Site Structure and Photocatalytic Role of Sulfur or Nitrogen-Doped Titanium Oxide with Uniform Mesopores under Visible Light

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Anion doping to titanium oxide (TiO2) has been extensively studied to explore visible light-responsive photocatalysts. Among them, sulfur doping was most effective; however, the site structure and the implication to promoted photocatalysis have not been reported yet, except for valence state information based on X-ray photoelectron spectroscopy. Sulfur and/or nitrogen was doped to TiO2 with a narrow pore size distribution, at 3 nm, using thiourea or urea. They were compared to the uniform mesoporous TiO2 modified via the chemical vapor deposition (CVD) of hydrogen sulfide and the titanate/TiO2 nanotube synthesized hydrothermally using TiS2. In ethanol and O2 under visible light (wavelengths of >370, >420, >480, >520, or >580 nm), water formation was promoted by a factor of 12, in clear contrast to the only 2.3× enhancement for acetaldehyde formation by doping sulfur. These anion-doped mesoporous TiO2 catalysts were characterized using Ti and S K-edge extended X-ray absorption fine structure for the first time. The Ti–S bonds were detected at 2.283–2.44 Å for sulfur-doped mesoporous TiO2 using thiourea and sulfur-doped mesoporous TiO2 via CVD, demonstrating the presence of substitutional anionic S on the O sites. The doped anionic sulfur created impurity level(s) at 0.8–2.2 eV below the conduction band (CB) minimum of mesoporous TiO2. It enabled the electron excitation to the CB and then to O2 to convert to water under visible light. In contrast, the impurity level(s) at 0.8–2.2 eV below the CB minimum was/were not effective to (directly or indirectly) receive electrons from the substrate (ethanol/ethanol). Preferential water formation under visible light was also observed for TiO2 nanotubes that were synthesized hydrothermally from TiS2.

Introduction

The band gap value (Eg) is critical in the performance of solar cells and photocatalysts. Titanium oxide (TiO2) has been extensively studied for photocatalysis under UV and/or visible light.1,2 Because the Eg values for anatase and rutile-type TiO2 are 3.2 and 3.0 eV, respectively, corresponding to the energies of UV light, modification of the TiO2 is necessary to be responsive under visible light. Transition-metal cations were doped on/in TiO2 to reduce the Eg value, but the doped cation sites often enhance the charge carrier recombination seriously and affect the interfacial charge transfer to the substrate, depending on the doped amount on/in TiO2.2

The density of states (DOS) was evaluated for doped TiO2 by density functional theory (DFT) calculations using the full-potential linearized-augmented-plane-wave method. Nonmetal anion doping to TiO2 was predicted to reduce the Eg value, form a DOS derived from the anion near valence band (VB) maximum or deeper level, and maintain the conduction band (CB) minimum enough high to donate electrons to the oxidants in photocatalysis.3 Since then, visible-light-excited photocatalysis has been intensively studied over TiO2 doped with B,4 C,5–10 N,11 S,2 N,22–28 F,29–31 Cl and Br,32 and I33–35 for the decomposition of methylene blue, water, 2-propanol, acetaldehyde, phenol derivatives, nitric oxide, and other volatile organic chemicals (VOCs) and dyes (see Table 1).

<table>
<thead>
<tr>
<th>Emission</th>
<th>Reaction</th>
</tr>
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<tbody>
<tr>
<td>UV</td>
<td>Reduction of water</td>
</tr>
<tr>
<td>UV</td>
<td>Photocatalytic oxidation of alcohols</td>
</tr>
<tr>
<td>UV</td>
<td>Photocatalytic oxidation of amines</td>
</tr>
<tr>
<td>UV</td>
<td>Photocatalytic oxidation of aldehydes</td>
</tr>
</tbody>
</table>

Table 1. Photocatalytic Reactions Promoted by Doped TiO2

Site structure and the photocatalytic role of nitrogen-doped TiO2 were reported using electron paramagnetic resonance (EPR), and DFT calculations were reported using the plane-wave-pseudopotential method.16 The impurity level due to substitutional N was calculated at a level 0.14–0.59 eV above the valence band (VB) maximum. The electron of substitutional N0 or N− level is excited to CB and then irreversibly reduced O2 to O2− (adsorbed), based on EPR measurements under visible light. The effects of reduced Ti3+ level to donate an electron to the substitutional N level16 of and oxygen vacancies (F center)16,36 were also discussed.

The band gap reduction and photocatalytic promotion under visible light were most pronounced for sulfur-doped TiO2 (see Table 1).22–28 Both substitutional cationic S5+/S6+ on the Ti sites starting from thiourea or sulfuric acid22,24–27 and substitutional anionic S on the O sites starting from TiS2, CS2, or H2S,23,28,37 have been reported; however, the site structure and the implication to promoted photocatalysis have not been reported yet.

