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# Surface Chlorination of $TiO_2$-Based Photocatalysts: A Way to Remarkably Improve Photocatalytic Activity in Both UV and Visible Region

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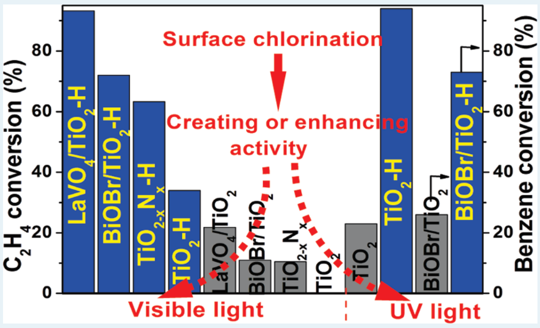
S *Supporting Information*

**ABSTRACT:** Endeavoring to the imperative and challenging issue of developing efficient and applicable visible light responsive photocatalysts, we demonstrate a general and versatile route for modifying $TiO_2$-based photocatalysts through surface chlorination, making the chlorinated photocatalysts work efficiently in both the UV and visible regions. The chlorine acted not only as a key component, endowing $TiO_2$ with fascinating visible light activity, but also as an effective promoter, rendering both visible light and UV photocatalysts with remarkably enhanced activity. The increase in oxygen vacancies and the chain transfer reaction initiated by chlorine radicals were mainly responsible for the remarkable improvement in activity.



**KEYWORDS:** Photocatalysis, chlorine, visible light, $TiO_2$

## 1. INTRODUCTION

The search for photocatalysts with high efficiency and good activity stability has attracted great attention, since this is the key factor affecting the practical applications of photocatalysis. During past decades, although the remarkable progress has been made in the synthesis of new photocatalysts working in the UV or visible light regions, $TiO_2$-based materials are still considered to be one of the superior candidates for solving environmental concerns due to $TiO_2$'s many desirable properties. Its large band gap, however, requires ultraviolet light for excitation, which limits the efficient utilization of solar energy. Diverse strategies were thus designed to modify $TiO_2$ for extending its absorption into the visible region, such as incorporation of transition metal ions,[1,2] doping nonmetal elements,[3−10] and a composite of two semiconductors.[11−13] Among them, nitrogen-doped $TiO_2$[3,4] ($TiO_{2-x}N_x$) has been intensively investigated as one of the most successful and promising materials and has exhibited good photocatalytic activity toward various reactions under visible light irradiation, but their reactivities, stabilities and quantum efficiencies are in a lower level compared with UV case, and this is also the threshold limiting their practical applications. So the design of more powerful and durable visible-light photocatalysts is still a great challenge in this field.

Different from the above-mentioned methods in which the photocatalysts were usually synthesized in critical conditions, such as high temperature and complex equipment, the Berman[14] and Ollis groups[15−18] pioneered work that the photocatalytic reaction rate can be significantly improved under UV irradiation through the introduction of trichloroethylene into the reaction system or, alternatively, prechlorination of $TiO_2$ with HCl solution. This substantial enhancement was attributed to the promoting effect of chlorine radicals. Unfortunately, they proceeded the photocatalytic reactions only under UV irradiation due to $TiO_2$ with a large band gap, and the more significant breakthrough toward visible-light photocatalysis with chlorine involved has not yet been achieved.

Here, we report a feasible and general pathway, surface chlorination, for modifying the existing $TiO_2$-based photocatalysts, avoiding the need for expensive equipment and complicated procedures. Surface chlorination of photocatalysts was performed by photocatalytic degradation of trichloromethane ($CHCl_3$) under UV irradiation or impregnation with HCl solution. One UV photocatalyst ($TiO_2$) and three visible light photocatalysts ($TiO_{2-x}N_x$, $BiOBr/TiO_2$, and $LaVO_4/TiO_2$) were selected. Importantly, the straightforward surface chlorination can render $TiO_2$ with fascinating visible light activity for ethylene probe molecules, conversion ∼3.5 times higher than that of $TiO_{2-x}N_x$. Furthermore, the chlorinated visible light photocatalysts exhibited distinct improvements in photocatalytic efficiency and activity stability in both UV and visible region. This would undoubtedly be beneficial to the efficient utilization of solar light in applications.

