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

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Received: December 9, 2008; Revised Manuscript Received: February 20, 2009

Anion doping to titanium oxide (TiO_2) 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 TiO_2 with a narrow pore size distribution, at 3 nm, using thiourea or urea. They were compared to the uniform mesoporous TiO_2 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 >580nm), water formation was promoted by a factor of 12, in clear contrast to the only $2.3 \times$ 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 TiO_2 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 TiO_2 . It enabled the electron excitation to the CB and then to O_2 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/ethoxyl). Preferential water formation under visible light was also observed for TiO_2 nanotubes that were synthesized hydrothermally from TiS_2 .

Introduction

The band gap value (E_g) 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 E_g 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 E_g 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 fullpotential linearized-augmented-plane-wave method. Nonmetal anion doping to TiO₂ was predicted to reduce the E_g 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,^{3,11–21} S,^{22–28} F,^{29–31} Cl and Br,³² and I^{33–35} 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). 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 N[•] 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 and of 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 S^{4+}/S^{6+} on the Ti sites starting from thiourea or sulfuric acid^{22,24–27} 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,^{38,39} Fe,³⁸ Zr,³⁸ Nb,³⁸ Mo,^{38,40} 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 nanotubes 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

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	heteroanion		TiO ₂					
element	precursor	precursor	synthesis route	visible light absorption (shoulder, tail) (nm)	$E_{ m g}$ (eV)	reactant of photocatalysis	promoted ratio	reference
В	BH ₃	TiCl ₄	sol-gel	400-800		MTBE	$6 \times$ that of anatase	4
00	CO ₂	Ti metal	pyrolysis	410-560	2.32	water (electrochemical)	$7.7 \times$ that of TiO ₂	ŝ
ט נ	HU(CH2)2UH NBu4 ⁺ OH ⁻	TiCl ₄	anouization (iv 1) sol-gel	400 - 700	2.2 3.17 - 3.02	water (electrochemical) 4-chlorophenol	$76 \times \text{that of TiO}_2$	0 1-
C	TiC	TiC	calcined	380 - 600	2.9	CCI ₃ CO ₂ H	$14 \times \text{that of TiO}_2$	8
C	TiC	TiC	calcined	390 - 600		2-propanol	$0.1 \times \text{that of N-TiO}_2$	6
C	TiC	TiC	calcined	390-600		methylene blue		6
Z	$\rm NEt_3$	$Ti(O^{-i}Pr)_4$	sol-gel	380 - 690		Methylene Blue		11
Z	NEt ₃ , etc.	$Ti(O-Bu)_4$	hydrothermal	380 - 600	2.95 - 2.70	Rhodamine B, 2,4-dichlorophenol	$1.1-2.8 \times$ that of TiO ₂	12
Z	$N_4(CH_2)_6$	TiCl ₃	solvothermal	390 - 600	2.48 - 2.29	nitric oxide	$5 \times$ that of P25	13
z;	N_2	anatase/rutile	sputtering	390-600		Methylene Blue	8× that of anatase/rutile	ς, ω
Z	$N_4(CH_2)_6$, urea	P25	milling	400 - 600		nitric oxide	$1-4 \times$ that of P25	14
Z	TiN	NiT	calcined	420 - 600	2.94	acetaldehyde	$20 \times$ that of P25	15
Z	$NH_4^+CI^-$	$Ti(O'Pr)_4$	sol-gel	400 - 580		Methylene Blue	$1.3 \times$ that of TiO ₂	16
Z	$\rm NH_3$	titanate NT	hydrothermal	400 - 500	3.17	2-propanol		17
Z	NH3	anatase	CVD	380 - 500		formic acid	$4 \times$ that of anatase	18
Z	$\rm NH_4^+OH$	TiCl ₄	sol-gel	390-700	2.8	Methyl Orange		20
Z	urea	titanate	impregnated	380 - 500	2.46	4-chlorophenol	$8 \times$ that of TiO ₂	21
N, C	$Ti[OC(NH_2)_2]_6Cl_3$	$Ti[OC(NH_2)_2]_6Cl_3$	calcined	380 - 550	1.87	Methyl Orange	$1.7 \times \text{that of P25}$	19
S	thiourea	$Ti(O^{-i}Pr)_4$	impregnated	410-600	2.4 - 2.3	water (solar cell)		22
S	TiS_2	TiS_2	calcined	380 - 580		Methylene Blue		23
S	thiourea	$Ti(O^{-i}Pr)_4$	sol-gel	400 - 600		Methylene Blue	$1.0-10\times$ that of TiO ₂	24
S	thiourea	$Ti(O^{-i}Pr)_4$	sol-gel	400 - 600		2-propanol	$0.9 - 10 \times$ that of TiO ₂	25
S	thiourea	$Ti(O^{-i}Pr)_4$	sol-gel	380 - 600		Methylene Blue	$10 \times \text{that of TiO}_2$	26
S	H_2SO_4/TiS_2	$Ti(O^{-i}Pr)_4/TiS_2$	sol-gel			Rhodamine 6G	$10 \times \text{that of TiO}_2$	27
S	CS_2	Ti(O-Bu) ₄	supercritical	390-700	2.6	Methylene Blue	$7.9 \times$ that of TiO ₂	28
Ц	$\rm NH_4^+F^-$	$Ti(O^{-i}Pr)_4$	sol-gel	400-520	2.90	acetone	$1.3 \times$ that of P25	29
F, N	H_2TiF_6	TiCl ₄	pyrolysis	390 - 550		acetaldehyde	$7 \times$ that of P25	30
F, N	$(NH_4^+)_2 TiF_6^{2-}$	$(NH_4)_2 TiF_6$	sol-gel	380 - 550	2.34	water		31
Cl, Br	HBr	TiCl4	hydrothermal	370-500		water	$3 \times$ that of P25	32
$(I_2)_n$	I crystal	$Ti(O'Pr)_4$	sol-gel	425-770		Methylene Blue	$10 \times$ that of P25	33
Π	HIO ₃	$Ti(O-'Pr)_4$	hydrothermal (template)	400 - 600		Methylene Blue	7× of P25	34
I	HIO_3	$Ti(O-Bu)_4$	sol-gel	380 - 650		phenol	$6 \times$ of P25	35

