Enhanced Photocatalytic Fuel Denitrification over TiO$_2$/α-Fe$_2$O$_3$ Nanocomposites under Visible Light Irradiation

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With increasingly stringent environmental regulations, the removal of nitrogen-containing compounds (NCCs) from gasoline fuel has become a more and more important research subject. In this work, we have successfully synthesized TiO$_2$/α-Fe$_2$O$_3$ heterogeneous photocatalysts with different mass ratios of TiO$_2$ vs. α-Fe$_2$O$_3$. Taking photocatalytic denitrification of typical alkali NCCs, pyridine, in gasoline fuel under visible light irradiation (λ ≥ 420 nm) as the model reaction, the TiO$_2$/α-Fe$_2$O$_3$ hybrids have exhibited enhanced photocatalytic activity compared with pure TiO$_2$ and α-Fe$_2$O$_3$, giving a pyridine removal ratio of ~100% after irradiation for 240 min. The improved photocatalytic performance can be attributed to the integrative effect of the enhanced light absorption intensity and more efficient separation of photogenerated electron-hole pairs. Importantly, this type of heterogeneous photocatalysts can be easily separate in the reaction medium by an external magnetic field that is very important for industrial purpose. In addition, major reaction intermediates have been identified by the liquid chromatograph-mass spectrometer (HPLC-MS) and a tentative photocatalytic denitrification mechanism has been proposed.

The nitrogen-containing compounds (NCCs) in gasoline fuel are one of the most alarming environmental concerns to date. Crude gasoline fuel naturally contains a high concentration of NCCs, such as pyridine, indoles, nitrides and their derivatives$^1$. Once released into the atmospheric environment, their combustion products (e.g., NO$_x$, NO and unburned hydrocarbon particles) will cause photochemical smog and resulting in serious hazardous effects on ecosystems and human health$^1, 2$. The removal of nitrogen containing compounds from gasoline is currently achieved by catalytic hydrodenitrification, adsorptive denitrogenation, oxidative denitrogenation, and photocatalytic denitrogenation$^3$–$^8$. Among the above methods, photocatalytic is a promising technique since it achieves the one-pot removal of NCCs by utilizing sunlight$^7, 8$.

Semiconductor titanium oxide (TiO$_2$) has always been regarded as one of the most common photocatalyst for the treatment of NCCs, because of its physical and chemical stability, simple preparation, nontoxicity, low cost, and unique electronic and optical properties$^9, 10$. Nevertheless, two main drawbacks should be tackled before TiO$_2$ can meet the actual application in large-scale NCCs denitrogenation. First, due to its large band gap (3.2 eV), TiO$_2$ does not absorb photons in the visible region of the electromagnetic spectrum, which significantly reduces its solar energy conversion efficiency. Even worse, as frequently reported, the low charge mobility in TiO$_2$ contributed to higher recombination rate of photogenerated electrons and holes, thereby limiting the catalytic activity$^{11, 12}$. Many attempts have been made to realize the actual applications of TiO$_2$ photocatalysts, such as nanostructuring (nanofibers, hollow sphere)$^{13, 14}$ and coupling with other materials (CuS, graphene, noble metal)$^{15-20}$. Actually, combining TiO$_2$ with other semiconductors to construct heterostructures is considered as one of the best approaches to effectively improve its solar energy conversion and effectively accelerate the separation of photoexcited charge carriers$^{21}$. Therefore, the exploration of efficient semiconductor-coupled TiO$_2$

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nanocomposites with highly visible-light photocatalytic denitrogenation performance has become an attractive area of investigation.

