One-Pot Synthesis of Anionic (Nitrogen) and Cationic (Sulfur) Codoped High-Temperature Stable, Visible Light Active, Anatase Photocatalysts

Suresh Pillai  
Technological University Dublin, suresh.pillai@dit.ie

Declan McCormack  
Dublin Institute of Technology, declan.mccormack@dit.ie

Steven Hinder

Pradeepan Periyat  
Dublin Institute of Technology, pradeepan.periyat@dit.ie

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Suresh C. Pillai
Declan McCormack
John Colreavy
Pradeepan Periyat
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Pradeepan Periyat, Declan E. McCormack, Steven J. Hinder, and Suresh C. Pillai

Centre for Research in Engineering Surface Technology (CREST), FOCUS Institute, Dublin Institute of Technology, Camden Row, Dublin 8, Ireland, School of Chemical and Pharmaceutical Sciences, Dublin Institute of Technology, Kevin Street, Dublin 8, Ireland, and The Surface Analysis Laboratory, School of Engineering, University of Surrey, Guildford, Surrey GU2 7XH, U.K.

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An efficient and straightforward method for the preparation of nitrogen and sulfur (N, S) codoped high-temperature stable, visible light active, anatase titania is reported. For the first time simultaneous nitrogen and sulfur doping was achieved using a single source, ammonium sulfate [(NH₄)₂SO₄], as the modification agent of the titanium isopropoxide (TTIP) precursor. A stoichiometric modification of 1:8 TTIP:(NH₄)₂SO₄ composition (TNS8) was found to be the most effective in extending the stability of anatase to higher temperatures. This particular modification resulted in 100% anatase at 850 °C and 41% anatase at 900 °C, whereas the control titania contained only 12% anatase at 700 °C and completely transformed to rutile at 800 °C. Codoped (N, S) titania was investigated by a range of characterization techniques including XRD, Raman spectroscopy, XPS, and FTIR. XPS indicated the existence of nitrogen as an anion dopant and sulfur as a cation dopant within the TiO₂ lattice. The UV/visible and visible light photocatalytic studies were carried out using the rhodamine 6G dye as a model system. The visible light photocatalytic activity of the TNS8 sample calcined at 850 °C was double that of Degussa P25, and the rate constant calculated by pseudo-first-order kinetics was 0.019 min⁻¹ for the TNS8 sample and 0.008 min⁻¹ for Degussa P25. This higher photocatalytic activity was attributable to a combination of improved anatase phase stability, higher surface area, and codoped (N, S) titania lattice. Moreover, this codoped (N, S) sample also exhibits excellent photocatalytic activity under UV/visible light.

1. Introduction

Nanocrystalline titania is considered to be an eco-friendly material and has found applications in various fields such as photovoltaics, photocatalysis, self-cleaning coatings, and nanochromatic display devices. 1-5 Among the three forms of titania (anatase, rutile, and brookite), anatase usually exhibits the highest photocatalytic activity. The higher adsorption affinity toward organic compounds, along with the lower electron—hole recombination rate of anatase, phase makes it a superior photocatalyst. 5,7 The anatase phase is irreversibly converted to the less reactive rutile phase at 500—600 °C under normal conditions, 5,8,9 which limits its suitability for high-temperature applications. Many proposed innovative and commercial applications for photocatalytically active stable titania-coated materials such as bathroom tiles, sanitary wares, and self-cleaning glass for the control of organic contaminants require high processing temperatures and hence high-temperature stability. 2,11,12 High consumer demand is projected for these materials. To date most of the work reported to improve the thermal stability of anatase titania utilizes metal ion doping. 13-15 This method, which involves the addition of inorganic oxides (e.g., Al₂O₃, CeO₂) to generate metal ions at higher temperatures, has successfully been used to control the anatase-to-rutile transformation temperature as well as improve the photocatalytic activity of titania. However, the drawback of this method is the generation of secondary impurity phases (e.g., Al₂TiO₅, CeTi₂O₇, and Ce₂Ti₂O₇) which affects phase purity and thus reduces the photocatalytic activity of titania. 16

