One-Step Synthesis of Bifunctional TiO2 Catalysts and Their Photocatalytic Activity

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In this paper, we have investigated in detail the preparation of anatase TiO2 catalysts by the controlled thermal decomposition of ammonium titanyl sulfate ((NH4)2TiO(SO4)2) and their catalytic activity. The structures of anatase TiO2 catalysts have been characterized by powder X-ray diffraction, N2 adsorption–desorption isotherms, diffuse reflectance UV–vis spectroscopy, infrared spectroscopy, X-ray photoemission spectroscopy, NH3 temperature-programmed desorption, and solid-state MAS NMR spectrometer. We report for the first time that the anatase TiO2 catalyst prepared by calcination of (NH4)2TiO(SO4)2 at 600 °C (TiO2-600) is a very active bifunctional catalyst. TiO2-600 is doped with N and S and thus very active in the photodegradation of methyl orange under visible light illumination (λ > 420 nm); meanwhile, it also has a large number of Brønsted acid sites arising from the covalently bonded sulfuric acid groups and thus is active in the esterification of ethanol and acetic acid to ethyl acetate. The Pt/TiO2-600 photocatalysts with different Pt loadings were prepared via the incipient wetness impregnation method and their photocatalytic activity for the H2 production from water splitting was evaluated with methanol as a sacrificial electron donor under both all-wavelength light and visible light (λ > 400 nm) irradiation. All Pt/TiO2-600 photocatalysts show considerable photocatalytic activity of water splitting. The optimum Pt loading on TiO2-600 is 1 and 0.1 wt % for the all-wavelength light and visible light photocatalytic reaction, respectively. Our results demonstrate a facile method to prepare highly active bifunctional TiO2 catalysts promising in both visible-light-driven photocatalysis and acid catalysis.

1. Introduction

TiO2 is versatile in catalysis. TiO2-based materials are very promising photocatalysts,1–4 and they also have wide applications in heterogeneous catalysis, particularly as a support of both metal and oxide catalysts.5–7 Therefore, it is very attractive to prepare TiO2 catalysts with multifunctions.8–11 TiO2 catalysts prepared by the immersion of anatase TiO2 into H2SO4 solutions, a kind of solid acid, have recently been introduced as photocatalysts for their higher catalytic activity compared with pure TiO2 in the photodegradation of some organic compounds,8–13 however, they were only responsive to UV light. Several mechanisms of the enhanced photocatalytic activity of SO42-/TiO2 solid acids were proposed, including the enhanced adsorption capacity for the reactants,12 the improved photooxidation ability, and the decreasing recombination possibility between electrons and holes.10,13 Active sulfate-promoted rutile TiO2 nanoparticles responsive to visible light were directly prepared via precipitating Ti(SO4)2 in NaOH solution followed by peptizing in HNO3 without the phase transformation from anatase to rutile.14 Fang et al.15 recently reported that the thermal decomposition of the precipitation formed by titanyl oxalate complex ([TiO(C2O4)2]2–) and ammonium hydroxide at 400 °C could prepare visible-light-active N-doped anatase TiO2 photocatalysts; meanwhile, the N-doped anatase TiO2 photocatalyst had Brønsted acid sites arising from the covalently bonded dicarboxyl groups. They also demonstrated that the Brønsted acid sites greatly enhanced the adsorption capacity of TiO2 toward methyl orange. Although the N-doped TiO2 photocatalysts have demonstrated remarkable photocatalytic activity for many photocatalytic reactions under visible light illumination,16–19 their photocatalytic activity for the photocatalytic H2 production from water splitting under visible light illumination has not been extensively explored.20–23 The N-doped TiO2 photocatalysts were reported to be active in the photocatalytic splitting of water to produce H2 under visible light illumination,20–22 and their photocatalytic activity could be enhanced by the loading of Pt23 because the overpotential of H2 evolution on Pt is the lowest.