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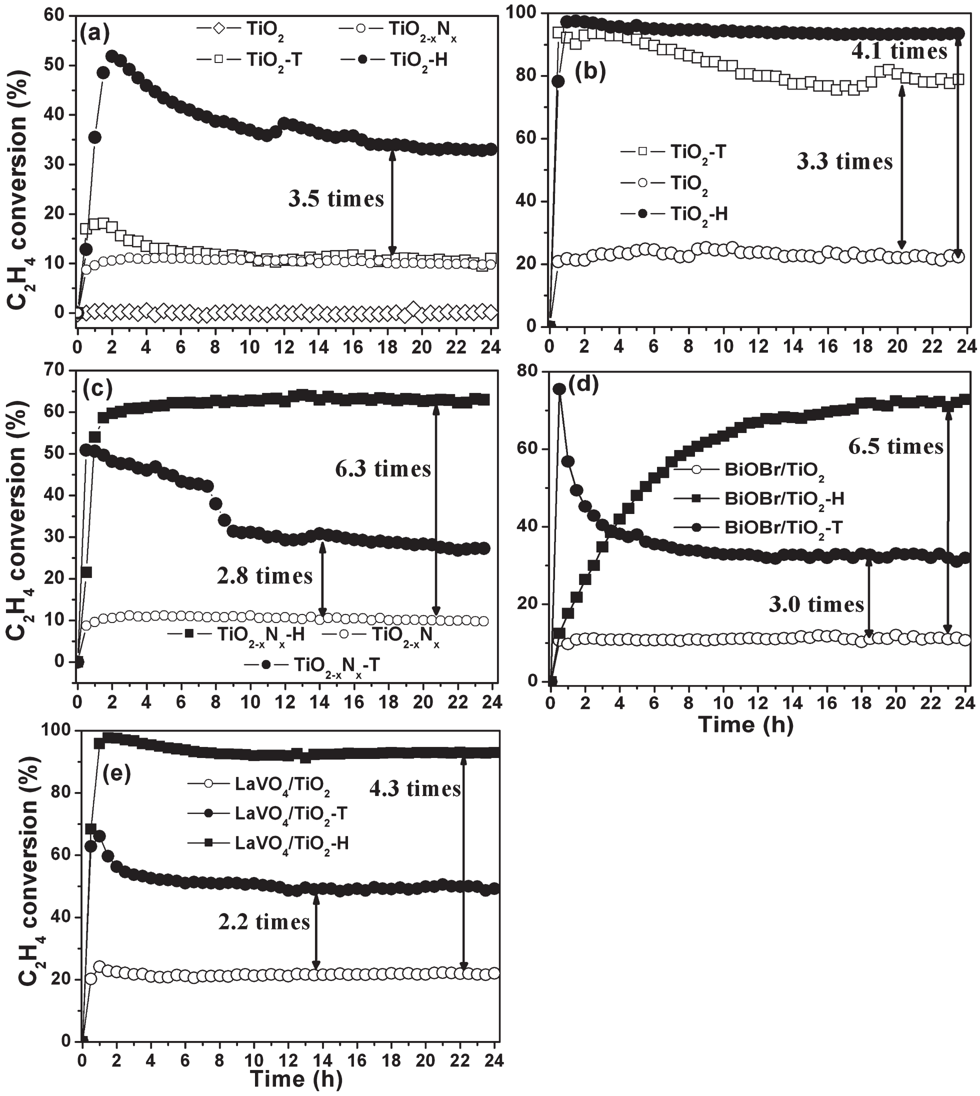


**Figure 1.** Photocatalytic degradation of ethylene over different photocatalysts before and after chlorination: (a) TiO$_2$ under visible light, (b) TiO$_2$ under UV irradiation, (c) TiO$_{2-x}$N$_x$ under visible light, (d) BiOBr/TiO$_2$ under visible light, and (e) LaVO$_4$/TiO$_2$ under visible light.

## 2. EXPERIMENTAL SECTION

**2.1. Catalyst Preparation .** TiO$_2$ (anatase, 99%, Alfa Aesar) was used as received. The LaVO$_4$/TiO$_2$ was prepared according to the same process reported by Huang.[11] The above-mentioned TiO$_2$ was calcined under flowing NH$_3$ gas (flow rate: 200 mL/min) at 600 °C for 3 h, followed by naturally cooling to room temperature under NH$_3$ to obtain the TiO$_{2-x}$N$_x$ sample. The BiOBr was synthesized by the same procedure described in the literature, except that the initial reagent NaBr was changed to KBr.[19] The bicomponent BiOBr/TiO$_2$ was prepared using a sol–gel method similar to the LaVO$_4$/TiO$_2$, except with the modification that the initial ratio of BiOBr to TiO$_2$ was fixed at 10 wt %.