Chemical modification of a precursor is considered a superior method to the conventional method of metal ion doping, since it eliminates the secondary impurity phase formation. Sulfate impregnation of TiO₂ has recently been reported to improve the photocatalytic activity of titania. 17-19 For example, Colon et al. reported using this methodology to improve the phase stability of anatase up to 700 °C. They also noted the higher photocatalytic activity for the impregnated sample compared to the unmodified one. However, these materials converted to rutile phase at 800 °C, and subsequently the photocatalytic activity was also reduced. 18 The (NH₄)₂SO₄ impregnation on TiO₂ reported by Ortiz-Islas et al. showed brookite and mascagnite phase as an impurity. 20 Furthermore, the complete phase transformation to rutile occurred in the range 650—50 °C. The effect of the SO₄²⁻ and Cl⁻ ions on the formation of anatase by the low-temperature, microemulsion modified hydrothermal method has also been reported. 21 Bokhimi et al. reported a comparative study of two different Cu precursors (CuCl₂ and CuSO₄) for anatase stabilization, and the CuSO₄ addition retained 98% anatase at 800 °C. 22 However the stabilization explained in this study was due to the combined effect of metal ion (Cu²⁺) and SO₄²⁻. Moreover the secondary impurity phases bonattite and antiferite were generated after annealing the sample at 400 and 800 °C, respectively. We have recently reported the chemical modification of titanium isopropanoxide by using different nonmetallic chemical reagents such as...
as urea, sulfuric acid, and trifluoroacetic acid to improve the
anatase stability and the photocatalytic activity by doping with
nitrogen, sulfur, and fluorine, respectively.2,23

This paper outlines the preparation of an N, S codoped anatase
titania having high-temperature stability and visible-light pho-
tocatalytic activity by chemically modifying titanium isopro-
poxide precursor. The codoping (N, S) was achieved by using a
double dopant precursor ammonium sulfate [(NH₄)₂SO₄]. This
effectively performs a dual role during the chemical modification
process by stabilizing the anatase phase at higher temperature
and serving as a source for both nitrogen and sulfur dopants to
improve the photocatalytic activity of the high-temperature
stabilized anatase titania. With this method the phase composi-
tion can be tuned by simply varying the molar ratio of
ammonium sulfate to titania precursor. This modification has
also resulted in increased temperature stability of anatase phase
up to 900 °C (41% anatase), an increase in surface area, and a
higher visible light photocatalytic activity than the standard
Degussa P25. Recent studies using thiourea showed that either
nitrogen or sulfur was doped in the titania lattice.24,28 Surpris-
ingly here we achieved combined anionic (nitrogen) and cationic
(sulfur) doping in the titania lattice from the use of the single
precursor ammonium sulfate [(NH₄)₂SO₄].

2. Experimental Section

2.1. Procedure. The reagents used in this study were titanium
isopropoxide (TTIP, 97%, Aldrich), ammonium sulfate [(NH₄)₂SO₄
99%, Riedel-de Haen, Germany], and deionized water. In a typical
experiment conducted to prepare a 1:1 titanoprecursor:ammonium
sulfate precursor solution, 29.7 mL (100 mmol) titanium isopro-
poxide (Ti(OPr)₄) was placed in 250 mL beaker. To the above
solution was slowly added, 5 mL at a time with stirring, a solution
of 13.2 g (100 mmol) of (NH₄)₂SO₄ dissolved in 180 mL of water.

This was stirred for a further 15 min and then dried at 100 °C in
an oven for 24 h. A similar procedure was adopted to synthesize
1:4 1:8, 1:10, and 1:12 samples. Samples were named as TNS1,
TNS4, TNS8, TNS10, and TNS12, respectively. For TNS12 sample
preparation, the ammonium sulfate did not dissolve completely in
180 mL of water but formed a highly saturated solution. This was
used for further reaction with TTIP. A control sample without any
ammonium sulfate was also prepared to act as a comparison. All
samples were calcined at 700, 800, 850, and 900 °C. X-ray
diffraction (XRD) patterns of the calcined sample were obtained
with a Siemens D 500 X-ray diffractometer in the diffraction angle
range 2θ = 10°–70° using Cu Kα radiation. The amount of anatase
in the sample was estimated using the Spurr equation (eq 1).\\n\\n\[ F_A = 100 - \left( 1 - \frac{I_A(101)}{I_B(110)} \right) \times 100 \] (1)

where \( F_A \) is the mass fraction of anatase in the sample, \( I_A \) (101)
and \( I_B \) (110) are the integrated main peak intensities of anatase
and rutile, respectively.