In this paper, sulfur and/or nitrogen was doped during template mesoporous synthesis. The co-doping syntheses successfully formed a TiO2 matrix with mesopores of narrow pore size distribution at 3 nm, similar to reported mesoporous TiO2 that has been doped with Al,38 V,39 Fe,38 Zr,38 Nb,38 Mo,40 and Ce.38,41 Thus-obtained sulfur-doped mesoporous TiO2 was compared to mesoporous TiO2 modified via the chemical vapor deposition (CVD) method and titanate/TiO2 nanotube synthesized hydrothermally, starting from TiS2. The intentions are to compare the photocatalytic effects of homogeneously distributed sulfur in a matrix via co-doping versus sulfur near the TiO2 surface via CVD method and also the effects of randomly
<table>
<thead>
<tr>
<th>Element</th>
<th>Precursor</th>
<th>Synthesis Route</th>
<th>Visible Light Absorption (Shoulder, Tail) (nm)</th>
<th>E_g (eV)</th>
<th>Reactant of Photocatalysis</th>
<th>Promoted Ratio</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>BH₄</td>
<td>TiCl₄ sol–gel</td>
<td>400–800</td>
<td>2.32</td>
<td>MTBE</td>
<td>6× that of anatase</td>
<td>4</td>
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<tr>
<td>C</td>
<td>CO₂</td>
<td>Ti metal pyrolysis</td>
<td>410–560</td>
<td>2.32</td>
<td>water (electrochemical)</td>
<td>7.7× that of TiO₂</td>
<td>5</td>
</tr>
<tr>
<td>C</td>
<td>HO(CH₂)₂OH</td>
<td>Ti metal anodization (NT)</td>
<td>400–700</td>
<td>2.2</td>
<td>water (electrochemical)</td>
<td>6× that of TiO₂</td>
<td>6</td>
</tr>
<tr>
<td>C</td>
<td>NBu₄⁺OH⁻</td>
<td>TiCl₄ sol–gel</td>
<td>380–600</td>
<td>2.9</td>
<td>4-chlorophenol</td>
<td>76× that of TiO₂</td>
<td>7</td>
</tr>
<tr>
<td>C</td>
<td>TiC</td>
<td>TiCl₄ calcined</td>
<td>380–600</td>
<td>2.9</td>
<td>2-propanol</td>
<td>8× that of TiO₂</td>
<td>7</td>
</tr>
<tr>
<td>C</td>
<td>TiC</td>
<td>TiCl₄ calcined</td>
<td>390–600</td>
<td>2.9</td>
<td>methyl blue</td>
<td>8× that of N-TiO₂</td>
<td>9</td>
</tr>
<tr>
<td>N</td>
<td>NE₃⁺, etc.</td>
<td>Ti(O-iPr)₄ sol–gel</td>
<td>380–600</td>
<td>2.95–2.70</td>
<td>Rhodamine B, 2,4-dichlorophenol</td>
<td>1.1–2.8× that of TiO₂</td>
<td>11</td>
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<tr>
<td>N</td>
<td>N₃(CH₂)₆</td>
<td>TiCl₃ solvothermal</td>
<td>390–600</td>
<td>2.48–2.29</td>
<td>nitric oxide</td>
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<td>13</td>
</tr>
<tr>
<td>N</td>
<td>N₂</td>
<td>anatase/rutile sputtering</td>
<td>390–600</td>
<td>2.94</td>
<td>acetaldehyde</td>
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<td>NH₄⁺Cl⁻</td>
<td>Ti(O-iPr)₄ sol–gel</td>
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<td>3.17</td>
<td>2-propanol</td>
<td>1.3× that of TiO₂</td>
<td>15</td>
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<tr>
<td>N</td>
<td>NH₃</td>
<td>titanate CVD</td>
<td>380–500</td>
<td>2.8</td>
<td>formic acid</td>
<td>6× that of anatase</td>
<td>16</td>
</tr>
<tr>
<td>N</td>
<td>NH₄⁺OH⁻</td>
<td>TiCl₄ sol–gel</td>
<td>390–700</td>
<td>2.8</td>
<td>Methyl Orange</td>
<td>8× that of TiO₂</td>
<td>17</td>
</tr>
<tr>
<td>N</td>
<td>urea</td>
<td>titanate impregnated</td>
<td>380–500</td>
<td>2.46</td>
<td>4-chlorophenol</td>
<td>8× that of TiO₂</td>
<td>18</td>
</tr>
<tr>
<td>N, C</td>
<td>Ti[OC(NH₂)₂]₃Cl₂</td>
<td>Ti[OC(NH₂)₂]₃Cl₂ calcined</td>
<td>380–550</td>
<td>1.87</td>
<td>Methyl Orange</td>
<td>1.7× that of P25</td>
<td>19</td>
</tr>
<tr>
<td>S</td>
<td>thiourea</td>
<td>Ti(O-iPr)₄ impregnated</td>
<td>410–600</td>
<td>2.4–2.3</td>
<td>water (solar cell)</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>TiS₂</td>
<td>TiS₂ calcined</td>
<td>380–580</td>
<td>2.4–2.3</td>
<td>Methylene Blue</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>thiourea</td>
<td>Ti(O-iPr)₄ sol–gel</td>
<td>400–600</td>
<td>2.4–2.3</td>
<td>Methylene Blue</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>thiourea</td>
<td>Ti(O-iPr)₄ sol–gel</td>
<td>400–600</td>
<td>2.4–2.3</td>
<td>Methylene Blue</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>thiourea</td>
<td>Ti(O-iPr)₄ sol–gel</td>
<td>380–600</td>
<td>2.4–2.3</td>
<td>Methylene Blue</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>H₂SO₄/TiS₂</td>
<td>Ti(O-iPr)₄/TiS₂ sol–gel</td>
<td>390–700</td>
<td>2.6</td>
<td>Rhodamine 6G</td>
<td>10× that of TiO₂</td>
<td>27</td>
</tr>
<tr>
<td>S</td>
<td>CS₂</td>
<td>Ti(O-Bu)₄ supercritical</td>
<td>390–700</td>
<td>2.6</td>
<td>Methylene Blue</td>
<td>7.9× that of TiO₂</td>
<td>28</td>
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<tr>
<td>F</td>
<td>NH₄⁺F⁻</td>
<td>Ti(O-iPr)₄ sol–gel</td>
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<td>2.90</td>
<td>acetone</td>
<td>1.3× that of P25</td>
<td>29</td>
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<tr>
<td>F, N</td>
<td>H₂TiF₆</td>
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<td>2.34</td>
<td>water</td>
<td>7× that of P25</td>
<td>30</td>
</tr>
<tr>
<td>F, N</td>
<td>(NH₄⁺)₂TiF₆⁻</td>
<td>(NH₄⁺)₂TiF₆ calcined</td>
<td>380–550</td>
<td>2.34</td>
<td>water</td>
<td>3× that of P25</td>
<td>31</td>
</tr>
<tr>
<td>Cl, Br</td>
<td>Br⁻</td>
<td>TiCl₄ hydrothermal</td>
<td>370–500</td>
<td>2.34</td>
<td>Methylene Blue</td>
<td>10× that of P25</td>
<td>32</td>
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<tr>
<td>I</td>
<td>I crystal</td>
<td>Ti(O-iPr)₄ sol–gel</td>
<td>425–770</td>
<td>2.34</td>
<td>Methylene Blue</td>
<td>7× that of P25</td>
<td>33</td>
</tr>
<tr>
<td>I</td>
<td>HIO₄</td>
<td>Ti(O-iPr)₄ hydrothermal (template)</td>
<td>400–600</td>
<td>2.34</td>
<td>phenol</td>
<td>6× that of P25</td>
<td>34</td>
</tr>
<tr>
<td>I</td>
<td>HIO₄</td>
<td>Ti(O-Bu)₄ sol–gel</td>
<td>380–650</td>
<td>2.34</td>
<td>phenol</td>
<td>5× that of P25</td>
<td>35</td>
</tr>
</tbody>
</table>
distributed sulfur via co-doping versus sulfur distributed along the nanotubes.