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,⁴ C 1s,^{6,7,9,10} N 1s,^{3,11–13,18,20,21} S $2p_{3/2}$,^{24,25,27,28,37} and I $3d_{5/2}$,^{34,35} X-ray photoelectron spectroscopy (XPS). To judge the dopant sites (substitutional or interstitial), valence (cationic, neutral, or anionic), and geometric distribution (at surface or in bulk) on/in the TiO₂ matrix, synthesized sulfur- or nitrogen-doped TiO₂ were investigated using Ti K-edge extended X-ray absorption fine structure (EXAFS) for the first time to nonmetal-doped TiO₂. S K-edge 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,⁹ nitrogen-doped,¹⁷ sulfur-doped,²⁵ or vanadium-doped TiO_2^{42} from 2-propanol to acetone and then to $CO/CO_2^{9,17,25}$ or from ethanol to acetaldehyde, then to formic acid, and finally to CO/CO_2 .⁴² The effects of dopants to facilitate band-gap exitation were discussed under visible light. The reaction mechanism of photo-oxidation of methanol, ethanol, and 1-propanol was already discussed in detail, including the formation of •OH radicals and hole oxidation for adsorbed intermediates but over undoped TiO₂ under UV light.^{43,44} Therefore, in this work, the difference of ethanol oxidation reactivity under visible light among synthesized sulfur- or nitrogen-doped mesoporous TiO₂ (or TiO₂ nanotubes) was discussed based on analyzed site structures of doped sulfur or nirogen and their associated band structures. The role of sulfur or nitrogen in the reduction of O_2 and the oxidation of alcohol is presented.

Experimental Section

Reagents and Catalyst Syntheses. Rutile-type TiO₂ (<5 μ m in size, >99.9% purity, Wako Pure Chemicals), anatase-type TiO₂ (<5 μ m in size, >99.9% purity, Wako Pure Chemicals), and FeTiO₃ (>99.8% purity, Alfa Aesar) were used as received.