Ammonium titanyl sulfate ((NH4)2TiO(SO4)2, ATS) was previously used as a molecule precursor to prepare nanocrystalline anatase TiO2,24,25 and the obtained anatase TiO2 were only reported to exhibit a comparable UV-light-driven photocatalytic activity in the photodegradation of phenol and methylene blue to the commercial Degussa P-25. However, after considering the molecular structure of ATS, we believe that it should be possible to prepare TiO2 photocatalysts with the covalently bonded sulfuric acid groups by the controlled thermal decomposition of ATS. In this paper, we have investigated in detail the thermal decomposition process of ATS and found that the anatase TiO2 catalyst prepared by calcination of ATS at 600 °C is doped with N and S; meanwhile, it has a large number of

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Brønsted acid sites arising from the covalently bonded sulfuric acid groups. As a consequence, the anatase TiO₂ catalyst is very catalytically active in both the photodegradation of methyl orange under visible light (λ > 420 nm) illumination and in the esterification of ethanol and acetic acid to ethyl acetate. The anatase TiO₂ catalyst prepared by the calcination of ATS at 700 °C is doped with S but it does not contain any Brønsted acid sites, and thus it is only active in the photodegradation of methyl orange under visible light illumination. The photocatalytic activity of TiO₂-600 and Pt/TiO₂-600 in the water splitting to produce H₂ has also been investigated under both all-wavelength light and visible light (λ > 400 nm) illuminations.

2. Experimental Section

2.1. Catalyst Preparation. Both 50 g of Ti(SO₄)₂ and 25.5 g of (NH₄)₂SO₄ were added into 100 mL of distilled water under stirring until the formation of a clear solution. The solution was then evaporated at 70 °C and a white powder was obtained. The white powder was used as the precursor and calcined in air at the desired temperatures for 2 h to prepare the TiO₂ catalyst. The commercial Degussa P-25 purchased from EVONIK INDUSTRIES was employed for the comparison. Pt/TiO₂-600 was further used as the support to prepare Pt/TiO₂-600 photocatalysts by the incipient wetness impregnation method. A calculated amount of H₂PtCl₆·6H₂O was loaded onto TiO₂-600 in the aqueous solution, and the impregnated TiO₂-600 was dried at 110 °C for 24 h and then reduced in 5 vol % H₂/Ar flow (flow rate: 30 mL/min) at 300 °C for 2 h. The Pt loading in Pt/TiO₂-600 ranged from 0.1 to 3 wt %, and the acquired photocatalyst was denoted as xPt/TiO₂ in which x is the weight ratio in percentage of Pt.

2.2. Catalyst Characterization. Thermogravimetric analysis (TGA) was performed on a Shimadzu DTA60H analyzer with a heating rate of 10 deg/min in an air flow. The thermal decomposition of the ATS precursor was also studied with temperature-programmed reaction spectroscopy (TPRS) in which 0.02 g of catalyst precursor dried at 70 °C was loaded in a quartz reactor and heated linearly with a rate of 2 deg/min in an air flow, whose products were online analyzed by a Hiden QIC-20 gas analysis system. Powder X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert PROS diffractometer using a nickel-filtered Cu Kα (0.15418 nm) radiation source with the operation voltage and operation current being 40 kV and 50 mA, respectively. N₂ adsorption–desorption isotherms were measured on a Micromeritics ASAP 2020 M¹ system to online analyze the composition of the stream. A 0.05 g sample of catalyst in a quartz reactor was degassed at 300 °C for 2 h and subsequently purged with Ar until NH₃ could not be detected in the stream. Then the catalyst was heated at a ramping rate of 5 deg/min in an Ar atmosphere and the desorption trace of NH₃ was online monitored. A flow rate of 20 mL/min was employed in the NH₃-TPD experiments.

2.3. Catalytic Activity Measurement. The photocatalytic activity of TiO₂ catalysts was probed by the photodegradation of methyl orange both under all-wavelength light and visible light illumination. To simulate the sun light spectrum, a 500W Xe arc lamp (BL-GHX-CH500, Xi'an Depai Biotech. Co. Ltd., China) was applied as the light source, which was positioned inside a cylindrical Pyrex vessel surrounded by a circulating water jacket to cool the lamp. In a typical run, 0.12 g of catalyst was added to 40 mL of methyl orange aqueous solution (methyl orange concentration: 20 mg/L). The suspension was stirred in darkness for 1 h to reach the adsorption–desorption equilibrium of methyl orange on the catalyst surface prior to illumination. Then the suspension was exposed under light irradiation from the Xe lamp. For visible light illumination experiments, a UV cutoff glass filter (λ > 420 nm) only allowing the photons with wavelengths above 420 nm to pass was used between the Xe lamp and the tube containing the reaction suspension, which was about 9 cm from the light source. Approximately 4 mL of aqueous solution was collected at regular intervals and centrifuged. The concentration of methyl orange in the centrifuged aqueous solution was determined by measuring the absorbance at 490 nm of methyl orange aqueous solution was determined by measuring the absorbance at 490 nm of methyl orange on a Shimadzu UV-2450 UV–visible spectrophotometer, from which the photocatalytic activity was calculated.