Raman measurements were taken using an Instruments S.A.
(Jobin Yvon) Labram 1B. A helium–neon laser (514 nm) was
used as laser source. BET (Brunauer, Emmett and Teller) surface
area and pore size measurements were carried out by nitrogen
desorption using a Quantachrome NOVA 2000e surface area
analyzer. The measurements were carried out at liquid nitrogen
temperature after degassing the powder samples for 2 h at 200
°C. The FTIR spectra of the sample were measured using a
Spectrum GX-FTIR spectrophotometer in the range 4000–400
cm⁻¹ using 32 scans per sample. X-ray Photoelectron Spectro-
microscopy (XPS) analysis was performed on a Thermo VG
Scientific (East Grinstead, U.K.) Sigma Probe spectrometer. The
instrument employs a monochromated Al Kα X-ray source (hν
= 1486.6 eV) which was used at 140 W. The area of analysis
was approximately 500 μm diameter for each sample analyzed.

2.2. Photocatalysis Studies. The visible and UV/visible light
photocatalytic activity was performed by the following approach.
In a typical experiment 0.06 g of calcined sample was dispersed
in 50 mL of rhodamine 6G solution having a concentration 5 \times 10⁻⁶ M. The above suspension was stirred for 30 min in the
dark to obtain adsorption–desorption equilibrium to eliminate
the error due to any initial adsorption effect. This was then
irradiated in a Q-Sun Xenon solar simulator chamber having a
wavelength range from 200 to 800 nm with an irradiation power
0.68 W/m². A cutoff filter (λ = 420 nm) was used for the visible
light photocatalysis to eliminate the UV light coming from the
solar simulator. Degradation was monitored by taking 3-mL
aliquots at different intervals of time. These aliquots were
centrifuged for 15 min prior to absorbance measurements in
order to eliminate the error due to scattering. Photocatalysis
studies under UV/visible light were carried out by the same
method without a filter.

3. Results

3.1. Anatase Phase Stability by XRD and Raman Studies.
XRD analysis of the codoped (N, S) samples displayed higher
anatase phase stability compared to the control titania prepared
under identical conditions. Table 1 represents the fraction of
anatase and rutile present in the codoped (N, S) and control
sample at different calcination temperatures calculated using
eq 1. All codoped samples show only anatase phase (100%) at
700 °C. In contrast the control sample was predominately rutile
phase (88%). Even though (NH₄)₂SO₄ modification is effective
in extending anatase phase stability in all instances, the effect
is less in the lower molar ratio samples. The trend is clearly
evident from Table 1 and Figures 1, 2, and 3. At 800 and 850
°C the TNS8 sample is 100% anatase phase, whereas the control
titania was already completely converted to rutile phase at 800
°C. The TNS4 and TNS8 modification was found to be very
effective in increasing the anatase phase stability (9% and 41% anatase phase, respectively, at 900 °C). The optimum level
of modification is identified as TNS8. Raman spectroscopy was
also applied to study the high-temperature stability of codoped
titania as anatase and rutile phases and different Raman active
modes.25,26 Figure 4, spectra a and b, are respectively the Raman
spectra of the TNS8 and control sample calcined at 800 °C.
All the peaks present in the TNS8 sample were due to the
anatase phase at 399, 513, and 639 cm⁻¹.2,25,26 In contrast the
control sample with peaks at 230, 446, and 612 cm⁻¹ is clearly
rutile phase.25,26 At 900 °C (Figure 4c) the TNS8 sample shows
41% anatase (as per XRD) which is confirmed by anatase peaks
at (399, 513, and 639 cm⁻¹) along with rutile peaks. These
Raman results are consistent with the XRD data.