Based on its abundance, stability, nontoxic nature, and much smaller band gap (2.3 eV), iron oxide (α-Fe₂O₃) in particular is a promising candidate for the development of efficient solar photocatalysts. However, α-Fe₂O₃ has one significant drawback: its photocatalytic performance is limited by the high recombination rate of the photogenerated charge carriers. The introduction of magnetic component α-Fe₂O₃ might not only offer some synergetic enhancement of the catalytic activity by forming the hybrid structure, but also prevent the agglomeration of the catalyst nanoparticles during recovery. TiO₂ could be one of the best surface catalysts due to its matched band position with α-Fe₂O₃. Thus, it is reasonable to believe that this heterostructure has the enormous potential to increase the separation and transfer efficiency of photogenerated charge carriers and meanwhile conquer the drawbacks of pure TiO₂ and α-Fe₂O₃. Although there have been some reports on TiO₂ or α-Fe₂O₃ photocatalysts. It should be noted that they always focus on the elimination of NOx from the flue gas. Especially, the utilization of TiO₂/α-Fe₂O₃ composites in photocatalytic denitification of NCCs from the original gasoline fuel has remained unavailable so far.

Herein, we report for the first time that the TiO₂/α-Fe₂O₃ composites can be utilized as photoactive and durable photocatalysts toward the denitification of one kind of typical NCCs, pyridine, in original gasoline fuel under ambient conditions. Alkali nitride, pyridine, has been chosen as the target of the research owing to its widely application. This is further confirmed from a representative HRTEM image of the TiO₂/Fe₂O₃-5 composite. From the Fig. 2(i), we could clearly observe two different crystal lattices corresponding to anatase-TiO₂ (d₁₀₁ = 0.35 nm) and α-Fe₂O₃ (d₁₁₀ = 0.25 nm). The EDS elemental mapping also confirms that Fe, Ti and O elements are uniformly distributed in the TiO₂/Fe₂O₃-5 (Fig. S1).

### Results

**Characterizations.** Figure 1 shows the XRD patterns of the as-prepared TiO₂, Fe₂O₃ and TiO₂/α-Fe₂O₃ composites (with 30, 50, and 70 wt.% of Fe₂O₃, designated as TiO₂/Fe₂O₃-3, TiO₂/Fe₂O₃-5, and TiO₂/Fe₂O₃-7, respectively). It is obvious that the all the diffraction peaks of the TiO₂ belong to pure anatase structure of TiO₂ (JCPDS 21–1272). Meanwhile, six crystal peaks at 2θ = 24.1°, 33.2°, 35.6°, 40.8°, 49.5°, and 54.1° can be indexed as (012), (104), (110), (113), (024) and (116) reflection of α-Fe₂O₃ (JCPDS 89–8103). For the TiO₂/Fe₂O₃ composites with different mass ratios, all the reflection peaks could be indexed to hematite phases of Fe₂O₃ and anatase phases of TiO₂, indicating the successfully combined anatase TiO₂ with α-Fe₂O₃ in the composites. No peak from impurity phase was found, indicating the high purity of the as-prepared composites. It is easy to observe that the main characteristic diffraction peaks of the TiO₂/Fe₂O₃ composites did not noticeably change after TiO₂ hybridized with α-Fe₂O₃, suggesting that the calcination process could not destroy the crystal of TiO₂.