Water (40 mL) was added dropwise to a mixture of titanium tetraisopropoxide (28.0 mmol; >95% purity, Wako Pure Chemicals), thiourea (14.0 mmol; >98% purity, Wako Pure Chemicals), and dodecylamine (14.0 mmol; >95% purity, Wako Pure Chemicals) at 273 K. A measured quantity (1.6 mL) of hydrogen chloride (0.1 M; Precious Analytical grade, Wako Pure Chemicals) was added, and the mixture was left still overnight. The mixture then was transferred to a Teflon container and maintained at a temperature of 333 K for 4 days. The solid was filtered and washed with methanol (>99.8%, Wako Pure Chemicals) and diethyl ether (>99.5%, Wako Pure Chemicals). The obtained powder was dried at 373 K for 1 day and then evacuated at 453 K in a Pyrex glass tube that was connected to a vacuum system (10^{-6} Pa) for 2 h. The tube was sealed by fire and kept at 453 K for 10 days. The resulting solid was washed with carbon disulfide (>99%, Wako Pure Chemicals), an ethanol (>99.5%, Wako Pure Chemicals) solution of *p*-toluenesulfonic acid (>99%, Wako Pure Chemicals), and finally ethanol (see Table 2A). The washing was repeated until no dodecylamine or its decomposed compounds was detected for the filtrate in the UV-visible spectra. The powder was evacuated (10^{-6} Pa) at 373 K for 2 h. After the heating, no organic compounds (<10 nmol) were detected in gas chromatography (GC) measurements. The thus-synthesized sample is denoted as SN-doped mesoporous TiO₂.

Mesoporous TiO₂ was synthesized based on the literature⁴⁵ (see Table 2A). The synthesis route of nitrogen-doped mesoporous TiO₂ was similar to that for mesoporous TiO₂. Urea (14.0 mmol, >99% purity, Wako Pure Chemicals) was used as a nitrogen dopant. Note that the carbon from the urea or thiourea may remain in the catalysts, but identification of the source was difficult: it was either from urea/thiourea or dodecylamine/ ethanol. Hence, these samples are simply denoted as SN-doped/N-doped mesoporous TiO₂. The filtered powder after heating at 333 K for 4 days was washed only with diethyl ether (see Table 2A). The washing was repeated until no dodecylamine, nor its decomposed compounds, was detected for the filtrate in the UV-visible spectra.

After intact mesoporous TiO₂ was evacuated (10^{-6} Pa) at 290 K for 3 h, 101 kPa of H₂S was introduced and the temperature was elevated from 290 K to 583 K or 623 K, with a ramping rate of 6 K/min. Thus-synthesized samples are denoted as S-doped mesoporous TiO₂-583 or TiO₂-623 (see Table 2B).

Titanate nanotubes were synthesized based on the literature method,⁴⁶⁻⁴⁹ 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 (TVS-1-30, Taiatsu Techno) 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 thussynthesized sample is denoted as "TiO₂ nanotube".⁴⁷ A nanotube sample that contained tetravalent titanium (Ti^{IV}) 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 (referenced hereafter as TiO_2 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-reflectance 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, $\alpha \times h\nu \propto (h\nu - E_g)^2$, in which α , h, and ν are absorption coefficient, Planck constant, and wavenumber, respectively.^{7,19–22,28,50,51}

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 $2\theta_{Bragg} = 1.5^{\circ}-50^{\circ}$. Conditions involved 30 kV, Cu K α 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

				(A) Doping during Ten	mplate Synthesi	S				
				Washin	ng Medium after	r Heating				
Sample	additive	molar ratio ^a	TiO ₂ phase	at 333 K		at 453 K	S content (wt $\%)^l$	mesopore $d_{\rm XRD} (\rm nm)^c$	$S_{\rm BET}$ (m ² /g)	$\stackrel{E_{\mathrm{g}}}{(\mathrm{eV})}$
mesoporous TiO ₂ SN-doped mesoporous TiO ₂ N-doped mesoporous TiO ₂	$(H_2N)_2C=S$ $(H_2N)_2C=O$	S/Ti = 1/2 N/Ti = 1/1	amorphous amorphous amorphous	methanol, diethyl ether methanol, diethyl ether diethyl ether	r <i>p</i> -toluenest CS ₂ , <i>p</i> -tolu	ulfonic acid/ethanol lenesulfonic acid/ethanol ılfonic acid/ethanol	1.7	2.7 2.9	608 229	2.9 2.2 2.8
				(B) CVD D(oping					
sample	addi	itive $T(0)$	K) TiO ₂	phase S content	: (wt %) ^b	mesopore d_{XRD} (nm) ^c	$S_{\rm BET}~({ m m}^2/{ m g})$	$E_{\rm g} ({ m eV})$		
S-doped mesoporous TiO ₂ -5 S-doped mesoporous TiO ₂ -6	583 H ₂ 523 H ₂	² S 58 ² S 62	3 amor 3 amor	phous 0.4 phous 0.7	48 77	not detected not detected	1.9 2.6	3.0(1.7) 0.8		
				(C) Hydrothermal	1 Synthesis					
						lanotube Dimensions ^d				
sample	source	Ti/NaOl	H molar ratio ^a	TiO ₂ phase	$d_{\rm TEM}({ m nm})$	t_{TEM} (mm) l	rem (nm) Sbet	$(m^2/g)^d$ E	$_{g} (eV)^{e}$	
titanate/TiO ₂ nanotube	TiO ₂ (P25)		1/4	amorphous ^d anatase ^e	7.9	2.3	29	334	3.1	
titanate/TiO ₂ nanotube-S	TiS_2		1/37	amorphous ^d anatase ^e	3.9	0.83	62	110	3.1	