The energy level(s) created between the VB maximum and the CB minimum due to doping must be critical to control the photocatalysis of anion-doped TiO₂. The chemical states of dopants were reported based on B 1s, C 1s, N 1s, K 3d, and I 3d. X-ray photoelectron spectroscopy (XPS) was also applied to evaluate the amount of doped sulfur or nitrogen and their valence state.

XAFS spectra were also applied to evaluate the amount of doped sulfur and the valence state. The photo-oxidation reactions of aliphatic alcohols were reported over carbon-doped, nitrogen-doped, sulfur-doped, or vanadium-doped TiO₂ from 2-propanol to acetone and then to CO/CO₂. The effects of dopants to facilitate photocatalysis of anion-doped TiO₂ were reported based on B 1s, C 1s, N 1s, and I 3d.

Titanate nanotubes were synthesized based on the literature method as a reference of two-dimensional reaction space of a few nanometers. Two grams of TiO₂ (Degussa P25, anatase, rutile = 7/3) and 10 mL of sodium hydroxide (97%, Wako) solution (10 M) were mixed and heated in an autoclave in a Pyrex glass tube that was connected to diffusion and rotary pumps (90 kPa in a vacuum system) with a capacitance manometer (ULVAC, Models CCMT-1000A and GM-2001). The samples were evacuated at a temperature of 423 K for 1 day. The precipitate was filtered and washed with HCl solution (0.1 M) until the filtrate became neutral. The powder was finally washed with distilled water and dried at 353 K for 2 days. The obtained titanate nanotubes were calcined at 673 K for 2 h. The thus-synthesized sample is denoted as “TiO₂ nanotube-S”. A nanotube sample that contained tetravalent titanium (TiIV) was also synthesized using 0.3 g of TiS₂ powder (>99% purity, Alfa Aesar) in a route similar to that for the titanate nanotube. The thus-synthesized titanate nanotube-S was calcined at 673 K for 2 h (referred hereafter as TiO₂ nanotube-S).

Characterization. Optical spectra were recorded on a UV-visible light spectrometer (Jasco, Model V-650), using an integrating sphere (Jasco, Model ISV-469) for diffuse-refectance measurements and D₂ and halogen lamps for wavelengths below and above 340 nm, respectively. Measurements were performed at 290 K in the wavelength range of 200–900 nm. The absorbance was obtained by the transformation based on the Kubelka–Munk equation. The band-gap values were evaluated based on the Tauc equation for the allowed indirect transition, α × hν = (hν – Eg)², in which α, h, and ν are absorption coefficient, Planck constant, and wavenumber, respectively. When the absorption edge is a straight line on a log-log plot, this indicates an indirect transition.

Nitrogen adsorption measurements were performed at a temperature of 77 K and pressures of 1.0–90 kPa in a vacuum system that was connected to diffusion and rotary pumps (10⁻⁶ Pa) and equipped with a capacitance manometer (ULVAC, Models CCMT-1000A and GM-2001). The samples were evacuated at a temperature of 393 K for 2 h before measurements. X-ray diffraction (XRD) data were obtained using a Rigaku MiniFlex II diffractometer at a Bragg angle of 2θ = 1.5°–50°. Conditions involved 30 kV, Cu Kα emission, and a nickel filter. Transmission electron microscopy (TEM) images were taken using field-emission-type TEM equipment (JEOL, Model JEM-4000FX) with an accelerating voltage of 400 kV. Samples were dispersed in ethanol and mounted on amorphous carbon-coated copper mesh.

Ti K-edge X-ray absorption fine structure (XAFS) spectra were measured in transmission mode in the Photon Factory (PF) at the High-Energy Accelerator Research Organization (Tsukuba) on beamlines 9A, 9C, and 12C. The storage-ring energy was 2.5 GeV, and the ring current was between 451 mA and...
TABLE 2: Synthetic Conditions and Physicochemical Properties of Mesoporous TiO$_2$-, S-, or N-Doped Mesoporous TiO$_2$, and Titanate/TiO$_2$ Nanotubes, Created via (A) Doping during Template Synthesis, (B) CVD Doping, or (C) Hydrothermal Synthesis

(A) Doping during Template Synthesis

<table>
<thead>
<tr>
<th>Sample</th>
<th>additive</th>
<th>molar ratio$^a$</th>
<th>TiO$_2$ phase</th>
<th>Washing Medium after Heating</th>
<th>at 333 K</th>
<th>at 453 K</th>
<th>S content (wt %)$^b$</th>
<th>mesopore $d_{XRD}$ (nm)$^c$</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mesoporous TiO$_2$</td>
<td></td>
<td></td>
<td>amorphous</td>
<td>methanol, diethyl ether</td>
<td>608</td>
<td>2.9</td>
<td>2.7</td>
<td>608</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>SN-doped mesoporous TiO$_2$</td>
<td>(H$_2$N)$_2$C=S</td>
<td>S/Ti = 1/2</td>
<td>amorphous</td>
<td>methanol, diethyl ether</td>
<td>2.9</td>
<td>629</td>
<td>1.7</td>
<td>229</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>N-doped mesoporous TiO$_2$</td>
<td>(H$_2$N)$_2$C=O</td>
<td>N/Ti = 1/1</td>
<td>amorphous</td>
<td>diethyl ether</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</table>

(B) CVD Doping

<table>
<thead>
<tr>
<th>sample</th>
<th>additive</th>
<th>$T$ (K)</th>
<th>TiO$_2$ phase</th>
<th>S content (wt %)$^b$</th>
<th>mesopore $d_{XRD}$ (nm)$^c$</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-doped mesoporous TiO$_2$-583</td>
<td>H$_2$S</td>
<td>583</td>
<td>amorphous</td>
<td>0.48</td>
<td>not detected</td>
<td>1.9</td>
<td>3.0(1.7)</td>
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<tr>
<td>S-doped mesoporous TiO$_2$-623</td>
<td>H$_2$S</td>
<td>623</td>
<td>amorphous</td>
<td>0.77</td>
<td>not detected</td>
<td>2.6</td>
<td>0.8</td>
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</table>