3.2. BET Surface Area Analysis. The physicochemical
sorption properties and pore parameters of the TNS8 and control

<table>
<thead>
<tr>
<th>sample</th>
<th>700 °C</th>
<th>800 °C</th>
<th>850 °C</th>
<th>900 °C</th>
<th>1000 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>R</td>
<td>A</td>
<td>R</td>
<td>A</td>
</tr>
<tr>
<td>TNS4</td>
<td>100</td>
<td>0</td>
<td>59</td>
<td>41</td>
<td>22</td>
</tr>
<tr>
<td>TNS8</td>
<td>100</td>
<td>0</td>
<td>96</td>
<td>4</td>
<td>76</td>
</tr>
<tr>
<td>TNS10</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>TNS12</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>19</td>
</tr>
<tr>
<td>control</td>
<td>12</td>
<td>82</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

* Error ±5%.
Nitrogen, Sulfur Codoped Anatase TiO₂

Table 2: Surface area of the TNS8 and control titania at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Sample</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>TNS8</td>
<td>53.3</td>
<td>0.256</td>
</tr>
<tr>
<td></td>
<td>control</td>
<td>25.6</td>
<td>0.160</td>
</tr>
<tr>
<td>800</td>
<td>TNS8</td>
<td>30.1</td>
<td>0.120</td>
</tr>
<tr>
<td></td>
<td>control</td>
<td>1.9</td>
<td>0.007</td>
</tr>
<tr>
<td>900</td>
<td>TNS8</td>
<td>10.0</td>
<td>0.022</td>
</tr>
<tr>
<td></td>
<td>control</td>
<td>1.0</td>
<td>0.00</td>
</tr>
</tbody>
</table>

3.3. X-ray Photoelectron Spectroscopy (XPS). XPS measurements were carried out to investigate the N and S incorporation in the high-temperature stable anatase titania. The amount of nitrogen and sulfur in the TNS8 samples calcined at temperatures 600, 700, 800, and 900 °C are shown in Table 3. The amount of N and S at 600 °C is significant compared to those obtained at higher temperatures. Figure 5 represents the XPS spectra of nitrogen and sulfur present in the TNS8 sample calcined at 600 and 800 °C. In Figure 5a, the binding energy peak for N-doped TNS8 sample at 600 °C is broad, extends from 398 to 405 eV, and is centered at 402 eV. This value is clearly greater than the typical binding energy (396 eV) of the Ti–N bond, suggesting that there is no Ti–N bond formation.27 It was previously observed that the molecular chemisorbed...
TABLE 3: Amount of nitrogen and sulfur present in the TNS8 sample calcined at different temperatures

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>Nitrogen Content (atom %)</th>
<th>Sulfur Content (atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>1.5</td>
<td>3.5</td>
</tr>
<tr>
<td>700</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>800</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>900</td>
<td>0.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

*Error ± 5%.

The reactivity of transition metal alkoxides, particularly titanium (IV) alkoxide, particularly in relation to hydrolysis and condensation is rapid. This is due to the presence of vacant d orbitals in the transition metals which help in the co-ordination expansion. Titanium (IV) alkoxide compounds when reacting with water increase the co-ordination number of the metal from 4 to 6, by accepting the lone pair of electrons from the oxygen of the nucleophilic ligand $–O–H$ to form $\text{Ti(OH)}_2\text{H}_2\text{O}_{(c–)}^{-}$.

This structure undergoes dehydration and condensation to form a final precipitate of titanium hydroxide which generates crystalline titania ($\text{TiO}_2$) on further heat treatment. In order to avoid the fast reactivity toward hydrolysis and condensation, chemical additives (complexing molecules) are often added to moderate the rate of the reaction.

In the present study a readily available compound, ammonium sulfate, was used as a chemical modifier which is able to generate a high-temperature, stabilized N, S codoped anatase titania. The initial reaction between ammonium sulfate and titanium isopropanoxide precursor led to the formation of a mixture of compounds including ammonium titane and titanium oxysulphate (Figure 8b). It undergoes structural changes on heat treatment due to the instability of ammonium and sulfate species present in the compound to form the high-temperature stabilized anatase titania above 600 °C. The formation of these compounds suggests that both ammonium and sulfate species are capable of inhibiting the crystallization of rutile titania at a lower temperature (below 600 °C), thereby retaining anatase titania to higher temperatures (above 600 °C). The XRD of the TNS8 sample at 100 °C shows mainly ammonium sulfate (JCPDS file no. 41-0621). This is stable up to 300 °C; however, the formation of anatase $\text{TiO}_2$ in very small quantity is also visible here which is represented by a broad peak around the 2θ value at 25.3 in Figure 8a. Further heat treatment performed for this compound at a temperature of 400 °C generated the ammonium titane and titanium oxysulphate (Figure 8b). Above 400 °C this forms the nitrogen-doped titanium oxysulphate structure (Figure 8e, JCPDS file no. 81-1566) due to the decomposition of ammonium ions. Our previous report showed that the titanium oxysulphate decomposes at a temperature of 620 °C to produce the sulfur-doped anatase titania. Therefore, further heat treatment of the above titanium oxysulphate causes its decomposition over a temperature above 600 °C to produce the N, S codoped anatase titania. The general reaction series can be represented by the following equations.