The Brønsted acid catalysis activity of TiO₂ was probed by the esterification of ethanol and acetic acid to ethyl acetate. The mixture containing 0.2 mol of ethanol, 0.02 mol of acetic acid, and 0.1 g of TiO₂ catalyst was kept at 60 °C under stirring in the absence of light. A certain amount of cyclohexane was also added to the mixture as the internal standard for the quantitative analysis. Approximately 1 mL of aqueous solution was collected at regular intervals and centrifuged. The composition of the centrifuged aqueous solution was analyzed on an Agilent Technologies 6890N Network GC system and the amount of ethyl acetate was quantitatively determined by heteronuclear multiple quantum correlation (HMQC) NMR spectra of the samples were recorded on a Varian Infinity plus-400 spectrometer and collected at 399.9 MHz with use of a single-pulse sequence with a π/4 pulse and a 4s recycle delay with a spinning speed of 10 kHz. The ¹H chemical shift was referred to the ¹H chemical shift of adamantane at 1.74 ppm. Before the measurements the samples were dehydrated at 200 °C under a pressure below 10⁻² Pa for 12 h. NH₃-thermal programmed desorption (NH₃-TPD) experiments were performed in a homemade apparatus employing a Hiden QIC-20 gas analysis system to online analyze the composition of the stream. A 0.05 g sample of catalyst in a quartz reactor was degassed at 300 °C for 1 h and cooled to room temperature (rt) in an Ar atmosphere. The catalyst was then exposed to an atmosphere of 5% NH₃ in Ar for 2 h and subsequently purged with Ar until NH₃ could not be detected in the stream. Then the catalyst was heated at a ramping rate of 5 deg/min in an Ar atmosphere and the desorption trace of NH₃ was online monitored. A flow rate of 20 mL/min was employed in the NH₃-TPD experiments.
method for hydrogen evolution by a Shimazu GC 14CPTF gas chromatograph equipped with a thermal conductivity couple (TCD).

3. Results and Discussion

The XRD pattern of the catalyst precursor, the white powder prepared by evaporating Ti(SO$_4$)$_2$ and (NH$_4$)$_2$SO$_4$ aqueous solution at 70 °C, is presented in Figure 1, whose diffraction peaks could be well indexed to those of ATS (JCPDS card No. 34-0732). The infrared spectrum of the catalyst precursor is shown in Figure 2. The observed vibration peaks could also be assigned to ATS, for example, the bands at 3157 and 1402 cm$^{-1}$ could be assigned to the stretching and bending vibration of the N–H bond, respectively; the bands at 1257 and 1133 cm$^{-1}$ could be assigned to the asymmetric and symmetric stretching vibration of the S=O bond, respectively; the bands at 1030 and 976 cm$^{-1}$ could be assigned to the asymmetric and symmetric stretching vibration of the S–O bond, respectively; and the bands at 3430 and 1640 cm$^{-1}$ could be assigned to the stretching and bending vibration of the O–H bond of water molecules in ATS, respectively. Therefore, the XRD and IR results demonstrate that the precursor prepared by evaporating Ti(SO$_4$)$_2$ and (NH$_4$)$_2$SO$_4$ aqueous solution at 70 °C is ATS. The thermal stability of ATS in air was investigated by means of TGA and TPRS, whose results are shown in Figure 3. It could be seen that two obvious weight losses occur between 50 and 200 °C and 400 and 600 °C, respectively. Inferred from the TPRS results, the weight loss between 50 and 200 °C results from the desorption of water and ammonia whereas the weight loss between 400 and 600 °C results from the decomposition of ATS. Water, NH$_3$, NO, and SO$_2$ were detected as the products of the thermal decomposition. We considered the thermal decomposition in two steps: the first is the decomposition of ATS to H$_2$TiO(SO$_4$)$_2$, producing water, NH$_3$, and NO; the second is the further decomposition of H$_2$TiO(SO$_4$)$_2$, producing SO$_2$ and water. It is interesting that SO$_3$ was not detected during the course of thermal decomposition.