(C) Hydrothermal Synthesis

<table>
<thead>
<tr>
<th>sample</th>
<th>source</th>
<th>Ti/NaOH molar ratio$^a$</th>
<th>TiO$_2$ phase</th>
<th>Nanotube Dimensions$^d$</th>
<th>$d_{TEM}$ (nm)</th>
<th>$t_{TEM}$ (nm)</th>
<th>$l_{TEM}$ (nm)</th>
<th>$S_{BET}$ (m$^2$/g)$^d$</th>
<th>$E_g$ (eV$^f$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>titanate/TiO$_2$ nanotube</td>
<td>TiO$_2$ (P25)</td>
<td>1/4</td>
<td>amorphous$^e$</td>
<td>anatase$^e$</td>
<td>7.9</td>
<td>2.3</td>
<td>29</td>
<td>334</td>
<td>3.1</td>
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<tr>
<td>titanate/TiO$_2$ nanotube-S</td>
<td>TiS$_2$</td>
<td>1/37</td>
<td>amorphous$^e$</td>
<td>anatase$^e$</td>
<td>3.9</td>
<td>0.83</td>
<td>62</td>
<td>110</td>
<td>3.1</td>
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</table>

$^a$ Introduced amounts during catalyst synthesis. $^b$ Based on the edge-jump values of S K-edge XAFS. $^c$ Average diameter, as determined via XRD. $^d$ Using an as-synthesized titanate nanotube. Dimensions are given as $d_{TEM}$ (average diameter, as determined by TEM analysis), $t_{TEM}$ (average wall thickness, as determined by TEM analysis), and $l_{TEM}$ (average length, as determined by TEM analysis). $^e$ After calcining at 673 K.
255 mA. A Si(111) double-crystal monochromator and cylindrical double mirror were inserted into the X-ray beam path. The parallellness of double crystals was adjusted using a piezo translator and set to 65% intensity to maximum flux. The slit opening size was 1.0 mm × 1.0 mm in front of the I0 ionization chamber. The I0 and I1 ionization chambers were purged with the mixture of helium and N2 (7:3) and N2, respectively. The powder samples were ground as fine as possible and mounted on tape. The Ti K-edge energy for titanium metal was calibrated to 4964.5 eV.52,53

S K-edge XAFS spectra were measured also in PF on beamline 9A. The setup was basically similar to that for Ti K-edge, but the Si(111) monochromator was fully tuned using a piezo translator.54 The I0 and I1 ionization chambers were purged with helium and N2, respectively. Standard samples were prepared by thoroughly mixing TiS2 with mesoporous TiO2 to 1.6 and 4.5 wt % of sulfur. A small amount (1.4 mg) of powder samples was ground as fine as possible and mounted onto tape. The sulfur contents in SN-doped samples were evaluated based on the comparison of edge-jump values to those for standard samples previously mentioned. The maximum of the first pre-edge feature in the spectrum of Na2S2O3 • 5H2O (99% purity, Wako Pure Chemicals) was assigned to 2472.02 eV.55

The XAFS data were analyzed with XDAP (XAFS Services International).56 The pre-edge background was approximated by the modified Victoreen function, C2/E2 + C1E + C0. The background of post-edge oscillation was approximated by a smoothing-spline function, calculated using an equation for the number of data points (N).

\[
\sum_{i=1}^{N} \frac{(\mu_i - B G_i)^2}{\exp(-0.075k_i^2)} \leq \text{smoothing factor}
\]

Multiple shell analyses were performed for the Fourier-filtered \(k^3\)-weighted EXAFS data in \(k\)- and \(R\)-space using empirical parameters extracted from EXAFS for rutile-type TiO2 and TiS2 for Ti–O, Ti(–O)–Ti, and Ti–S bonds based on reported crystal structures (see Table 3).57–59 The \(\sigma^2\) values listed in Table 4 were relative to those of the references. The many-body reduction factor \(S_\sigma^2\) was assumed to be equal for the sample and reference. The goodness of fit was given as requested by the Committee on Standards and Criteria in X-ray Absorption Spectroscopy.

**Ethanol Photo-oxidation Tests.** The reaction was performed in a closed circulating system (loop volume of 108 mL). One hundred milligrams of catalyst was spread homogeneously in a quartz reaction cell60 (bottom plate area is 23.8 cm2) connected to the circulation loop. The sample was under vacuum (10^-6 Pa) at 290 K and illuminated for 10 h with a xenon arc lamp operated at 480 W (Ushio, Model UXL-500D-O) filtered using L37 (>370 nm, Kenko). After the pretreatment, no gas desorption was detected (<10 nmol) for all the catalysts based on the online GC equipped with thermal conductivity detector (Shimazu, Model GC-8AT). The pretreatment conditions were

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**TABLE 3: Empirical Fit Parameters for Ti K-Edge EXAFS Analyses**

<table>
<thead>
<tr>
<th>shell</th>
<th>compound</th>
<th>Model</th>
<th>Data Ranges Used</th>
<th>(R (\text{Å}))</th>
<th>(N)</th>
<th>(k (\text{Å}^{-1}))</th>
<th>(R (\text{Å}))</th>
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<tr>
<td>Ti(–O)–Ti</td>
<td>rutile-type TiO2</td>
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<td>12</td>
<td>1.92–15.00</td>
<td>2.34–2.87</td>
<td>57, 58</td>
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</tr>
<tr>
<td>Ti–S</td>
<td>TiS2</td>
<td>2.430</td>
<td>6</td>
<td>2.85–14.12</td>
<td>1.54–2.39</td>
<td>59</td>
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---