The first route to surface chlorination was performed by photocatalytic decomposition of trichloromethane (CHCl$_3$) under UV irradiation in a tubular vessel microreactor operating in a continuous-flow mode. CHCl$_3$ diluted in O$_2$ was used to afford a reactant stream (flow rate: 20 mL/min), and the initial concentration of CHCl$_3$ was fixed at 80 ppm. Analysis of the reactor effluent was conducted by a gas chromatograph (HP6890, Agilent Technologies, Wilmington, USA). The concentrations of CHCl$_3$ and carbon dioxide were determined by using a flame ionization detector and a thermal conductivity detector, respectively. After 5 h of reaction, the flow of the CHCl$_3$ gas was turned off , and O$_2$ was continued until no CO$_2$ and CHCl$_3$ were detected by gas chromatography.

Surface chlorinated photocatalysts were also obtained by impregnation of 1 g of photocatalysts into 3 mL of 4 mol/L HCl, followed by a drying process at room temperature for about 1 day, and with a further 50 °C treatment before use.

The resulting samples were denoted as P—T for photodegradation of CHCl$_3$ and P—H for impregnation with HCl, where P is the photocatalyst employed.

**2.2. Photocatalytic Activity.** The measurement of photocatalytic activity under UV irradiation was carried out using the same photocatalytic equipment mentioned above. The UV source was provided by four 4-W UV lamps with a wavelength centered at 254 nm (Philips, TUV 4W/G4 T5). In the case of visible light reaction, a 1.8 × 2.6 × 1 cm$^3$ fixed-bed quartz reactor was employed instead of a tubular one. A 500 W Xe-arc lamp (CHF-XM500, Beijing Trusttech Co.) equipped with an IR-

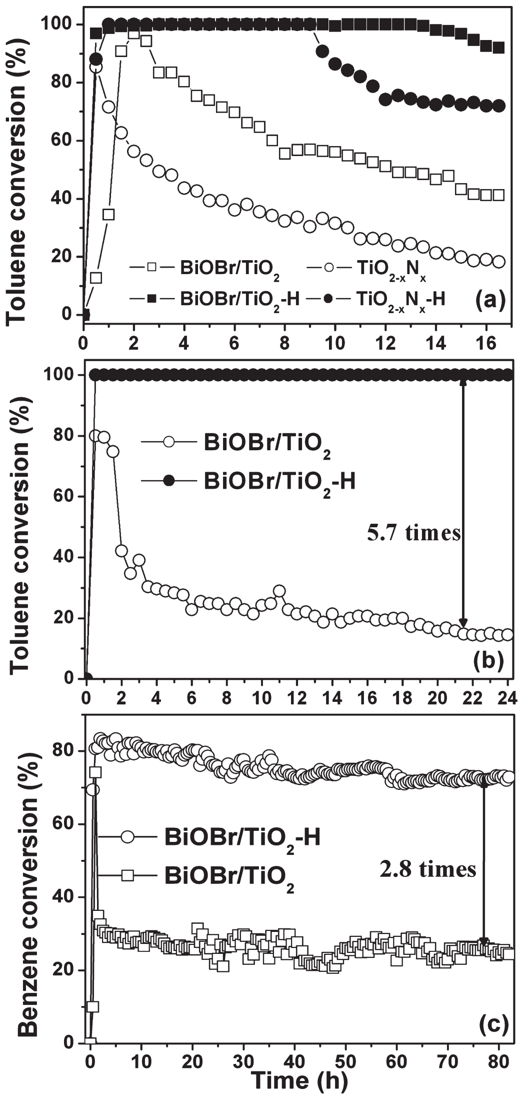


**Figure 2.** Photocatalytic degradation of (a) toluene under visible light, (b) toluene under UV, and (c) benzene under UV.

cutoff filter ($\lambda$ < 800 nm) and an UV-cutoff filter ($\lambda$ > 420 nm) was used as the visible light source. The weights of other photocatalysts were 0.3 g, except that 0.36 g of $LaVO_4/TiO_2$ and $BiOBr/TiO_2$ was used, with a particle size of 0.21−0.25 mm. Prior to the photocatalytic experiment, the catalysts were allowed to reach adsorption equilibrium in the dark. Since a steady conversion for ethylene on $BiOBr/TiO_2$−H was obtained after more than 10 h, both the photocatalysts used for degradation of toluene and benzene were employed for the degradation of ethylene. All the model molecules, such as ethylene, toluene, benzene, hexane and propylene, were diluted in oxygen at a concentration of 160, 115, 150, 280, 300 ppm, respectively.