On basis of the TGA and TPRS results, we calcined ATS at 600, 700, and 800 °C, and the resulting TiO$_2$ catalysts were denoted as TiO$_2$-600, TiO$_2$-700, and TiO$_2$-800, respectively. The XRD results (Figure 1) demonstrate that all these TiO$_2$ catalysts are with a pure anatase phase (JCPDS card No. 83-2243). It was reported that the pure TiO$_2$ sample generally underwent the phase transformation from anatase to rutile at ca. 600 °C.$^{26}$ Therefore, anatase TiO$_2$ prepared by the thermal decomposition of ATS is resistant to the anatase-to-rutile phase transformation. Figure 4 shows the N$_2$ adsorption–desorption isotherms of TiO$_2$ catalysts and their pore size distribution of mesopores. Different from TiO$_2$-700 and TiO$_2$-800, TiO$_2$-600 exhibits a bimodal pore size distribution of mesopores. Table 1 summarizes the macroproperties of TiO$_2$ catalysts obtained from XRD and N$_2$ adsorption–desorption isotherms. With the increasing calcinations temperature of TiO$_2$ catalysts, their average crystalline size increases, and their BET surface area and pore volume decrease.
As shown in Figure 2, the infrared spectrum of TiO2-600 still displays an obvious vibration feature at 927 cm\(^{-1}\), demonstrating that some sulfonic acid groups still remain on TiO2-600. Increasing the calcination temperature to 700 °C and above completely annihilates these sulfonic acid groups and only weak vibration features at 3430 and 1640 cm\(^{-1}\) arising from surface hydroxyls appear in the infrared spectra of TiO2-700 and TiO2-800. The TPRS result (Figure 3) also shows that SO2 is not produced above 700 °C. XPS was employed to investigate the surface composition of TiO2 catalysts. The results are shown in Figure 5. The Ti 2p, O 1s, and C 1s XPS features are similar for all three catalysts. The Ti 2p\(_{3/2}\) binding energy and the O 1s binding energy of the major O 1s component respectively locate around 458.2 and 529.5 eV, which could be assigned to Ti\(^{4+}\) and O\(^{-2}\) in TiO2.\(^{27}\) The O 1s shoulder with the binding energy at 531.7 eV could be assigned to surface hydroxyls on TiO2,\(^{28}\) but the O 1s binding energy of oxygen in sulfonic acid groups is within 531.2–532.0 eV.\(^{27}\) Inferred from the C 1s XPS spectra, there is mainly the adventitious carbon on TiO2. The XPS results

### TABLE 1: Macroproperties of TiO2 Catalysts

<table>
<thead>
<tr>
<th>catalyst</th>
<th>(d_{XRD}) (nm)</th>
<th>BET surface area (m(^2)/g)</th>
<th>pore vol (cm(^3)/g)</th>
<th>av pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2-600</td>
<td>22.7</td>
<td>58</td>
<td>0.291</td>
<td>19.4</td>
</tr>
<tr>
<td>TiO2-700</td>
<td>38.0</td>
<td>32</td>
<td>0.147</td>
<td>18.8</td>
</tr>
<tr>
<td>TiO2-800</td>
<td>50.5</td>
<td>12</td>
<td>0.063</td>
<td>24.4</td>
</tr>
</tbody>
</table>

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![Figure 4](image.png)

**Figure 4.** (Left) The N\(_2\) adsorption–desorption isotherms of TiO2 catalysts. (Right) The size distributions of mesopores of TiO2 catalysts.

![Figure 5](image.png)