**TABLE 4: Best Fit Results of Ti K-Edge EXAFS Spectra for Mesoporous TiO2 and Doped Mesoporous TiO2**

<table>
<thead>
<tr>
<th>(R (\text{Å}))</th>
<th>(\Delta\sigma_t^2 (\text{Å}^2))</th>
<th>(\Delta\sigma_r^2 (\text{Å}^2))</th>
<th>(\Delta\sigma_{if} (\text{Å}))</th>
<th>(\Delta\sigma_{if} (\text{Å}))</th>
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<tr>
<td>1.75 (±0.02)</td>
<td>2.3 (±0.6)</td>
<td>0.0025 (±0.0019)</td>
<td>0.0017 (±0.0020)</td>
<td>2.0 (±0.6)</td>
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<tr>
<td>2.00 (±0.06)</td>
<td>1.19 (±0.5)</td>
<td>0.0052 (±0.0018)</td>
<td>0.0039 (±0.0025)</td>
<td>2.00 (±0.06)</td>
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<tr>
<td>1.73 (±0.02)</td>
<td>3.2 (±0.8)</td>
<td>0.0059 (±0.0011)</td>
<td>0.0059 (±0.0011)</td>
<td>1.88 (±0.0003)</td>
</tr>
<tr>
<td>2.00 (±0.06)</td>
<td>2.0 (±0.6)</td>
<td>0.0030 (±0.0014)</td>
<td>0.0030 (±0.0014)</td>
<td>2.0 (±0.06)</td>
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<td>2.0 (±0.06)</td>
<td>0.44 (±0.5)</td>
<td>0.0095 (±0.0004)</td>
<td>0.0095 (±0.0004)</td>
<td>1.88 (±0.0001)</td>
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<td>1.74 (±0.02)</td>
<td>4.4 (±0.5)</td>
<td>0.0095 (±0.0004)</td>
<td>0.0095 (±0.0004)</td>
<td>2.0 (±0.06)</td>
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</table>
compared to anatase-type TiO$_2$. The g value was evaluated to 3.0 eV (see curve e in the inset of Figure 1, and Table 2B). The specific SA decreased to 229 m$^2$/g for the SN-doped mesoporous TiO$_2$ (see Table 2A). For S-doped mesoporous TiO$_2$ via CVD, the specific SA decreased to 1.9–2.6 m$^2$/g (see Table 2B). The specific SA for titane nanotubes was 110–334 m$^2$/g on a level similar to SN-doped mesoporous TiO$_2$ (see Tables 2C and 2A).

Narrow pore size distribution centered at 2.7 nm ($\theta_{\text{BET}}$ = 3.34°) for mesoporous TiO$_2$ was preserved for SN-doped mesoporous TiO$_2$ centered at 2.9 nm ($\theta_{\text{BET}}$ = 3.09°; see Table 2A). The lower angle XRD peak disappeared for S-doped mesoporous TiO$_2$-583/623 (Table 2B). High-resolution TEM images were taken to observe the nanotube structure. The average tube diameter, wall thickness, and length, which were 7.9, 2.3, and 29 nm, respectively, for titane nanotube changed to 3.9, 0.83, and 62 nm, respectively, for the thinner and longer nanotube-S (see Figure 2). This is the first report of titane/TiO$_2$ nanotube synthesis starting from TiS$_2$.

The sulfur contents in SN-doped mesoporous TiO$_2$ and S-doped mesoporous TiO$_2$-583/623 samples were evaluated to 1.7, 0.48, and 0.77 wt %, respectively, based on the S K-edge XAFS spectra. The three near-edge spectra all consisted of an intense peak at 2482.2–2482.4 eV, accompanied by peaks at 2473.9–2474.4 eV (w), 2489.3–2489.4 eV (w), and 2498.2–2499.0 eV (w,br). The peak positions were similar to those for TiS$_2$: 2482.4 eV (s), 2472.8 eV (m), 2489.2 eV (w), and 2498.9 eV (w,br).

**Ti K Pre-edge Region.** The Ti K-edge spectra in the pre-edge region for mesoporous TiO$_2$, doped mesoporous TiO$_2$, and titane nanotubes are depicted in Figure 3A. The spectra for standard Ti compounds were also shown (see Figure 3B).

The pre-edge region for mesoporous TiO$_2$ consisted of an intense peak at 4969.3 eV, accompanied by weaker peaks at 4967.2 and 4972.6 eV (see spectrum a in Figure 3A). The spectral pattern in this energy region resembled that for FeTiO$_3$ (see spectrum c in Figure 3B), except that the peak at 4972.6 eV did not appear for FeTiO$_3$. The pre-edge (spectrum a in Figure 3A) and post-edge peak patterns well resembled that for amorphous TiO$_2$ that has been reported elsewhere.39,45,62

All the pre-edge spectral patterns for N-doped and SN-doped mesoporous TiO$_2$ and S-doped mesoporous TiO$_2$-583 and 623...
The amplitude of $k^{3}$-weighted EXAFS function and its associated Fourier transform for S-doped mesoporous TiO$_2$-623 resembled the corresponding data for SN-doped one (see spectra e and c in Figure 4). The best-fit result for the former in the region of $1.13 - 3.17$ Å was Ti–O bonds at 1.879 Å with $N = 4.4$, Ti–S bonds at 2.283 Å with $N = 0.7$, and Ti(–O)–Ti bonds at 3.05 and 3.24 Å with a total of $N = 8.4$ (see spectrum c in Table 4).

The $k^{3}$-weighted EXAFS function and its associated Fourier transform for S-doped mesoporous TiO$_2$-583 resembled the corresponding data for SN-doped one (see spectra e and c in Figure 4). The best-fit result for the former in the region of $1.03 - 3.18$ Å with four shells of Ti–O, Ti–S, and two Ti(–O)–Ti was similar to that for the latter, but the Ti–S bond distance was longer at 2.40 Å and Ti–O and Ti(–O)–Ti coordination was greater (6.2 and 10.8, respectively), compared to values obtained for the SN-doped one (see entries e and c in Tables 4).

Ethanol Photo-oxidation Reactions under Visible Light.