**2.3. Characterization.** A Varian Cary 500 UV−vis spectrophotometer was used to record the UV−vis diffuse reflectance spectra of various samples. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI Quantum 2000 XPS system (Physical Electronics, Inc., Chanhassen, USA) with a monochromatic Al Kα X-ray source and a charge neutralizer. Electron spin resonance (ESR) spectra were obtained using a Bruker model ER200D instrument with a 500-W Xe-arc lamp equipped with an IR-cutoff filter ($\lambda$< 800 nm) and an UV-cutoff ($\lambda$ > 420 nm) as visible light source or a 200-W mercury−xenon lamp with a wavelength centered at 254 nm for the UV case. The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer using Cu Kα irradiation. The chlorine content of the chlorinated $TiO_2$ sample by photocatalytic degradation of $CHCl_3$ was analyzed using an ion chromatograph (881 Compact IC Pro, Metrohm, Zofingen, Switzerland) equipped with a conductivity detector and an ion exchange column (Metrosep A Supp 5, Metrohm). In situ FT-IR spectra were performed on a Nicolet Nexus 670 FT-IR spectrometer (GMI Inc., Ramsey, USA) at a resolution of 4 $cm^{-1}$. The sample was pressed into a self-supporting thin wafer and put into the sample holder. The wafer was degassed in dynamic vacuum ($10^{-2}$ Pa) at 120 °C for 3 h, and then the spectrum was recorded. Temperature programmed desorption (TPD) of oxygen molecules was carried out by using a Micrometrics TPD/R2910 (Micro-Metrics Co., Cumming, USA) chemisorbed instrument. The sample (0.2 g) was pretreated at 150 °C under He gas for 2 h. The sample was then cooled to ambient temperature. Continuous pulses of oxygen were subsequently injected over the catalyst until the sample reached the adsorption equilibrium. After this, the sample was heated from 30 to 850 °C at a rate of 10 °C/min using He as carrier gas (flow rate: 10 mL/min). The desorption of oxygen molecules was monitored by a thermal conductivity detector. The amount of adsorbed oxygen was calculated according to the area of the $O_2$-desorption peaks.

## 3. RESULTS AND DISCUSSION

**3.1. Photocatalytic Activity of the Chlorinated $TiO_2$.** Figure 1a and b shows the photocatalytic degradation of ethylene over $TiO_2$ before and after chlorination under both visible light and UV. Under visible light, pure $TiO_2$ was without any activity, but the ethylene conversions were improved greatly after chlorination by both methods. The $TiO_2$−T showed a similar conversion to $TiO_{2-x}N_x$ that was known as a highly efficient visible light photocatalyst. Significantly, after treatment with HCl, the sample presented a conversion ~3.5 times higher than that of $TiO_{2-x}N_x$. In the case of UV irradiation, the chlorinated $TiO_2$ samples ($TiO_2$−T and $TiO_2$−H) showed a high conversion of 80% and 95%, about 3.3 and 4.1 times higher than pure $TiO_2$. This suggests that simple surface chlorination not only enhanced noticeably the photocatalytic activity of $TiO_2$ but also endowed the $TiO_2$ with high visible light activity.

**3.2. Photocatalytic Activity of the Chlorinated Three Visible Light Photocatalyst.** For three visible light photocatalysts, their photocatalytic behaviors for ethylene under visible light are shown in Figure 1c−e. The chlorinated photocatalysts through photocatalytic degradation of $CHCl_3$ exhibited 2.2−3.0 times higher conversion than that before chlorination. Especially, the conversions of ethylene over the HCl treated $TiO_{2-x}N_x$ and $BiOBr/TiO_2$ were improved notably, more than 6 times higher than that before chlorination. The measurement of $CO_2$ yield (Figure S1, Supporting Information) also confirms the beneficial effect of chlorination treatment. Surface chlorination of three visible light photocatalysts promoted largely ethylene conversion.

Aromatic compounds are an important class of gas pollutants, mainly benzene and toluene. Especially, benzene has a very stable aromatic structure and is less susceptible to photocatalytic oxidation. Therefore, toluene and benzene were chosen as the model molecules to investigate the effect of chlorination on their photocatalytic degradations.

