenol of the MWCNT−TiO_2 nanocomposites, even much higher than the commercial P25 TiO_2. Mainly on the basis of the measurements of O_2 TPD curves (Figure 10C) and SPS responses, it is suggested that the MWCNT is favorable to increase the RhB adsorption on the surface of composite so as to accelerate the photosensitization oxidation reactions, which is unfavorable for O_2 adsorption, leading to the low photocatalytic activity for degradation of colorless pollutants. Importantly, the phosphate modification greatly increases the amount of O_2 adsorbed on the MWCNT, and hence responsible for the improved separation of charge carrier and then to the considerable photoactivities for degrading colorless pollutants by the resulting nanocomposites. Hence, it is confirmed that it is crucial for efficient photocatalysts to degrade colorless pollutants so as to promote the O_2 adsorption on the CNTs as electron receptors in the fabricated nanocomposites by phosphate modification.

3.2.2. For Graphene/Fe_2O_3. Graphene, as an atomic-layer-thick 2D nanostructured carbon, has attracted great attention due to its large specific surface area and exceptional storing and transferring electron features.[69,70] It is well-known that it possesses obvious advantages over CNTs.[71] Thus, it is meaningful to couple TiO_2 or Fe_2O_3 with graphene to improve its photocatalytic activities. From the point of practical application by utilizing solar light, it is more feasible to use visible-response Fe_2O_3 as a photocatalyst. Considering the role of adsorbed O_2, it is anticipated that visible-light photoactivities of α-

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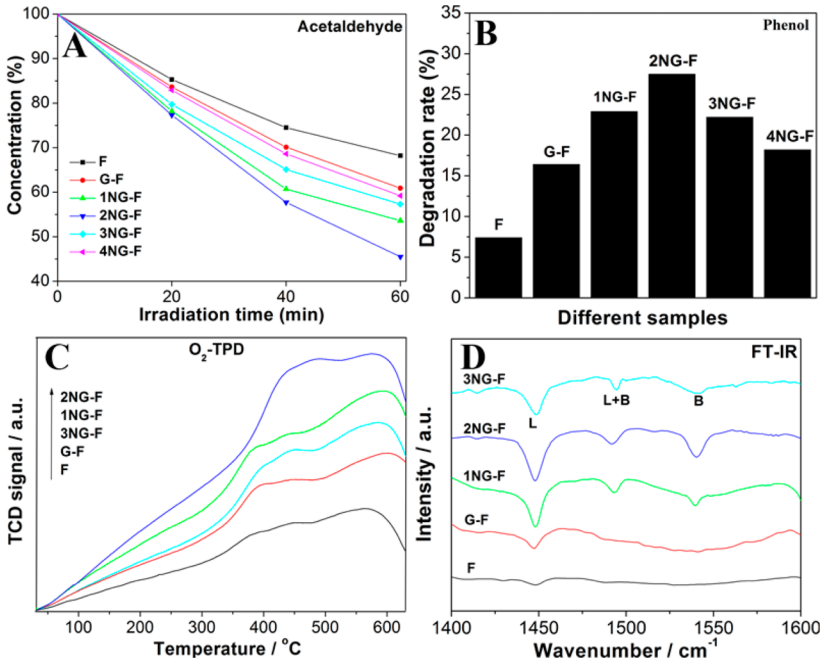

Figure 12. Photocatalytic degradation rates of gas-phase acetaldehyde (A) and liquid-phase phenol (B) on F, G-F, and different NG-F samples under visible irradiation; curves of O_2 temperature-programmed desorption (C) and the surface acidity-related pyridine-adsorbed FT-IR spectra (D) of different Fe_2O_3-based samples (L, Lewis acid sites; B, Brönsted acid sites). (N means the doped N, and the number indicates the used N amount). Reprinted with permission from ref 75. Copyright 2014, American Chemical Society.

Fe_2O_3 could be greatly improved after coupling with a proper amount of graphene, particularly with the phosphate-modified one (Figure 11A,B).