Over mesoporous TiO$_2$, acetaldehyde (2.1 $\mu$mol h$^{-1}$ g$_{cat}$$^{-1}$) and water (3.4 $\mu$mol h$^{-1}$ g$_{cat}$$^{-1}$) were formed in the ethanol oxidation reaction under visible light (>420 nm) (see Figure 5a and entry a in Table 5). A similar acetaldehyde formation rate (2.3 $\mu$mol h$^{-1}$ g$_{cat}$$^{-1}$) was reported, but the water formation rate in the literature (16 $\mu$mol h$^{-1}$ g$_{cat}$$^{-1}$) decreased to 21% (see entry a in Table 5). Because the pretreatment of catalyst was extended from 2 h under vacuum (from ref 65) to 10 h under vacuum, under UV–visible light (>370 nm) in this work, the difference of surface hydroxyl group density over TiO$_2$ may be critical for the photo-oxidation of O$_2$. Pretreated under the more-severe condition, the products were exclusively acetaldehyde and water and no CO$_2$, acetic acid, or formic acid were detected.

The product formation rates over N-doped and SN-doped ones were 1.1–1.8 times and 2.3–6.8 times greater, respectively, than corresponding values over mesoporous TiO$_2$ (see spectra a in Table 4). The promotion of water formation was greater by S-doping than N-doping.

Next, the SN-doping effect was compared to S-doping effect via CVD on mesoporous TiO$_2$. The acetaldehyde formation was not promoted, but the water formation rate was 11 times greater over S-doped mesoporous TiO$_2$-583 compared to under doped one (see spectra d in Table 4). The promotion of acetaldehyde formation over S-doped mesoporous TiO$_2$-623 was 1.9 times similar extent to SN-doped and N-doped ones (1.8–2.3 times). Water formation was dramatically promoted.
by a factor of 12 times over S-doped mesoporous TiO$_2$-623 than that over mesoporous TiO$_2$ (see spectra e and a in Table 5). The photocatalytic result over TiO$_2$ nanotube-S was similar to that for S-doped mesoporous TiO$_2$-583 (see Table 5f).

In summary, S-doping was effective to mesoporous TiO$_2$ for the O$_2$ reduction to water under visible light (>420 nm). Even small amount of S in TiO$_2$ nanotube-S was as effective as relatively greater amounts of S in SN-doped mesoporous TiO$_2$ and S-doped mesoporous TiO$_2$-623. In contrast, the promotion of acetaldehyde formation was only 0.90–2.3 times greater, upon doping with either sulfur or nitrogen.

The formation rate dependences on the cut-off wavelength (370–580 nm) were plotted for water and acetaldehyde (see Figure 5B). The S-doped mesoporous TiO$_2$-623 catalyst that exhibited extended visible-light absorption tailing (see spectrum e in Figure 1) was used. The water formation rate under visible light with a wavelength of >580 nm was still 33% of that under visible light with a wavelength of >420 nm in Figure 5B. The water formation rate decreased similar to the decomposition rates of Methylene Blue$_2^{24}$ and 2-propanol$_2^{25}$ over S-doped TiO$_2$ as the cutoff wavelength progressively increased. These dependences were effectively less steep, compared to the ethanol oxidation over V-doped mesoporous TiO$_2$,$_x$N$_y$,$_z^{3}$ and the water decomposition over Ti$_{1-x}$N$_x$F$_y$ and Ga$_{1-x}$Zn$_x$N$_y$.$_z^{67}$

Discussion

N-Doped Mesoporous TiO$_2$. Nitrogen was doped in/on TiO$_2$ with uniform mesopores. Nitrogen doping using urea during template synthesis negligibly affected the optical spectra (see spectra a and b in Figure 1). The $E_g$ value was 2.8 eV (see Table 2A). The $E_g$ values were 2.46–3.17 eV for N-doped TiO$_2$,$_x$,$_y$,$_z^{12,15,17,20,21}$ except for that synthesized from hexamethylenetetramine and TiCl$_4$ solvo-thermally, which was 2.29 eV (Table 1).$^{13}$ The Ti 1s–3d pre-edge peak pattern did not change because of the nitrogen doping (see spectra a and b in Figure 1A), demonstrating an amorphous TiO$_2$ matrix.

Based on Ti K-edge EXAFS analyses, the bond distances for two Ti–O (or Ti–N) and two Ti(−O–)Ti (or Ti(−N–)Ti) shells changed only within 0.03 Å, but the total N for Ti–O (or Ti–N) bonds effectively increased, starting from 4.2 to 6.2, because of the nitrogen doping (see spectra a and b in Table 4). This suggests a transition from unsaturated TiO$_{1-x}$N$_x$ octahedra. Thus, N atoms substituted on the O sites of the TiO$_2$ matrix with uniform mesopores to form O−Ti–N bonds, in accord with EPR and DFT study.$^{16}$ The matrix was not distorted much, based on similar Ti–O (or Ti–N) and Ti(−O–)Ti (or Ti(−N–)Ti) bond distances (see spectra a and b in Table 4), because the atomic sizes of the O and N atoms are similar. The doping effect of nitrogen was a promotion of acetaldehyde formation by only 1.8 times under visible light (see spectra a and c in Table 5).

S-Doped Mesoporous TiO$_2$. Sulfur was doped in/on TiO$_2$ with uniform mesopores via co-doping or CVD. The absorption tailing in the visible-light region grew progressively in the following order: TiO$_2$ nanotube-S < S-doped mesoporous TiO$_2$-583 ≈ mesoporous TiO$_2$ < SN-doped mesoporous TiO$_2$ < S-doped mesoporous TiO$_2$-623 (see spectra g, d, a, c, and e in Figure 1). Corresponding $E_g$ values were 3.1, 3.0 (1.7), 2.9, 2.2, and 0.8 eV, respectively (see Table 2). The $E_g$ values of 2.3–2.6 eV were reported for S-doped TiO$_2$ (see Table 1).$^{22,28}$ The sulfur doping via CVD (see spectrum e in Figure 1) at 623 K may be excessive.
Although the average pore size remained unchanged in the range of 2.7–2.9 nm by SN-doping (see Table 2A), the uniform mesopore structure was destroyed for S-doped TiO$_2$ via CVD, because of the high reaction temperature (583–623 K). With the increase in the amount of doped heteroatom, the bonding strain of solid progressively increases and uniform mesopores should become unstable. In fact, the specific SA decreased from 608 m$^2$/g to 229 m$^2$/g (SN-doped mesoporous TiO$_2$) (see Table 2A), similar to the progressive decrease of specific SA for vanadium-doped mesoporous TiO$_2$. The retardation of phase transition from the anatase phase to the rutile phase in the temperature range of 973–1173 K was reported by doping of S and N, resulting in the relatively higher specific SA (53.3–10.0 m$^2$/g), compared to that for undoped TiO$_2$. In this work, the doped S/N partially inhibited uniform mesostructure formation consisted of amorphous Ti oxide/hydroxide and dodecylamine, resulting in a relatively lower SA, compared to that for undoped mesoporous TiO$_2$. The specific SA decreased to 1.9–2.6 m$^2$/g for S-doped mesoporous TiO$_2$-583 and 623 (Table 2B), which is consistent with the loss of uniform mesopores.