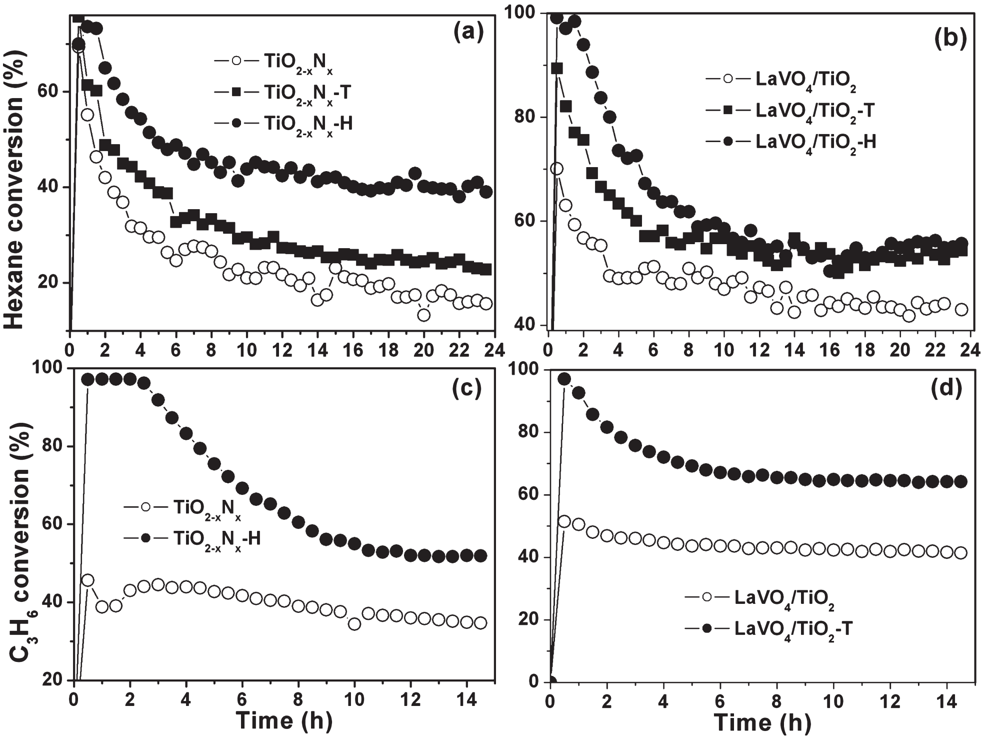


**Figure 3.** Visible light photocatalytic degradation of (a, b) hexane and (c, d) propylene over $TiO_{2-x}N_x$ and $LaVO_4/TiO_2$ before and after chlorination.

As shown in Figure 2a, both $TiO_{2-x}N_x$—H and $BiOBr/TiO_2$—H exhibited high toluene conversion, about 70% and 90%, respectively, after 16 h under visible light, whereas those before chlorination had conversion of 20% and 40%, respectively. In the case of UV irradiation, $BiOBr/TiO_2$—H (as an example) in Figure 2b and c presented a very high conversion of about 100% and 73% for toluene and benzene, respectively, about 5.7 and 2.8 times higher than that before chlorination, respectively.

The $CO_2$ yield (Figure S2, Supporting Information) further demonstrated that toluene and benzene was mostly mineralized. This phenomenon differs from Ollis group's result that the chlorine was ineffective for rate enhancement toward benzene,[16] possibly due to the UV light source with a different wavelength. Moreover, no noticeable deactivation was observed after 80 h during photocatalytic degradation of benzene on $BiOBr/TiO_2$—H (Figure 2c), suggesting it has excellent activity stability. In addition, hexane and propylene conversions under visible light (Figure 3) were also enhanced by chlorination. These results imply that surface chlorination can improve remarkably the photocatalytic activity and make it operable under UV and visible light for highly efficient degradation of many pollutants.