The surface morphology and microstructure information of the as-synthesized samples have been characterized by SEM and TEM. As seen in Fig. 2(a), the as-prepared TiO₂ exhibit the 1D morphology with an average length of ca. 5–7 μm and an average diameter of ca. 50–100 nm, which is consistent with the previous report. After the deposition of α-Fe₂O₃ onto the TiO₂, microrods, Fe₂O₃ particles are densely coated onto the surface of the TiO₂ microrods to form a hetero-interface between TiO₂ microrods and Fe₂O₃ particles (Fig. 2(b–f)). It can be also found that, the quantity of α-Fe₂O₃ coated on the surface of the TiO₂ increases gradually along with the enhancement of the loading amount of α-Fe₂O₃. Simultaneously, it could be observed from the TEM images (Fig. 2(g and h)), α-Fe₂O₃ particles are tightly combined with TiO₂ microrods via a simple calcination process. This is further confirmed from a representative HRTEM image of the TiO₂/Fe₂O₃-5 composite. From the Fig. 2(i), we could clearly observe two different crystal lattices corresponding to anatase-TiO₂ ([d₁₀₁ = 0.35 nm] and α-Fe₂O₃ ([d₁₁₀ = 0.25 nm]. The EDS elemental mapping also confirms that Fe, Ti and O elements are uniformly distributed in the TiO₂/Fe₂O₃-5 (Fig. S1). All these results gave solid evidence that TiO₂ microrods and α-Fe₂O₃ were successfully coupled together to form TiO₂/Fe₂O₃ photocatalysts.
X-ray photoelectron spectroscopy (XPS) is performed to study the structural and chemical state of the elements present in TiO$_2$/Fe$_2$O$_3$ nanocomposites. As shown in Fig. 3(a), the survey spectrum of the TiO$_2$/Fe$_2$O$_3$-5 shows the pronounced featured signal of O 1 s, Fe 2p and Ti 2p, indicating that the Fe$_2$O$_3$ particles are successfully immobilized on the surface of the TiO$_2$. The weak signal of Ti is maybe due to the covering effect of Fe$_2$O$_3$ in the TiO$_2$/Fe$_2$O$_3$-5. Figure 3(b) shows the high-resolution XPS spectrum of the O1s. Beside the component of O1s lattice centered at 529.4 eV, two bands at 530.8 eV and 532.1 eV are detected and attributed to the presence of coordinatively unsaturated oxygen species (surface defects) which belong to the lattice oxygen combined with Fe$^{3+}$ and Ti$^{4+}$. Figure 3(c) shows the high-resolution XPS spectra of Fe 2p. The binding energies of 710.3 and 724.2 eV with a satellite signal at 718.9 eV are characteristic of Fe(III) in Fe$_2$O$_3$, which is due to spin-orbit splitting. The peak separation, namely, $\Delta = 2p_{1/2} - 2p_{3/2} = 13.9$ eV, which is very similar to those reported for $\alpha$-Fe$_2$O$_3$. Figure 3(d) shows peaks at 458.5 and 464.1 eV and are assigned to Ti 2p $3/2$ and Ti 2p $1/2$ core levels. The difference between the Ti 2p core levels is 5.6 eV, indicating the normal state of Ti$^{4+}$ in the anatase TiO$_2$. The shoulder of the Ti 2p $3/2$ peak corresponds to a band at 458.5 eV. This band is assigned to formation of a Ti-O-Fe bond in the interface of TiO$_2$/Fe$_2$O$_3$, which indicated the formation of TiO$_2$/Fe$_2$O$_3$. Similar observation was also reported for TiO$_2$/Fe$_2$O$_3$ coatings by Zhang and Lei. The amount of Fe$_2$O$_3$ deposited on TiO$_2$/Fe$_2$O$_3$ has been determined by ICP. It is found that the loading percentage of Fe$_2$O$_3$ in samples of TiO$_2$/Fe$_2$O$_3$, TiO$_2$/Fe$_2$O$_3$-3, TiO$_2$/Fe$_2$O$_3$-5 and TiO$_2$/Fe$_2$O$_3$-7 are 27.1%, 45.6%, 66.0%, respectively. It is also demonstrated that the calcination approach is an effective technique of immobilizing Fe$_2$O$_3$ onto the TiO$_2$, because the content of Fe$_2$O$_3$ only slightly less than the theoretical content. For further information of the surface acidity of TiO$_2$/Fe$_2$O$_3$ composites, the temperature-programmed desorption (TPD) of ammonia has been carried out. As shown in Fig. S2, the peaks at 560 °C can be assigned to desorption of ammonia from Lewis acid sites, which is due to the presence of unsaturated surface Ti$^{4+}$ ions. Moreover, The appearance of peak at 275 °C in NH$_3$-TPD curve of TiO$_2$/Fe$_2$O$_3$-5 can be associated with ammonia desorption from surface Fe$^{3+}$, which play role of medium Lewis acid centers. The NH$_3$-TPD measurements results have confirmed the strong surface acidity of TiO$_2$/Fe$_2$O$_3$ composites. Thus, the Lewis acid surface of TiO$_2$/Fe$_2$O$_3$ is benefit to absorbing Lewis base, pyridine to obtain a better photocatalytic activity.