$$\text{4Ti(OPr)$_2$} + (\text{NH}_4)\text{SO}_4 + 8\text{H}_2\text{O} \rightarrow \text{TiO}_2\text{S}_2\text{N}_4 + $$

$$\text{3TiO}_2\text{S}_2\text{N}_4 + 3\text{H}_2\text{O} \rightarrow 3\text{TiO}_2 + 6\text{SO}_2$$

$$\text{TiOSO}_4 + 16(\text{CH}_3–\text{CH(OH)}–\text{CH}_3) \rightarrow $$

$$\text{TiO}_2\text{S}_2\text{N}_4 + 3\text{O}_2 \rightarrow $$

$$\text{TiO}_2\text{S}_2\text{N}_4 + 3\text{H}_2\text{O}$$

$$\text{2TiO}_2\text{S}_2\text{N}_4 + 3\text{O}_2 \rightarrow $$

$$\text{TiO}_2\text{S}_2\text{N}_4 + 3\text{H}_2\text{O}$$

Therefore, the $\text{SO}_4^{2–}$ ion which is stable up to a temperature of 620 °C plays a major role in stabilizing the anatase structure along with $\text{NH}_4^+$ cation. IR spectroscopy reveals the role of the ammonium and sulfate species in the stabilization of the
Nitrogen, Sulfur Codoped Anatase TiO₂

**Figure 5.** XPS spectra of (a) nitrogen and (b) sulfur at 600 °C; (c) nitrogen and (d) sulfur at 800 °C.

**TABLE 4: Rate constants of the Degussa P25, TNS8, and control titania at different temperatures**

<table>
<thead>
<tr>
<th>light source</th>
<th>Degussa</th>
<th>TNS8</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV</td>
<td>0.281</td>
<td>0.259</td>
<td>0.156</td>
</tr>
<tr>
<td>visible</td>
<td>0.008</td>
<td>0.014</td>
<td>0.004</td>
</tr>
</tbody>
</table>

The IR spectra of the samples observed above 400 cm⁻¹ show the sulfate ion to decompose at this temperature. The XPS study shows that at 600 °C there is 1.53 atom % of nitrogen in the sample which is attributed to the decomposition of the NH₄⁺ cation. Above 400 °C ammonium ions are decomposed to produce N₂ molecules and NO species as explained in the XPS section 3.3. A further increase in temperature led to the doping of the nitrogen in the titania lattice by the replacement of the oxygen atom. This is confirmed by the XPS peak around 399.7 eV which is due to the formation of an O−Ti−N bond, suggesting that the nitrogen is doped in the lattice as an anion by the oxynitride bond formation (O−Ti−N). The interaction of sulfate ion becomes strong above 400 °C due to the strong binding of SO₄²⁻ with TiO₂. This is clearly evident from the IR spectra of the samples calcined at 500 and 600 °C (Figure 9e and f) where the absorption at 1104 cm⁻¹ is split into three distinct bands (1225, 1145, and 1044 cm⁻¹) due to the lowering of the symmetry of SO₄²⁻ ion from tetrahedral (Td) to C₂ point group as a result of a bidentate bond on formation of anatase titania. The XRD of the TNS8 sample at 600 °C (Figure 8h) displays an intense peak of anatase titania at 2θ value of 25.3° which shows that the sulfate ion began to decompose at this temperature. This is confirmed by the XRD spectra of TNS8 sample at 700 °C which shows codoped (N, S) anatase titania without any extra phase (Figure 1b). This sulfate decomposition was in agreement with previous results obtained. To confirm the effect of ammonium cation and sulfate anion on the anatase structure formation, all calcined TNS8 samples were treated with 1 M NaOH solution for 24 h. By treatment with NaOH and further washing with water, both the ammonium and sulfate ions were removed from the calcined samples. The FTIR spectra taken after NaOH treatment are shown in Figure 10. It reveals the absence of both species (ammonium and sulfate) with the spectra showing only the stretching vibration of the Ti−O−Ti bond below 1000 cm⁻¹, along with the bands around 1600 and 3400 cm⁻¹ corresponding to the bending and stretching of the OH group of both water molecules occluded and the OH group adsorbed on the surface of TiO₂. In addition to this the XRD pattern of these NaOH-treated samples shows no other peaks except the peak for anatase titania. At lower temperatures (100 and 300 °C) TNS8 samples
appear less crystalline, whereas the higher-temperature calcined sample (600 °C) has well crystallized anatase titania peaks (Supporting Information 2). This also suggests that both ammonium and sulfate species are capable of inhibiting the crystallization of titania at lower temperature (below 600 °C). Therefore, the modification using ammonium sulfate reveals that during the lower heat treatment regime the influence of ammonium ions is predominant, while as the temperature increases the sulfate interaction becomes more prominent. In the present study anatase stability was achieved up to a temperature of 900 °C.  