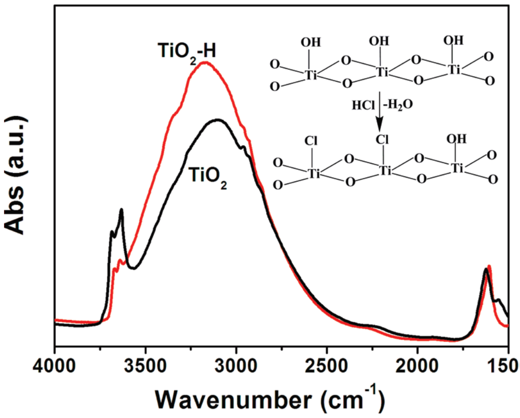


**Figure 4.** Infrared spectra of pure $TiO_2$ and $TiO_2$—H catalysts.

**3.3. Mechanism Discussion.** Since the chlorine content of the $TiO_2$ sample by photocatalytic degradation of $CHCl_3$ was not detected by XPS, its eluate solution after ultrasound-enhanced elution using water was measured by ion chromatography (Figure S4, Supporting Information). It was found that a small quantity of ionic chlorine existed in the acidic solution, indicating that the photocatalytic degradation of $CHCl_3$ will result in fixation of chlorine on the $TiO_2$ surface in the state of ionic chlorine.[20] Hence, the possible mechanism for improving photocatalytic efficiency by two routes is analogical. HCl molecules were chemisorbed on the surface of the partially hydroxylated $TiO_2$ by an ion-exchange reaction between the chlorine and hydroxyl groups,[21] as confirmed by the in situ IR spectra (Figure 4), exhibiting a significant decrease for two sharp bands at 3630 and 3690 $cm^{-1}$ corresponding to O—H stretching modes[22] due to the substitution of chloride groups for hydroxyl groups. Ollis's group reported that the surface-bound chloride groups could be converted to chlorine radicals by photogenerated holes if being irradiated by UV light,[15−18] but we found the formation of oxygen vacancies in the chlorinated $TiO_2$, corroborated by the ESR spectrum of the solid samples (Figure 5A).

After chlorination, a sharper signal at $g = 2.004$[23] appeared, which was attributed to the electrons trapped on oxygen vacancies. The ESR signal became stronger under visible light irradiation, indicating a sensitive visible light response, but no change was found for pure $TiO_2$ before and after visible light irradiation. Yu's group reported that the appearance of visible light photocatalytic activity in F-doped $TiO_2$ is due to extrinsic absorption through the creation of oxygen vacancies because the oxygen vacancy state was located between valence and conduc-

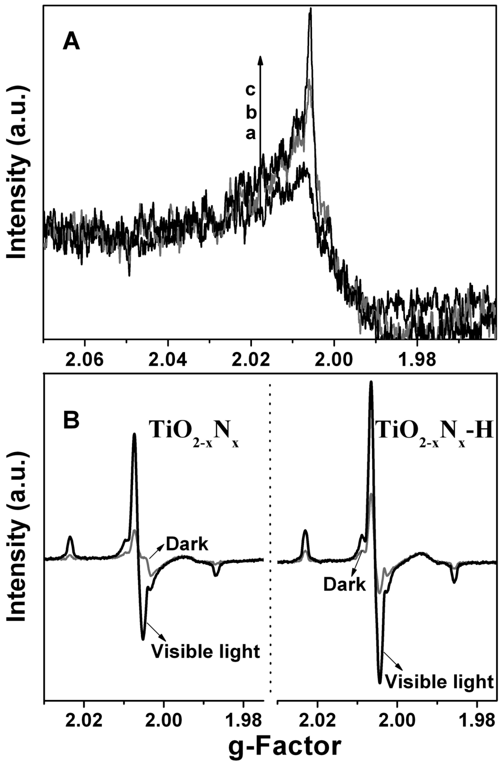


**Figure 5.** ESR spectra of (A) $TiO_2$ (a) and $TiO_2$−H (b) under dark conditions and (c) $TiO_2$−H under visible light irradiation and (B) $TiO_{2-x}N_x$ and $TiO_{2-x}N_x$−H under dark conditions and visible light irradiation.

tion bands and required less energy to activate.[24] It is expected that the oxygen vacancy states take part in a new photoexcitation process under visible light irradiation.

Considering that both samples exhibited negligible change in optical absorption, we think the high visible light activity for the chlorinated $TiO_2$ arose mainly from the formation of the oxygen vacancies. Meanwhile, the chemisorption capability toward $O_2$ was correspondingly improved, as further evidenced by $O_2$-TPD measurement (Figure 6). As the adsorbed $O_2$ scavenge the photoexcited electrons, the increase in the oxygen adsorption is favorable for the interfacial transfer of photoexcited electrons, which is a rate-determining step for various primary photocatalytic processes on $TiO_2$.[22] When the content of chlorine increased, more oxygen vacancies could be generated, resulting in $TiO_2$−H (0.31% obtained from XPS data, Figure S5 in Supporting Information) with a higher activity for ethylene than $TiO_2$−T. In the case of $TiO_{2-x}N_x$ (Figure 5B), its signal intensity for oxygen vacancies after chlorination increased greatly compared with before chlorination. This indicates that the chlorinated $TiO_{2-x}N_x$ may share same mechanism with the chlorinated $TiO_2$ in addition to an increase in the optical absorption in visible region.