The optical properties of the as-synthesized pure TiO$_2$, $\alpha$-Fe$_2$O$_3$ and TiO$_2$/Fe$_2$O$_3$ composites have been characterized by UV-vis diffuse reflectance spectroscopy (DRS) and the results are shown in Fig. 4. TiO$_2$ shows a typical absorption band edge at 390 nm, which originated from its band gap of 3.18 eV and in accordance with the reported value in the literatures. As for the $\alpha$-Fe$_2$O$_3$, it exhibits strong light absorption over the visible range, even extending to the infrared region, which is caused by $2(A_{1g}) \rightarrow (T_{1g})$ ligand field transition of Fe$^{3+}$. With the integration of Fe$_2$O$_3$, the optical absorption of the composites in the visible light region is greatly improved, which...
is in accordance with the color change of the samples from white to reddish brown. Therefore, the enhanced absorbance of light is expected to improve the visible-light-driven photocatalytic activity for a target reaction. This inference is well verified by the photocatalytic testing of TiO$_2$/Fe$_2$O$_3$ composites toward denitrogenation of NCCs under visible light irradiation.

**Photocatalytic properties.** The photocatalytic activities of TiO$_2$/$\alpha$-Fe$_2$O$_3$ composites have been evaluated by the photocatalytic denitrogenation of pyridine under visible light irradiation ($\lambda \geq 420$ nm). Blank experiments have been first carried out to demonstrate the photocatalytic nature of the reaction (Fig. S3). Apparently, the denitrogenation of pyridine hardly occurs in the absence of photocatalyst or light. Instead, the denitrogenation of pyridine proceeds smoothly in the presence of photocatalyst. Importantly, TiO$_2$/Fe$_2$O$_3$-5 composites exhibit much higher photocatalytic activity than that of TiO$_2$ (0%) and $\alpha$-Fe$_2$O$_3$ (44%) under identical
The reduction ratio is rapidly increased to ~100% after visible light irradiation (λ ≥ 420 nm) for 240 min. Moreover, such photoactivity is higher than that of TiO$_2$ + α-Fe$_2$O$_3$, which is prepared by simply mixing TiO$_2$ and α-Fe$_2$O$_3$ in proper proportions under identical conditions (Fig. 5(a)). Fig. 5(b) is the photocatalytic reaction kinetics of pyridine photocatalytic denitrogenation in octane based on the data plotted in Fig. 5(a). As can be observed, photocatalytic denitrogenation of pyridine approximately follows pseudo-first-order kinetics, as evidenced by the linear plot of ln(C$_0$/C$_t$) vs. reaction time t. As displayed in Fig. 5(b), the TiO$_2$/Fe$_2$O$_3$-5 composite has the highest rate constant (0.0097 min$^{-1}$) among all of the samples. The kinetic rate constants follow the order TiO$_2$/Fe$_2$O$_3$-5 (0.0097 min$^{-1}$) > TiO$_2$/Fe$_2$O$_3$-7 (0.0050 min$^{-1}$) > TiO$_2$/Fe$_2$O$_3$-3 (0.0047 min$^{-1}$) > α-Fe$_2$O$_3$ (0.0024 min$^{-1}$) > TiO$_2$ (0.0001 min$^{-1}$). Therefore, we can draw the conclusion that coating TiO$_2$ microrods with an ultrathin α-Fe$_2$O$_3$ layer could lead to the obvious photoactivity enhancement toward denitrogenation reactions. The results indicate that the effective interfacial hybridization between TiO$_2$ and α-Fe$_2$O$_3$ contributes to the remarkably enhanced photoactivity, thus making TiO$_2$/Fe$_2$O$_3$ composites be an efficient photocatalyst for denitrogenation of NCCs.