It is demonstrated that the improved visible-light activity is ascribed to the promoted charge carrier separation, which greatly depends on the increase in the capacity of charge carrier transportation (Figure 11C) and in the amounts of adsorbed O_2 after coupling with the phosphate-modified graphene (Figure 11D), which have been well proved from our work.[72] In addition, it is widely accepted that the physiochemical properties of nanostructured carbons, such as carbon nanotube and graphene, could be altered by doping heteroatoms, which further changes their activities, as evidenced by theoretical and experimental studies. Among the mostly investigated doped heteroatoms, greater attention has been focused toward nitrogen atom because it could obviously improve the electrochemical reduction currents of oxygen.[73,74] It is often suggested that the improved electrochemical-reduction currents of N-doped graphene are ascribed to the promoted charge transportation capacity and also the amount of adsorbed O_2.

This is in good agreement with our previous work,[75] about the visible-light enhanced photocatalytic activities of α-Fe_2O_3 for degrading gas-phase acetaldehyde (Figure 12A) and liquid-phase phenol (Figure 12B) after coupling graphene doped with a proper amount of N species in advance. It is deduced mainly by means of O_2-TPD curves (Figure 12C) and surface-acidity related pyridine adsorbed FT-IR spectra (Figure 12D) that the excess amount of doped quaternary-type N would be much beneficial for photoinduced charge carrier transfer and transportation and also for O_2 adsorption, resulting into the enhanced photogenerated charge carrier separation. It is worth noting that the improved O_2 adsorption for α-Fe_2O_3 is mainly attributed to the increased surface-acidity after graphene coupling, particularly for the quaternary-type N-doped one. This is in good agreement with our previous works, based on the surface modification with inorganic acids for efficient photocatalysis.

4. CONCLUSIONS AND PERSPECTIVES

In this review, it is clearly demonstrated that the surface modification with inorganic acids, especially with H_3PO_4, could promote the O_2 adsorption on oxide photocatalysts, such as TiO_2 and Fe_2O_3, and on nanostructured crystal carbons as the electron receptors, such as CNTs and graphene, in the fabricated heterojunctional nanocomposites also as photocatalysts, consequently making the photogenerated electrons captured effectively so as to improve the charge carrier separation. This leads to the greatly enhanced photoactivities for pollutant degradation. Thus, it is concluded that the step by which the photoelectrons are captured by the surface adsorbed O_2 is the rate-determining step for efficient photocatalytic processes for pollutants degradation, especially for the colorless ones. Moreover, it is confirmed that the promoted adsorption of O_2 is attributed to the increased surface acidity. Therefore, it is a feasible developed strategy for efficient photocatalysts to promote the adsorption of O_2 by increasing the surface acidity, such as surface modification with inorganic acids. This review helps us to understand well the crucial roles of adsorbed O_2 in the photocatalyitc degradation reactions for the environmental cleanup applications.

Currently, as for the decontamination of many emerging anthropogenic organic substances, especially those with great toxicity but at rather low concentration, semiconductor photocatalysis is a great potential technique. Especially, it is green and economic because it is completed by using molecular O_2 and solar energy both with rather abundance in the presence of semiconducting photocatalysts.

For the efficient photocatalysts to degrade pollutants, its key is to increase the surface acidity of semiconductor photocatalysts for promoting the adsorption of O_2 and then for enhancing the charge separation. Therefore, there should be rational strategies to promote the adsorption of O_2 by increasing the surface acidities. How is one to promote the surface acidity? On the basis of above analyses, the following points are suggested:

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(i) To modify with other inorganic acids, such as polyacid and heteropolyacid, in which the acid stability is required.
(ii) To comodify with several kinds of inorganic acids, in which the targeted modification is crucial.
(iii) To modify with HF molecules, in which F^- is fixed via the coordination bond form.
(iv) To dope nonmetal elements, such as N, and control different-facet exposure.

In a word, it is possible that the developed strategy for promoting the absorbed O_2 on semiconductor photocatalysts to degrade organic pollutants efficiently is feasible, with great significance from a scientific and engineering point of view. Besides, the studies in this field are currently unsystematic, and the degradation path and degree for pollutants, especially for mixed ones, are needed to be further explored in detail for a perfect environmental remediation. In addition, the developed strategies to promote the adsorption of O_2 could be also expanded to the wide applications related to the reduction of O_2, like the widely investigated fuel cell.

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Author Contributions

The paper was written through contributions of all authors. All authors have given approval to the final version of the paper.

Notes

The authors declare no competing financial interest.

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