**Figure 5.** The Ti 2p, O 1s, S 2p, N 1s, and C 1s XPS spectra of TiO2 catalysts.
clearly rule out the existence of doped carbon in TiO2 because the doped carbon in TiO2 exhibits a very low C 1s binding energy at ca. 282 eV.29 TiO2-600 exhibits two N components with the N 1s binding energy at 399.3 and 401.6 eV in the N 1s XPS spectrum of TiO2-600 whereas TiO2-700 and TiO2-800 do not show any N 1s XPS signals. The surface concentrations of N in these photocatalysts are summarized in Table 2. The assignment of observed N 1s XPS peak in N-doped TiO2 has been previously reported. The N 1s feature at ca. 397.0 eV is generally known as the “nitride” and has been assigned to N2− anions, which substitute for oxygen in the TiO2 lattice.30 Chen et al.31 reported an N 1s peak at 401.3 eV that was attributed to substitute N in O−Ti−N. Diwald et al.32 prepared N-doped rutile TiO2 (110) by heating in NH3 and observed two N 1s peaks at 396.7 and 399.6 eV. The peak at 399.6 eV was assigned to nitrogen likely located in an interstitial site in TiO2 and probably bound to hydrogen. They further proved this nitrogen state to be responsible for the observed shift of the photochemical threshold of rutile TiO2 (110) down to ~2.4 eV. Fang et al.15 also assigned the N 1s peak at 399.6 eV to nitrogen likely located in an interstitial site in TiO2 and probably bound to hydrogen. They further proved this nitrogen state to be responsible for the observed shift of the photochemical threshold of rutile TiO2 (110) down to ~2.4 eV. Fang et al.15 also assigned the N 1s peak at 399.6 eV to nitrogen likely located in an interstitial site in TiO2. Therefore, the N 1s feature at 399.3 eV could be assigned to the N species located in an interstitial site in TiO2, clearly demonstrating that TiO2-600 is N-doped. Another N 1s peak at 401.6 eV could arise from adsorbed N2 (γ-N2),24 NH4+,27 or adsorbed NO.33 On the basis of the TPRS results, we assigned the N 1s peak at 401.6 eV to adsorbed NH4+ or NO.

All TiO2 catalysts show obvious S 2p XPS features, and Table 2 summarizes the surface concentrations of S. The S 2p3/2 binding energy locates at 168.1, 167.9, and 167.8 eV for S species in TiO2-600, TiO2-700, and TiO2-800, respectively. It has been previously reported that the S(VI) cation substituting Ti in TiO2 due to cationic doping gave a S 2p3/2 binding energy at 167.8 eV.34,35 The TPRS and infrared results demonstrate that there are no sulfonic acid groups on TiO2-700 and TiO2-800; therefore, the S species with the S 2p3/2 binding energy at ca. 167.8 eV could be reasonably assigned to the S(VI) cation in TiO2-700 and TiO2-800. These results demonstrate that TiO2-700 and TiO2-800 are doped with S(VI) cations. Since the S element in sulfonic acid groups is with a S 2p3/2 binding energy at ca. 167.8 eV,27 we thus assign the S species observed in TiO2-600 to sulfonic acid groups, but the likely existence of S cationic doping in TiO2-600 could not be ruled out.

The diffuse reflectance UV–vis spectra (Figure 6) also demonstrate that the thermal decomposition of ATS leads to the preparation of doped TiO2. All TiO2 catalysts show certain absorption in the visible light region more or less. It is well-known that pure anatase TiO2 with a band gap of 3.2 eV is only responsive to UV light. Assuming the materials to be indirect semiconductors, as is TiO2, a plot of the modified Kubelka–Munk function \( F(R_\infty)E^{-1/2} \) vs the energy of absorbed light \( E \),36 as shown also in Figure 6, affords the band gap energy of ca. 3.2 eV for all TiO2 catalysts. This result indicates that the doped N or S only form the isolated energy levels in the band gap of anatase TiO2 but do not lead to the obvious band gap narrowing.

The Brønsted acid sites on the TiO2 catalysts were probed by means of NH3-TPD and 1H solid-state MAS NMR spectroscopy, whose results are presented in Figures 7 and 8, respectively. TiO2-600 shows a major NH3-desorption peak at 106 °C with a shoulder at 290 °C. The desorption peak at 290 °C disappears and that at 106 °C attenuates for TiO2-700 and TiO2-800, and TiO2-800 only shows a very weak desorption peak at 106 °C. The desorption temperature of NH3 accounts

### Table 2: The Surface Concentrations of Doped N and S (Atomic Ratio in Percentage) in Various Photocatalysts Evaluated from the XPS Measurements

<table>
<thead>
<tr>
<th></th>
<th>TiO2−600</th>
<th>TiO2−700</th>
<th>TiO2−800</th>
<th>0.1Pt/ TiO2</th>
<th>0.5Pt/ TiO2</th>
<th>1Pt/ TiO2</th>
<th>3Pt/ TiO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>0.4</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.8</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>S</td>
<td>1.0</td>
<td>0.6</td>
<td>0.6</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