The Ti 1s–3d pre-edge peak pattern remained unchanged for mesoporous TiO$_2$, SN-doped mesoporous TiO$_2$, S-doped mesoporous TiO$_2$-583, and S-doped mesoporous TiO$_2$-623.

Figure 5. Panel (A) shows the time course of ethanol oxidation reactions over (a) mesoporous TiO$_2$, (b) N-doped mesoporous TiO$_2$, (c) SN-doped mesoporous TiO$_2$, (d) S-doped mesoporous TiO$_2$-583, (e) S-doped mesoporous TiO$_2$-623, and (f) titanate nanotube-S under the illumination of xenon arc lamp filtered with L42 (>420 nm) in the first 2 h and L37 (>370 nm) in next 2 h. Panel (B) shows the rate dependence of acetaldehyde and water formation on the cutoff filter wavelength over S-doped mesoporous TiO$_2$-623.
Doped TiO$_2$ for O$_2$ Reduction under Visible Light


<table>
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<td>a</td>
<td>mesoporous TiO$_2$</td>
<td>2.1 3.4 0</td>
<td>this work</td>
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<tr>
<td>a'</td>
<td></td>
<td>2.3 16 0.3</td>
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<tr>
<td>b</td>
<td>SN-doped mesoporous TiO$_2$</td>
<td>4.8 23 0</td>
<td>this work</td>
</tr>
<tr>
<td>c</td>
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<td>this work</td>
</tr>
<tr>
<td>d</td>
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<td>this work</td>
</tr>
<tr>
<td>e</td>
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<td>3.9 42 0</td>
<td>this work</td>
</tr>
<tr>
<td>f</td>
<td>TiO$_2$ nanotube-S</td>
<td>1.9 39 0</td>
<td>this work</td>
</tr>
<tr>
<td>g</td>
<td>TiO$_2$(P25)</td>
<td>19 4.9 0.2</td>
<td>65</td>
</tr>
<tr>
<td>h</td>
<td>V-doped mesoporous TiO$_2$</td>
<td>23 16 0.3</td>
<td>60, 65, 66</td>
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</tbody>
</table>

*For entries a’, g, and h, the pre-treatment was evacuation for 2 h at 290 K. For entries a–f, the pretreatment was evacuation for 10 h at 290 K under UV-visible light (>370 nm).*

Photocatalytic Role of Doped S. The promotion of acetaldehyde formation by doping sulfur was in the order of TiO$_2$ nanotube-S ≈ S-doped mesoporous TiO$_2$-583 (0.48 wt % S) < S-doped mesoporous TiO$_2$-623 (0.77 wt % S) < SN-doped mesoporous TiO$_2$ (1.7 wt % S) in ethanol + O$_2$ under visible light (>420 nm) (Table 5) in the same order of sulfur contents (see Table 2) or the N value increase for Ti–S bonds obtained by EXAFS (see Table 4). The promotion by doped S (or SN) was only 0.90–2.3 times greater, which is comparable to the factor of 1.8 observed by doped N.

In contrast, the photoreduction of O$_2$ to water was enormously enhanced by doping sulfur. The promotion ratio was in the order of SN-doped mesoporous TiO$_2$ (6.8) < TiO$_2$ nanotube-S (11) < S-doped mesoporous TiO$_2$-583 (11) < S-doped mesoporous TiO$_2$-623 (12), which is much greater than the ratio of 1.1 observed for N-doped mesoporous TiO$_2$ (see Table 5). The sulfur contents and the N values for Ti–S bonds (0.7, 0.2, and 0.5 for SN-doped mesoporous TiO$_2$, S-doped mesoporous TiO$_2$-583, and S-doped mesoporous TiO$_2$-623, respectively) were not correlated to the promotion ratio for water formation. The preferential water formation (reduction side) rather than acetaldehyde (oxidation side) under visible light was also demonstrated as the less steep decrease of water formation rate than that for acetaldehyde as the cutoff wavelength progressively increased (see Figure 5B). Thus, anionic doped sulfur was the key to promote O$_2$ reduction to water under visible light, even in the presence of small amount of sulfur. The promotion was not enhanced more with further sulfur doping. The amount of sulfur (0.48 wt%) doped via the CVD method at 583 K was sufficient to effectively produce electrons and holes under visible light. Additional amounts of sulfur via CVD at 623 K (0.77 wt % S) or thiourea mixing (1.7 wt % S) were excessive. In contrast, the doped molar amount of nitrogen by mixing urea (N/Ti molar ratio = 1/1) may be fewer, because typical doped amounts for nitrogen were reported to be 0.1–2.5 at. % in TiO$_2$. Also, the change in UV–visible data was trivial upon nitrogen doping in this study (see Figure 1). The difference in doping amount should be one of the major reasons for the difference in reactivity on the reduction side (water formation) between S-doped and N-doped mesoporous TiO$_2$ (see Table 5).

The formation rate ratio of acetaldehyde and water was 0.62 over mesoporous TiO$_2$ and 1.4 over V-doped mesoporous TiO$_2$ (see entries a and h in Table 5) to 0.65. The reaction mechanism was listed in reactions 1–5. The reaction mechanism that was promoted by anionic sulfur is also proposed in reactions 1′–5′ (major route) and reactions 1′′–5′′ (minor route).