4.2. Photocatalysis. According to literature reports organic dyes such as methylene blue and rhodamine 6G undergo complete structural degradation by the photocatalytic reaction of TiO₂ through several intermediate steps. However, the photocatalytic activity of titania depends upon several factors, such as phase composition (anatase and/or rutile), surface area, crystallinity and crystallite size, adsorption properties of the dyes on the surface of TiO₂, used, rate of electron–hole recombination, and the number of electrons created. Which factor dominates the photocatalytic effect of titania is debatable. In this study, TNS8 samples calcined at all temperatures (700, 800, 850, and 900 °C) shows significantly higher photocatalytic activity than the control sample (Table 1) that the control sample is rutile at all temperatures, whereas the TNS8 sample is anatase. Anatase titania has been reported to be more photocatalytically active than the rutile form because the adsorption affinity of the organic dye molecule toward the anatase phase is stronger compared to that of rutile. The adsorption difference of the dye on TiO₂ phases is mainly due to the structural difference of anatase and rutile. Both anatase and rutile consist of tetragonal structures having [TiO₆] octahedra, which share edges and corners in a different manner, while keeping the overall stoichiometry as TiO₂. Rutile is characterized by a surface where the dissociation of adsorbed organic molecule takes place more easily than on the anatase. These essential differences in the surface chemistry of the two TiO₂ phases can explain their different photocatalytic properties because a photocatalytic reaction mainly takes place at the surface of the catalyst. All the codoped samples (except the TNS8 at 900 °C (41% anatase)) show only anatase phase, whereas the control samples show rutile phase (only at 700 °C 18% anatase phase presented) which explains the main reason for higher photocatalytic activity shown by the codoped samples. A further factor is the higher surface area of TNS8 samples (Table 2). As the specific surface area of the catalyst increases, it can adsorb a higher number of dye molecules. The TNS8 sample calcined at all temperatures shows the anatase phase with a significantly higher surface area (more than two times higher) compared to that of the control titania (Table 2). A further factor to consider is the effect of doping (N, S) which shifts the absorption edge of the titania toward the visible light region (Supporting Information 3) due to the synergistic effects of nitrogen and sulfur. The mixing of N₂p with O₂p states will effectively lead to the band gap narrowing of titania and the mixing of the Sₐ states of sulfur atoms with the valence band increases the width of the valence band which results in the decrease of band gap energy (Supporting Information 4, Table 1). These three factors, i.e., improvement in higher anatase phase stability, surface area, and doping (N, S) made the TNS8 sample more photocatalytically active than the control sample at all temperatures. Recent reports on the rhodamine dye degradation mechanism using TiO₂ and TiO₂/SiO₂ composites showed that the blue shift in absorption maxima represents the dye degradation pathway through the elimination of the diethyl group from the dye structure. In this study a gradual decrease in absorption maxima of the dye without any blue shift (Figures 6 and 7) was observed. Thus, it has been concluded here that active radical species (hydroxyl and superoxide radicals and holes) have a significant influence in improving the photocatalytic activity of these TiO₂ samples. Direct comparison of the crystal phase between the control and TNS8 sample shows
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5. Conclusions