For BiOBr/$TiO_2$ and $LaVO_4$/$TiO_2$, the introduction of chlorine led to an increase in the optical absorption in the visible region (Figure S6, Supporting Information), in good agreement with the good activity in this region, but no discriminable signals for oxygen vacancies were detected. Therefore, other mechanisms were probably involved in the photocatalysis in addition to oxygen vacancies. As for all the chlorinated $TiO_2$-based materials, the direct HCl impregnation process will preferentially afford more Brønsted and Lewis acidic sites, which could provide more surface chemisorption centers for target reactants.[22,25] This may be one factor accelerating the photocatalytic reaction but not the main reason, since the same treatment performed on both $TiO_2$-based materials by other Brønsted acids (such as HF and $HNO_3$) cannot obtain similar effects under identical gas−solid reaction conditions. Therefore, we preferred to believe that the enhanced reactivity primarily originated from the anions ($Cl^-$) rather than the protons only. Ollis's group has proposed a chain reactions initiated by chlorine radicals when investigating trichloroethylene-promoted photocatalytic oxidation of air pollutants under UV irradiation.[15,16]

Under irradiation with a certain energy, the trapping of the holes possessing a certain redox potential by surface-bound chlorines

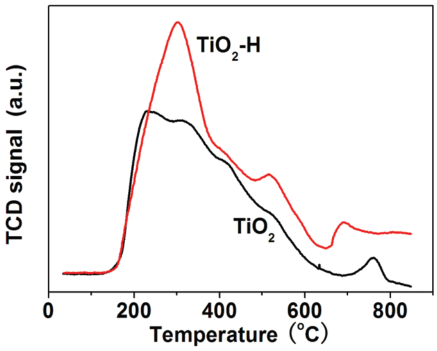


**Figure 6.** Oxygen temperature programmed desorption ($O_2$-TPD) profiles of $TiO_2$ and $TiO_2$−H samples.

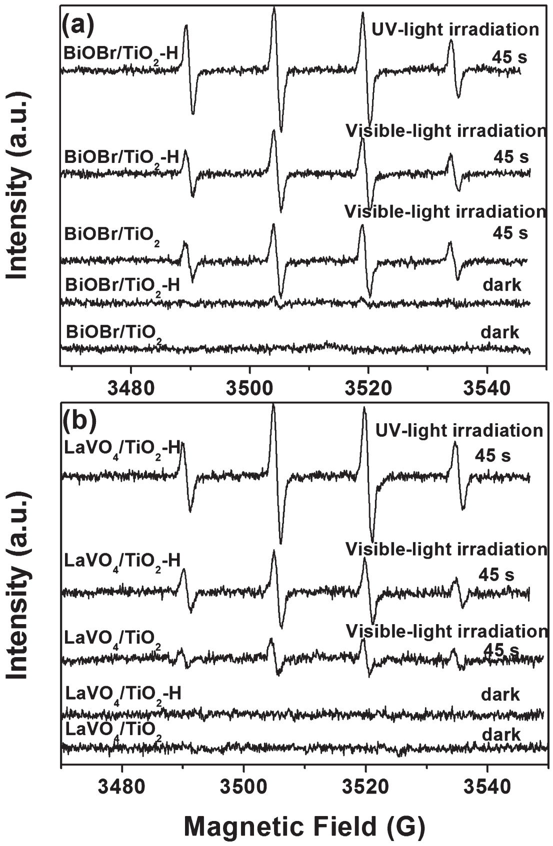
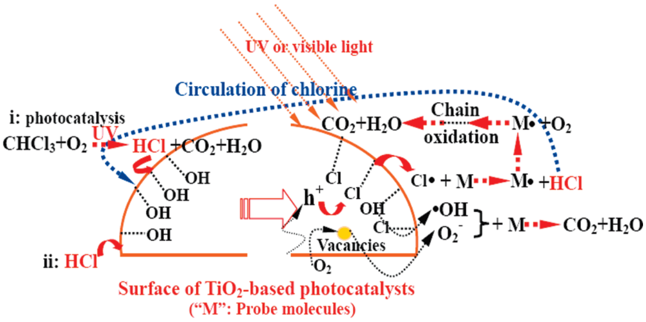


**Figure 7.** DMPO spin-trapping ESR spectra in (a) BiOBr/$TiO_2$ and BiOBr/$TiO_2$−H and (b) $LaVO_4$/$TiO_2$ and $LaVO_4$/$TiO_2$−H water dispersion under UV or visible light irradiation.