*a Not detected.
for the strength of acid sites. The NH3 desorption peaks at ca. 100 and 300 °C may be assigned to NH3 weakly adsorbed on the surface and NH3 adsorbed on Brönsted acid sites, respectively. The 1H solid-state MAS NMR spectrum of TiO2-600 consists of four peaks at 11.1, 7.5, 3.2, and 1.1 ppm. The signal at 11.1 ppm is absent in the 1H solid-state MAS NMR spectra of TiO2-700 and TiO2-800. The 1H solid-state MAS NMR spectrum of TiO2-700 shows three peaks at 7.0, 3.2, and 1.1 ppm and that of TiO2-800 shows two peaks at 6.6 and 1.1 ppm. The signal at 1.1 ppm arises from the background of the employed NMR rotor. On basis of previous 1H solid-state MAS NMR results of SO42−/TiO2, the signal at 11.1 ppm of TiO2-600 can be assigned to the hydroxyl groups directly connected to the S atom, i.e. the sulfonic acid groups on TiO2 (see Scheme 1a). This assignment is also consistent with the infrared and XPS results that sulfonic acid groups are present on TiO2-600, but not on TiO2-700 and TiO2-800. The signals at 7.5, 7.0, and 6.6 ppm for TiO2-600, TiO2-700, and TiO2-800 respectively are due to the “acidic” surface bridging hydroxyl groups. They were reported to show the 1H NMR signal at 6.6 ppm on anatase TiO2. The surface hydroxyl groups with a stronger acidity usually exhibit a larger 1H chemical shift value, thus the acidity of surface bridging hydroxyl groups follows the order: TiO2-600 > TiO2-700 > TiO2-800. As proposed by Zhang et al., the surface bridging hydroxyl groups in TiO2-600 are likely in close proximity to the bidentate sulfate anion (see Scheme 1b), and thus exhibit a strong acidity. We consider that the S element in Scheme 1b is actually the doped S species, thus the NMR result indicates that TiO2-600 is also doped by S; therefore, TiO2-600 is codoped by N and S. The 1H NMR results suggest that the chemical perturbing of the doped S species on the surface bridging hydroxyl groups on TiO2 decreases with the increasing calcinations temperature. The signal at 3.2 ppm can be assigned to the terminal titanol groups on TiO2. On the basis of the 1H NMR results, we can assign the NH3-desorption peak at 290 °C to NH3 adsorbed on the sulfonic acid groups on TiO2-600 and the NH3-desorption peak at 106 °C to NH3 adsorbed on the surface bridging hydroxyl groups on TiO2-600, TiO2-700, and TiO2-800.

The XPS and solid-state MAS NMR results clearly demonstrate that TiO2-600 is codoped by N and S and is also with a large number of Brönsted acid sites whereas TiO2-700 and TiO2-800 are doped by S but are with few Brönsted acid sites. Therefore, TiO2-600 should be a bifunctional catalyst. The photodegradation of methyl orange under visible light illumination and the esterification of ethanol and acetic acid to acetic ester were employed as the probe reactions for the photocatalysis and the acid catalysis, respectively. Figure 9 shows the UV−vis absorption spectra of the methyl orange solution during the photodegradation reaction catalyzed by TiO2-600 under visible light illumination. We observed that the color of the methyl orange solution changed from orange to red after the addition of TiO2-600, corresponding to the peak shift from 463 to 501 nm in the UV−vis absorption spectra. The pH value of methyl orange with TiO2-600 was measured to be 3.5, from which the capacity of TiO2-600 to release protons in water was estimated to be $8.43 \times 10^{-3}$ mol H⁺/mol TiO2. It could be seen from Figure 9 that the concentration of methyl orange decreases quickly with visible light illumination time.