Besides the excellent photo-denitrogenation efficiency, the stability and recyclability of photocatalysts is another significant factor in their practical application. To confirm the photostability of the as-prepared photocatalysts, the recycling tests for pyridine denitrogenation have been conducted with sample TiO$_2$/Fe$_2$O$_3$-5. After each cycling experiment, the photocatalyst was separated from the aqueous suspension by filtration and washed with ethanol several times. And then, the photocatalyst was centrifuged at 4500 rpm for 5 min and dried in vacuum at 100°C for 2 h. As shown in Fig. S4(a), the results of recycling tests indicate no significant loss of photocatalytic activities after four cycles, suggesting that the TiO$_2$/Fe$_2$O$_3$-5 photocatalyst is stable during the photocatalytic reaction. XRD results reveal that no significant changes are observed in the crystal structure of TiO$_2$/Fe$_2$O$_3$-5 before and after the catalytic reaction (Fig. S4(b)). Additionally, the separability of the TiO$_2$/Fe$_2$O$_3$-5 magnetic composites has also been tested by placing a magnet near the glass bottle after dispersing the TiO$_2$/Fe$_2$O$_3$-5 in octane (Fig. S4(c)). It is observed that the magnetic particles are attracted towards the magnet within 1 min. The magnetic properties of the resultant TiO$_2$/Fe$_2$O$_3$ have been investigated at room temperature by vibrating sample magnetometry (VSM) in the field range from -4 to +4 KOe (Fig. S5). The samples at room temperature have been measured to be 8.3 emu/g$^{-1}$, revealing strong magnetic properties. The curve presents a magnetic hysteresis loop, which also depicts the strong magnetic response to a varying magnetic field. The above results directly demonstrate the convenient separation of the TiO$_2$/Fe$_2$O$_3$-5 from liquids using an external magnetic field.
Discussion

In order to investigate the reasons for obvious photoactivity enhancement toward denitrogenation of pyridine over the photocatalysts, the surface area measurement and photoelectrochemical experiments have been performed. The Brunauer-Emmett-Teller (BET) surface areas of the as-prepared composites have been investigated using nitrogen adsorption-desorption experiments. As shown in Fig. S6, the isotherm for three samples exhibited a type IV with a H3 hysteresis loop according to the IUPAC classification. The BET surface areas of the pristine TiO$_2$ and Fe$_2$O$_3$ have been calculated to be 19.5 and 33.8 m$^2$/g, respectively. To clearly see the variations of original-TiO$_2$ after $\alpha$-Fe$_2$O$_3$ decoration, we summarize the BET surface areas of the samples in Table 1. The results show that after coupling with $\alpha$-Fe$_2$O$_3$, the surface area of the composites revealed a slight increase compared with TiO$_2$. However, for all of these samples, there are no line-relationship between the surface areas and the observed photoactivity order, that is, TiO$_2$/Fe$_2$O$_3$-5 $>$ TiO$_2$/Fe$_2$O$_3$-7 $>$ TiO$_2$/Fe$_2$O$_3$-3 $>$ $\alpha$-Fe$_2$O$_3$ $>$ TiO$_2$, cannot be attributed to the difference of surface area.

It is well established that TiO$_2$ and Fe$_2$O$_3$ are provided with matchable energy band position, together with intimate interfacial contact confirmed by our TEM results, which is able to result in the efficient charge carriers transfer. This reference is verified by the electrochemical impedance spectra (EIS). It can be obviously seen from Nyquist impedance plots (Fig. 6(a)) that the TiO$_2$/Fe$_2$O$_3$-5 shows damped semicircles at high frequencies as compared to blank TiO$_2$ and $\alpha$-Fe$_2$O$_3$, suggesting that the charge-transfer resistance decreases. Therefore, a consensus is reached that the integration of TiO$_2$ with $\alpha$-Fe$_2$O$_3$ could improve the transfer of charge carriers, thereby efficiently hampering the recombination of electron–hole pairs$^{40}$. The improved charge carrier separation and the