The pretreatment condition in this work (10 h under vacuum, in UV–visible light) decreased catalytic water formation rates, relative to the condition of 2 h under vacuum$^{65}$ for mesoporous TiO$_2$ (see entries a and a’ in Table 5). This difference is related to the surface concentration of the hydroxyl group. The more-severe condition in this work is more realistic in practical application, because the remarkably quick water formation in ref 65 (212 µmol h$^{-1}$ g$_{cat}^{-1}$) occurred only in the initial hour of reaction, and the rate gradually decreased in repeated catalytic tests$^{66}$ Under visible light (>420 nm), reaction 5 (one-to-one formation of acetaldehyde and water) proceeded over V-doped mesoporous TiO$_2$. Reductive reaction 4 of O$_2$, with the excited electrons formed when the doped cation impurity level was below the CB minimum of TiO$_2$ (see Scheme 1), should be less effective, compared to reaction 4′ or 4′′ proceeding at the CB of S-doped TiO$_2$, based on water formation rates in Table 5. Actually, the four electron-reduction reaction 4, 4′, or 4′′
consists of several elementary steps, probably including the formation of reactive hydroxyl radicals. \(^{1,14,60,72-75}\) Another possibility of the minor route is that the S\(-\)Ti that forms oxidizes surface OH to •OH radical. The •OH radical oxidizes ethanol and O\(_2\) is reduced similarly to reaction 4.

On the other hand, oxidative reaction 3 to produce acetaldehyde proceeded at the VB of V-doped mesoporous TiO\(_2\) (see entry h in Table 5), but the reaction \(^3\) was seriously inhibited at the S\(^2\) impurity level (see Scheme 1). Therefore, major route reaction \(^5\) proceeded in a manner in which photocreated holes were accumulated in the sulfur. The energy interval between the CB minimum and (highest) S impurity level was 0.8\(-\)2.2 eV, based on the UV\(\rightarrow\)visible spectra (see Table 2). Thus, the major reason seems energetic; the S\(^2\) impurity level would be enough high above the VB\(^3,26,61\) than the oxidation potential between ethanol and acetaldehyde and may not receive electron from the substrate (see Scheme 1). Alternative explanation based on kinetics is that HS-Ti should participate in the O\(_2\) reduction in reaction \(^4\), but the reactivity may be lower than that for HO-Ti and reaction \(^4\) may proceed slower than reaction \(^4\).

The coordinative unsaturation of Ti was demonstrated by the decrease of first and second coordination Ti\(-\)O and Ti\(-\)O\(\rightarrow\)Ti from 6 and 12, respectively, for standard compound (see Table 3) to 4.2\(-\)6.2 and 8.4\(-\)10.8, respectively, in addition to 0.2\(-\)0.7 of Ti\(-\)S coordination for S-doped mesoporous TiO\(_2\) samples (see Table 4). Therefore, it is consistent that adsorbed ethoxy group in reaction \(^2\) or \(^2\) has a tendency to remain stable on the surface\(^{53,54}\) and only O\(_2\) reduction to water proceeded catalytically over S-doped catalysts. The amount of hydrogen dissociated from ethanol (reaction \(^2\)) that was supplied for catalytic tests corresponds to water formed for 6.5 h over most active S-doped mesoporous TiO\(_2\) (see reaction \(^5\) and Table 5) and was not totally consumed in reaction tests for 4\(-\)5 h (see Figure 5).

In summary, sulfur that was doped on/in mesoporous TiO\(_2\) formed filled impurity level(s) located 0.8\(-\)2.2 eV below the CB minimum. The electron excitation from the S level(s) to CB and further to O\(_2\) was enabled under visible light. In contrast, the sufficiently high potential of the S level(s) than VB of mesoporous TiO\(_2\) was disadvantageous to receive electron (directly or indirectly) from ethanol/ethoxy. Thus, the reduction of O\(_2\) to water (and oxidation from ethanol to adsorbed ethoxy species) proceeded 6.8\(-\)12 times faster than mesoporous TiO\(_2\). The high potential nature of S-doped mesoporous TiO\(_2\) would be applied for the decomposition of volatile organic compounds (VOCs) or dyes of higher oxidation potential than the impurity S level or for the reverse reaction of water oxidation to O\(_2\) and proton reduction to H\(_2\) (water splitting).\(^{76}\)

**Conclusions**

SN-doped TiO\(_2\) with uniform mesopores centered at 2.9 nm was synthesized using thiourea. The specific surface area (SA) decreased from 608 m\(^2\)/g (mesoporous TiO\(_2\)) to 229 m\(^2\)/g, because of bonding strain at the doped sulfur and nitrogen in the solid. S-doped TiO\(_2\) was also synthesized via chemical vapor deposition (CVD) of H\(_2\)S over mesoporous TiO\(_2\) at 583 or 623 K. The specific SA seriously decreased to 1.9\(-\)2.6 m\(^2\)/g, in accord with the loss of uniform mesopores of TiO\(_2\). The absorption tailing in the visible-light region was ranked in the following order: S-doped mesoporous TiO\(_2\)-583 \(\approx\) mesoporous TiO\(_2\) < SN-doped mesoporous TiO\(_2\) < S-doped mesoporous TiO\(_2\)-623. The ultraviolet\(\rightarrow\)visible (UV\(\rightarrow\)vis) absorption data indicated the formation of S impurity energy level(s) located 0.8\(-\)2.2 eV below the conduction band (CB) minimum of mesoporous TiO\(_2\). The Ti\(-\)S bonds were detected at 2.283\(-\)2.44 Å for these samples by extended X-ray absorption fine structure (EXAFS), demonstrating the presence of substitutional anionic sulfur on the O sites of the TiO\(_2\) matrix.
The anionic sulfur doping enabled electron excitation from the impurity level(s) to the CB and then to O2 to form water (12 × promotion, compared to mesoporous TiO2) under visible light, but ethanol oxidation was promoted by only 2.3 times, because the sulfur impurity level(s) with relatively high electrochemical potential made receiving (directly or indirectly) the electron from ethanol/ethyl alcohol difficult. The kinetic effects of Ti–OH, Ti–SH, or OH radicals were also suggested. Nitrogen doping to mesoporous TiO2 was not effective. Although the amount of doped sulfur was minimal for TiO2 nanotube synthesized hydrothermally using TiS2, based on the optical spectrum, the photocatalytic result was similar to that over S-doped mesoporous TiO2. Even in the presence of a small amount of anionic sulfur on/in TiO2, the O2 reduction to water was promoted.

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References and Notes


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