Figure 10 compares the all-wavelength-light-driven and the visible-light-driven photocatalytic activity of various TiO2 catalysts and the commercial P25 in the photocatalytic degradation reaction of methyl orange. Comparing with TiO2-700, TiO2-600 exhibits a decreased capacity to adsorb methyl orange. This is reasonable because, with a pH value of 3.5, methyl orange mainly exists in the form of a neutral molecule and the surface of TiO2 with an isoelectric point (ISP) of ca. 5.5 is mainly positively charged. It could be seen that all the photocatalytic
reactions follow the pseudo-first-order reaction kinetics. Therefore, the reaction rate constant could be calculated by plotting $\ln(C_0/C)$ as a function of the reaction time, whose results are summarized in Table 3. Under all-wavelength light illumination, both TiO$_2$-600 and TiO$_2$-700 exhibit better photocatalytic activity than the commercial P25, and TiO$_2$-600 is most active with the highest reaction rate constant $k = 4.79 \times 10^{-3}$ min$^{-1}$. The photocatalytic activity of TiO$_2$-800 is a little bit inferior to that of P25. The visible-light-driven photocatalytic activity for the degradation of methyl orange also follows the order TiO$_2$-600 $>$ TiO$_2$-700 $>$ TiO$_2$-800, agreeing with the order of their concentrations of doped N and S summarized in Table 2. P25 does not show any detectable photocatalytic activity in the degradation of methyl orange under visible light illumination. It is reasonable because P25 with an absorption band edge of $\sim 400$ nm could not be excited by visible light with $\lambda > 420$ nm in our case. Recently acid orange 741,42 and methylene43 have been reported to readily undergo photocatalytic degradation under visible light illumination via a photosensitization mechanism. However, our results clearly demonstrate that the photosensitization mechanism can be ignored in the photocatalytic degradation of methyl orange catalyzed by our TiO$_2$ photocatalysts and P25 under visible light illumination. Therefore, the visible-light-driven photocatalytic activity of TiO$_2$-600, TiO$_2$-700, and TiO$_2$-800 arises from the visible-light photoexcitation of electrons from the isolated energy levels in the band gap formed by the doped N or S to the conduction band. Figure 11 shows the yield of acetic ester as a function of reaction time for the esterification reaction catalyzed by TiO$_2$-600, TiO$_2$-700, and P25. Since the active sites for the esterification reaction are Brønsted acid sites, TiO$_2$-600 with much more and much stronger Brønsted acid sites is far more active than TiO$_2$-700. The ethyl acetate yield reaches 85% after 6 h of esterification reaction catalyzed by TiO$_2$-600. This yield is comparable with that for the esterification reaction catalyzed by sulfonic acid functionalized mesoporous organosilicas under similar reaction condition.44–46 P25 exhibits a poorer activity than TiO$_2$-600 in the esterification reaction and the ethyl acetate yield reaches 38.8% after 6 h of reaction. This is reasonable because the surface hydroxyls on TiO$_2$ are known to have the Brønsted acidity.

TiO$_2$-600 was used as the support for the preparation of Pt/TiO$_2$ photocatalysts whose XRD patterns are displayed in Figure 12. TiO$_2$ retains the anatase phase and its average crystalline size is $\sim 24.5$ nm evaluated from the Sherrer equation in Pt/TiO$_2$. The diffraction peaks arising from Pt do not appear in Pt/TiO$_2$ until the Pt loading reaches 3 wt % whose XRD pattern shows a Pt (111) diffraction peak at 39.8° (2θ). These results indicate that Pt particles are highly dispersed on the TiO$_2$ surface in Pt/TiO$_2$ samples with a Pt loading below 3 wt %. Figure 13 shows the Pt 4f, N 1s, and S 2p XPS spectra of Pt/TiO$_2$ and TiO$_2$-600. The Ti 2p, O 1s, and C 1s XPS spectra of Pt/TiO$_2$ samples do not differ much from those of TiO$_2$-600. A “ghost” peak of the spectrometer at $\sim 75.5$ eV always appears in the Pt 4f XPS spectra whose origin could not be identified after a thorough investigation. The Pt 4f$_{7/2}$ binding energy in Pt/TiO$_2$ locates at 70.3 eV, a characteristic value for the metallic Pt,27 which implies that Pt in Pt/TiO$_2$ is metallic. An interesting observation is that, with the loading of Pt, the N 1s XPS peak with the binding energy at 401.6 eV weakens in 0.1Pt/TiO$_2$ and then disappears in Pt/TiO$_2$ with higher Pt loadings. This indicates that the loading of Pt on TiO$_2$ effectively disfavors the existence of adsorbed N species. The N 1s XPS peak with the binding energy around 399.6 eV corresponding to interstitial N species also weakens upon the loading of Pt but still remains for all Pt/TiO$_2$. The S 2p peak was only detected in 0.1Pt/TiO$_2$ but not in other Pt/TiO$_2$ samples. Table 2 summarizes the surface concentrations of doped N and S in Pt/TiO$_2$ photocatalysts. Pt is known to be one of the effective catalysts for the catalytic hydrodenitrification and hydrodesulfurization reaction under H$_2$ atmosphere.47,48 Therefore, the removal of N and S species in our Pt/TiO$_2$ photocatalysts might likely be due to the reduction treatment during the course of the catalyst preparation.