Scheme 1. The Possible Circulating Process of Chlorine during Photocatalysis



and the hydroxyl groups not replaced by Cl will result in the formation of chlorine[26,27] and hydroxyl radicals as important oxidizing species in $TiO_2$-based photocatalysis. The generation of OH• radicals is confirmed by the ESR spin-trap with DMPO (5,5-dimethyl-1-pyrroline-*N*-oxide) technique (Figure 7). Under visible light irradiation, the characteristic 1:2:2:1 quadruple peaks of the DMPO−OH• adduct have been obviously observed in the suspension of the $BiOBr/TiO_2$ and $LaVO_4/TiO_2$ samples before and after chlorination, whereas there is no signal for the suspension kept in the dark. This result provides direct evidence that the photocatalysts were activated when exposed to visible light and the photogenerated charge carriers possessed strong enough redox ability to form reactive oxygen species, such as hydroxyl radicals. Under UV irradiation, the quadruple peaks for $BiOBr/TiO_2$−H and $LaVO_4/TiO_2$−H became stronger, indicating the generation of more OH• radicals.

It should be possible for chlorine radicals to be formed under visible light irradiation in that chlorine radicals are less energetic than hydroxyl radicals.[17] Generally speaking, the chlorine radicals can attack organic substances having weakly bound branch hydrogen (such as ethylene, propylene, and hexane) and effectively destruct them into inorganic small molecules by a chain transfer oxidation that is faster than the corresponding reaction with hydroxyl radicals. For toluene and benzene, it is difficult to oxidize them by chlorine radicals directly under visible light. Since the holes and hydroxyl radicals are highly reactive in photocatalysis, especially for the cleavage of aromatic rings,[28,29] it is necessary for there to be present enough holes for the formation of hydroxyl radicals or direct oxidation. The consuming of the holes for the generation of chlorine radicals will certainly decrease the proportion of the total number of holes that could be converted to hydroxyl radicals. Only when the same photocatalyst was excited by a higher energy (i.e., UV) were more photogenerated holes and electrons produced. Thus, available holes for the formation of hydroxyl radicals and direct oxidation increased substantially, and the chlorine radical can attack the intermediates undergoing cleavage reactions, resulting in toluene and benzene having a higher conversion and mineralization rate simultaneously. In addition, $H_2O$ was one of the final products in the photocatalytic reaction and could be adsorbed and converted to surface hydroxyl groups by dissociating on acidic sites.[22] As a result, some of the HCl molecules generated from the chain transfer reaction were rechemisorbed and circulated into the reaction again (Scheme 1), resulting in good stability. The total content of chlorine for the $BiOBr/TiO_2$−H undergoing a continuous reaction for 80 h decreased by only 16%, compared with the fresh one, possibly as a result of the escape of a small protion of the gaseous HCl in that no chlorinated organic intermediates were detected in the gas phase by GC/MS.

## 4. CONCLUSIONS

We have demonstrated a versatile, economical and facile route for modifying both UV and visible-light photocatalysts through surface chlorination, avoiding the use of high temperature and complex equipment. The chlorine acted not only as a key component, endowing $TiO_2$ with fascinating visible light activity, but also as an effective promoter, rendering both visible light and UV photocatalysts with remarkably enhanced activity. Even for stable benzene molecules, a surprising promotion effect was also achieved under UV irradiation. We believe this method will offer an important and applicable pathway to create excellent photocatalysts for utilizing solar energy more efficiently. Furthermore, motivated by a similar promoting effect on several chlorinated wide band gap p-block metal semiconductors, a comprehensive study to elucidate the essential mechanism of a chlorine-promoting reaction for other photocatalysts is currently underway.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Yield of $CO_2$, $Cl^-$ concentrations by ion chromatograph, XPS analysis, UV−vis absorption spectra, and XRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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