![Figure 6](image_url)

**Table 1.** BET surface area, reaction rate constant and normalized rate constant of TiO$_2$, $\alpha$-Fe$_2$O$_3$ and TiO$_2$/Fe$_2$O$_3$ composites.

| Samples               | BET (m$^2$/g) | K [min$^{-1}$] | K'[g.min$^{-1}$.m$^{-2}$.x$^{10^{-5}}$] |
|-----------------------|---------------|----------------|----------------------------------------|
| TiO$_2$               | 19.5          | 0.0001         | 0.51282                                |
| $\alpha$-Fe$_2$O$_3$  | 33.8          | 0.0024         | 7.10059                                |
| TiO$_2$/Fe$_2$O$_3$-3 | 24.0          | 0.0047         | 19.5831                                |
| TiO$_2$/Fe$_2$O$_3$-5 | 27.1          | 0.0097         | 35.7934                                |
| TiO$_2$/Fe$_2$O$_3$-7 | 29.5          | 0.0050         | 16.9492                                |

**Figure 6.** (a) Transient photocurrent response of TiO$_2$, $\alpha$-Fe$_2$O$_3$ and TiO$_2$/Fe$_2$O$_3$ composites in 0.2 M Na$_2$SO$_4$ aqueous solution under irradiation of visible light ($\lambda \geq 420$ nm); (b) Nyquist impedance plots of TiO$_2$, $\alpha$-Fe$_2$O$_3$ and TiO$_2$/Fe$_2$O$_3$-5.
prolonged lifetime of photogenerated electron-hole pairs can be confirmed by the photo-electrochemical experiments. As displayed in Fig. 6(b), the introduction of \( \alpha - \text{Fe}_2\text{O}_3 \) enhances the photocurrent significantly, indicating a more efficient separation of the photoexcited electron-hole pairs.

A sequence of controlled experiments using different radical scavengers has been carried out in order to deeply understand the role of photogenerated radical species in the photocatalytic denitrogenation of pyridine over the photocatalysts. The results of adding different radical scavengers (ethanol for holes, CCl\(_4\) for electrons and isopropyl alcohol for OH·) over TiO\(_2/\alpha\)-Fe\(_2\)O\(_3\) systems are shown in Fig. S7. When the holes scavenger, ethanol is added into the reaction system, the removal ratio of pyridine remarkably decrease, manifesting that the denitrogenation of pyridine is mainly related to photoinduced holes. Thus, the adsorbed pyridine in solution interacts with holes to form the corresponding radical cations, which further reacts with the trace H\(_2\)O molecular and dioxygen, leading to the formation of CO\(_2\), H\(_2\)O, NH\(_3\) and HCOOH (Fig. S8). For further information of the denitrogenation pathway of pyridine, the liquid chromatograph-mass spectrometer (HPLC-MS) has been carried out. As displayed in Fig. S9, the peak intensity m/z 81.5 is reduced after the photocatalytic fuel denitrification, meaning that the pyridine has been degraded successfully. Two new peaks appeared at m/z 85.0 and m/z 46.1 after the photocatalytic fuel denitrification, meaning that the pyridine has been translated into the protonated of intermediate products C\(_4\)H\(_4\)O\(_2\) and CH\(_3\)NH\(_2\).