The photocatalytic activity of TiO$_2$-600 and Pt/TiO$_2$ in the water splitting to produce H$_2$ was evaluated and the results are shown in Figure 14. The calculated photocatalytic reaction rate of H$_2$ production catalyzed by various photocatalysts is summarized in Table 4. Under all-wavelength light illumination, all Pt/TiO$_2$ photocatalysts exhibit a remarkably enhanced activity compared with that of TiO$_2$-600. On Pt/TiO$_2$ photocatalysts, the

### Table 3: The Reaction Rate Constant $k$ ($\times 10^{-3}$ min$^{-1}$) of the Photocatalytic Degradation of Methyl Orange Catalyzed by Various TiO$_2$ Photocatalysts

<table>
<thead>
<tr>
<th>catalyst</th>
<th>all-wavelength light</th>
<th>visible light ($\lambda &gt; 420$ nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-600</td>
<td>4.79</td>
<td>1.76</td>
</tr>
<tr>
<td>TiO$_2$-700</td>
<td>2.68</td>
<td>0.94</td>
</tr>
<tr>
<td>TiO$_2$-800</td>
<td>1.80</td>
<td>0.57</td>
</tr>
<tr>
<td>P25</td>
<td>2.00</td>
<td>n.d.$^a$</td>
</tr>
</tbody>
</table>

$^a$ Not detected.
Pt particles have been reported to rapidly trap the photogenerated electrons after the formation of the photogenerated electron–hole pairs in the TiO₂ catalysts and then H⁺ in the water can accept the electron and be reduced on the Pt surface to produce H₂ whereas the photogenerated hole can be filled by the electron donor (CH₃OH in our case); therefore, the undesired recombination of the photoinduced charges could be effectively inhibited. Pt/TiO₂ photocatalysts with lower Pt loadings do not contain enough electron trap sites and thus the photoinduced charges recombination still happens. However, too much higher Pt loadings are also not good for the photocatalytic reaction. The Pt nanoparticles that trap excess electrons might become negatively charged and could attract positively charged holes, which causes an adverse effect on the photocatalytic activity. Meanwhile, the excessive coverage of Pt nanoparticles on the photocatalyst surface could also decrease the possibility of the holes reacting with the electron donors adsorbed on the photocatalyst surface, increasing the probability of electron–hole recombination and subsequently decreasing the photocatalytic activity.

Under visible light illumination, the photocatalytic activity of PtTiO₂ decreases with the increasing of Pt loading, agreeing with the concentration of doped N and S in the photocatalysts (Table 2). 0.1Pt/TiO₂ and 0.5Pt/TiO₂ are more active than TiO₂-600, demonstrating the positive effect of Pt; however, 1Pt/TiO₂ and 3Pt/TiO₂ are catalytically poorer than TiO₂-600, which could be reasonably attributed to the absence of doped S and the reduced concentrations of doped N in 1Pt/TiO₂. Therefore, our results demonstrate that the loading of Pt on N- or S-doped TiO₂ is likely to prepare photocatalysts active in the water splitting to produce H₂ under visible light illumination; however, appropriate methods must be found for the loading of Pt not to remove the doped N and S in the photocatalysts, such as photoinduced reduction and γ-ray irradiation induced reduction.

4. Conclusions

In summary, we demonstrate a novel approach to prepare active anatase TiO₂ catalysts by the controlled thermal decomposition of molecular precursor ATS. The calcination of ATS at 600 °C can prepare the sulfonic acid functionalized anatase TiO₂ doped with N and S that is highly active both in the acid catalysis and in the visible-light-driven photocatalysis. Therefore, TiO₂-600 is a promising bifunctional catalyst. The calcinations of ATS at 700 °C can prepare S(VI)-doped anatase TiO₂ photocatalysts highly active under visible light illumination. Meanwhile, the Pt/TiO₂-600 photocatalysts show considerable activity in the photocatalytic water splitting to produce H₂ under all-wavelength light illumination.
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References and Notes


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