Nitrogen, sulfur codoped high-temperature stable visible light active anatase titania was successfully synthesized by chemical modification of the precursor titanium isopropoxide using ammonium sulfate. These materials were characterized by various techniques such as XRD, Raman spectroscopy, FTIR, XPS, and BET surface area analysis. The phase analysis by XRD found the 1:8 TTIP:(NH₄)₂SO₄ composition (TNS8) was the most effective in extending the anatase-to-rutile phase transformation. It showed the formation of 100% anatase at 850 °C and 41% anatase at 900 °C, whereas the control titania completely transformed to rutile at 800 °C with only 12% anatase at 700 °C. XPS studies showed that nitrogen is doped as anion and sulfur as a cation. All the doped samples showed significantly higher photocatalytic activity compared to the control titania. The visible light photocatalytic activity comparison of the TNS8 sample calcined at higher temperature 850 °C with that of a commercial catalyst Degussa P25 showed that TNS8 has twice the activity of Degussa P25 and the rate constant calculated from first-order kinetics was 0.019 min⁻¹ for TNS8 and 0.008 min⁻¹ for Degussa P25, while the control sample showed a negligible amount of activity at this temperature. These N, S codoped samples also showed excellent photocatalytic activity in UV/visible light. The TNS8 composition calcined at 850 °C decolorized the rhodamine 6G dye within 4 min (pseudo-first-order rate constant 0.576 min⁻¹), whereas the Degussa P25 under identical conditions decolorized the dye only after 8 min (rate constant 0.281 min⁻¹). This higher photocactivity was explained by an improvement in anatase phase stability and higher surface area along codoping (N, S) in the titania lattice.

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Supporting Information Available: Figures giving type I isotherms of samples calcined at 800 °C, XRD patterns of the TNS8 samples at 100 and 600 °C after NaOH treatment, absorption spectra and reflectance spectra, band gaps of the N, S codoped samples also showed excellent photocatalytic activity in UV/visible light. The TNS8 composition calcined at 850 °C decolorized the rhodamine 6G dye within 4 min (pseudo-first-order rate constant 0.576 min⁻¹), whereas the Degussa P25 under identical conditions decolorized the dye only after 8 min (rate constant 0.281 min⁻¹). This higher photocactivity was explained by an improvement in anatase phase stability and higher surface area along codoping (N, S) in the titania lattice.

References and Notes

(9) Padmanabhan, S. C.; Pillai, S. C.; Colreavy, J.; Balakrishnan, S.;
(10) Kumar, K. N. P.; Keizer, K.; Burggraaf, A. J. Nature 1992, 358,
1958, 54, 1069.
2005, 88, 95.
107, 10871.
(13) Periyat, P.; Baju, K. V.; Pillai, K. P.; Mukundan, P.; Warrier,
(16) Periyat, P.; Baju, K. V.; Mukundan, P.; Pillai, P. K.; Warrier,
(17) Colon, G.; Hidalgo, M. C.; Munuera, G.; Ferino, I.; Cutrufello,
179, 20.
(18) Colon, G.; Hidalgo, M. C.; Munuera, G.; Ferino, I.; Cutrufello,
(20) Ortiz-Islas, E.; Lopez, T.; Navarrete, J.; Bokhimi, X.; Gomez, R.
109, 8673.
(23) Periyat, P.; Pillai, S. C.; McCormack, D. E.; Colreavy, J.; Hinder,
(25) Choi, S. Y.; Mamak, M.; Coombs, N.; Chopra, N.; Ozin, G. A.

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2007, 111, 96.
15, 41.
(30) Bringer, C. J.; Scherer, G. W. Sol-Gel Science; Academic Press:
32, 6001.
185, 19.
(37) Aronson, B. J.; Blanford, C. F.; Stein, A. Chem. Mater. 1997, 9,
1987, 83, 1591.
(43) Burda, C.; Lou, Y. B.; Chen, X. B.; Samia, A. C. S.; Stout, J.;
2003, 32, 330.