Based on the discussion presented above and the experimental results, a synergistic photocatalytic mechanism of the TiO\(_2/\alpha\)-Fe\(_2\)O\(_3\) catalyst was proposed, as illustrated in Fig. 7. It is clearly shown that the photogenerated electrons of \( \alpha - \text{Fe}_2\text{O}_3 \) will be excited from valence band (VB) to its different energy-level conduction band (CB) position under the excitation of visible light, including high-energy region (\(-0.05 \text{ eV} \sim -1.0 \text{ eV vs. SHE}\)) and low-energy region (0.1 eV \sim -0.05 eV vs. SHE) in this system. Thus, the photogenerated electrons at low-energy level would quickly relax to the VB bottom of \( \alpha - \text{Fe}_2\text{O}_3 \), then to recombine with holes. Meanwhile, partial high-energy electrons would thermodynamically transfer to the CB of TiO\(_2\) due to their matchable energy band position and intimate interfacial contact, thus resulting in the improved fate of photogenerated electron-hole pairs. Taking pyridine denitrogenation as the model reaction, the TiO\(_2/\alpha\)-Fe\(_2\)O\(_3\) photocatalysts have exhibited enhanced photocatalytic activity compared with pure TiO\(_2\) and \( \alpha - \text{Fe}_2\text{O}_3 \). The higher photoactivity of TiO\(_2/\alpha\)-Fe\(_2\)O\(_3\) can be attributed to the enhanced visible light absorption, efficient charge-carrier separation as well as the synergistic effect between TiO\(_2\) and \( \alpha - \text{Fe}_2\text{O}_3 \). To the best of our knowledge, this work represents the first example to use the TiO\(_2/\alpha\)-Fe\(_2\)O\(_3\) semiconductor composite photocatalyst for photocatalytic denitrification of NCCs. It is expected that our work could offer new inroads into explore heterojunction photocatalysts for photocatalytic denitrification of gasoline fuel.

**Methods**

**Reagents and chemicals.** All reagents and solvents were used as received from commercial suppliers without further purification. Tetrabutoxytitanium was supplied by Aladdin Reagent Co., Ltd. (Shanghai, China). Iron(III) nitrate nonahydrate (Fe(NO\(_3\))\(_3\)·9H\(_2\)O), ethylene glycol, pyridine, octane were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

**Synthesis of TiO\(_2\) sample.** TiO\(_2\) were prepared using the method previously reported by Peng et al.\(^{29}\). 3 mL of tetrabutoxytitanium was added to 30 mL ethylene glycol in a rockered flask. The solution was treated at 180°C for 2 h under continuous magnetic stirring, the white slurry was formed. Then the solution was cooled to room temperature naturally. The final white solid products were centrifuged and washed with ethanol several times to ensure total removal of the excess ethanol and the dried at room temperature. The assynthesized white solid products were titanium glycolate. Finally, the titanium glycolate precursor was calcined at 450°C for 2 h to form TiO\(_2\).

**Synthesis of TiO\(_2/\alpha\)-Fe\(_2\)O\(_3\) samples.** The TiO\(_2/\alpha\)-Fe\(_2\)O\(_3\) composites were synthesized by wet impregnation, drying, ethanol washing, and calcination process. Typically, 30 mL of 0.3 M (0.6 M or 0.9 M) Fe(NO\(_3\))\(_3\)·9H\(_2\)O in ethanol (EtOH) was added to 1.5 g of TiO\(_2\) powder, stirring for 30 min at room temperature and then sonicating...
for 30 min. After that, the suspension was evaporated at 50 °C to obtain solid sample. Then the sample was calcined at 300 °C for 10 min. Next, the sample was washed by ethanol thoroughly. Finally, the sample was once again calcined at 300 °C for 6 h. The loading of α-Fe2O3 in the composites was about 30, 50, and 70 wt% for 0.3, 0.6, and 0.9 M Fe(NO3)3·9H2O, designated as sample TiO2/Fe2O3-3, TiO2/Fe2O3-5, and TiO2/Fe2O3-7, respectively.

Characterization of materials. XRD patterns were carried on a Bruker D8 Advance X-ray diffractometer operated at 40 kV and 40 mA with Ni-filtered Cu Kα irradiation (λ = 0.15406 nm). The data were recorded in the 2θ range of 10°–80°. The Brunauer-Emmett-Teller (BET) surface area was measured with an ASAP2020M apparatus (Micromeritics Instrument Corp., USA). Before the test, the samples were degassed in vacuum at 240°C for 6 hours. The nitrogen adsorption and desorption isotherms were measured at 77 K. UV-vis diffuse reflectance spectra (UV-vis DRS) were obtained by a UV-vis spectrophotometer (Shimadzu UV-2700) with BaSO4 as a reflectance standard. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a PHI Quantum 2000 XPS system equipped with a monochromatic Al Kα X-ray source to obtain the surface elemental composition of the sample. The concentration of Fe2O3 in the sample was detected by the Ultima2 ICP optical emission spectrometer. The magnetization curves were measured at room temperature under a varying magnetic field from −4 to +4 kOe on a BHV-55 vibrating sample magnetometer (VSM). Temperature-programmed desorption (TPD) of ammonia was conducted in a flow apparatus on a Micrometrics 2910AutoChem analyzer. In a typical NH3-TPD experiment, about 0.2 g of the sample was loaded in a U-shaped quartz cell above a small amount of quartz wool. Before the experiments, the samples were pretreated for 2 h at 400 °C in a flow of helium. NH3-TPD was carried out in helium flow after purging the sample at 50°C during 60 min to decrease the amount of physisorbed ammonia. The temperature was increased with a rate of 10 °C/min up to 700 °C. The electrochemical measurements were performed in a conventional three electrode cell, Ag/AgCl electrode was used as the reference electrode and a Pt plate was used as the counter electrode. The photocurrent measurements were conducted with a BAS Epsilon workstation. The liquid chromatograph-mass spectrometer (HPLC-MS) methods for analyzing pyridine was performed using an Agilent 1200 series (Palo Alto, CA, USA) equipped with an Agilent Zorbax Eclipse XDB-C18 column (2.1 mm × 100 mm, 3.5 μm). The column was maintained at 30 °C during the sample analysis. The measurement for pyridine was performed in an isocratic elution program with methanol/acetone = 70:30 (v/v) as mobile phase. Flow rate was kept at 0.2 mL/min, and the injection volume was 10 μL.

Evaluation of photocatalytic activity. Simulated NCCs-containing gasoline fuel of 100 μg/g was prepared by dissolving 70 mg of pyridine in 1.0 L of octane. The octane interaction with hydroxylated surfaces of TiO2/Fe2O3 has been shown to be very weak and nonspecific, while the interaction of polar compounds such as pyridine is expected to be stronger. Furthermore, considering that octane is the main ingredient of gasoline, which is low-cost and low toxicity, therefore, we have chosen octane as the optimum reaction solvent in our reaction system. The photocatalytic denitration of pyridine was carried out at 30°C in a 100 mL quartz reactor containing 40 mg of TiO2/Fe2O3 and 40 mL of pyridine/octane solution (100 μg/g). The suspension was stirred in the dark for 1 h to ensure the establishment of adsorption-desorption equilibrium, the suspensions were irradiated by a 300 W Xe lamp (PLS-SXE 300, Beijing Perfectlight Co. Ltd) with a UV-CUT filter to cut off light of wavelength < 420 nm. During illumination, 2 mL of suspension was taken from the reactor at a scheduled interval and centrifuged to separate the photocatalyst. The pyridine content in the supernatant solution was determined colorimetrically at 251 nm using a Cary 50 UV-vis spectrophotometer (Varian Co.). In order to quantitatively understand the reaction kinetics of the pyridine photocatalytic denitration in our experiments, we applied the pseudo-first order model as expressed by Eq. (1), which is generally used for photocatalytic degradation process if the initial concentration of pollutant is low:

$$\ln\left(\frac{C_0}{C_t}\right) = kt$$  \hspace{1cm} (1)

where $C_0$ and $C_t$ are the concentrations of the pollutants in solution at time 0 and t, respectively, and k is the pseudo-first order rate constant.

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Author Contributions
X.W., L.W. and G.Y. designed project and carried out data analyses. R.L. performed the materials characterization. H.F. and S.Y. participated in analyzing the results. R.H. wrote the manuscript. All authors reviewed and commented on the manuscript.

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