TABLE 2: Synthetic Conditions and Physicochemical Properties of Mesoporous TiO₂-, S-, or N-Doped Mesoporous TiO₂, and Titanate/TiO₂ Nanotubes, Created via (A) Doping during Template Synthesis, (B) CVD Doping, or (C) Hydrothermal Synthesis

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), and l_{TEM} (average length, as determined by TEM analysis). ^e After calcining at 673 K.

		Mode	el	Data Rang	ges Used	
shell	compound	\overline{R} (Å)	Ν	k (Å ⁻¹)	<i>R</i> (Å)	reference
Ti-O	rutile-type TiO ₂	1.959	6	1.92-15.00	1.27-1.75	57, 58
Ti(-O-)Ti	rutile-type TiO ₂	3.058	12	1.92 - 15.00	2.34 - 2.87	57, 58
Ti-S	TiS ₂	2.430	6	2.85 - 14.12	1.54 - 2.39	59

255 mA. A Si(111) double-crystal monochromator and cylindrical double mirror were inserted into the X-ray beam path. The parallelness 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 I_0 ionization chamber. The I_0 and I_t 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 I_0 and I_t 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 preedge 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, $C_2/E^2 + C_1/E + C_0$. The background of post-edge oscillation was approximated by a smoothing-spline function, calculated using an equation for the number of data points (*N*).

$$\sum_{i=1}^{N} \frac{(\mu x_i - BG_i)^2}{\exp(-0.075k_i^2)} \le \text{smoothing factor}$$

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 σ^2 values listed in Table 4 were relative to those of the references. The many-body reduction factor S_0^2 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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Ti-O (or $Ti-N$)				Ti-S		–)íľ	-0–)Ti [or Ti(-	-N-)Ti]	
N $\Delta \sigma^2 ({\rm \AA}^2)$ $R ({\rm \AA})$	$\Delta \sigma^2$ (Å ²) R (Å)	R (Å)		Ν	$\Delta\sigma^2$ (Å ²)	<i>R</i> (Å)	Ν	$\Delta\sigma^2$ (Å ²)	goodness of fit
$\begin{array}{llllllllllllllllllllllllllllllllllll$	-0.00025 (± 0.0019) -0.0017 (± 0.0020)			(a) Mesol	oorous TiO ₂ Sample	2.918 (±0.011) 3.191 (±0.005)	1.6 (±0.3) 7.1 (±0.9)	$\begin{array}{c} -0.0054 \ (\pm 0.0018) \\ 0.0058 \ (\pm 0.0002) \end{array}$	$2.6 imes 10^5$
3.2 (土0.8) 0.0052 (土0.0018) 3.0 (土0.6) 0.0039 (土0.0025)	0.0052 (土0.0018) 0.0039 (土0.0025)			(b) N-Doped N	Aesoporous TiO ₂ Sample	2.89 (±0.02) 3.181 (±0.008)	$\begin{array}{c} 0.8 \ (\pm 0.3) \\ 8.8 \ (\pm 0.8) \end{array}$	$-0.0046 (\pm 0.0005)$ $0.0092 (\pm 0.0009)$	2.1×10^{5}
$4.4 \ (\pm 0.5) \qquad 0.0059 \ (\pm 0.0011) \qquad 2.283 \ (\pm 0.003)$	0.0059 (土0.0011) 2.283 (土0.003)	2.283 (土0.003)		(c) SN-Doped] 0.7 (土0.04)	Mesoporous TiO₂ Sample −0.00002 (±0.0004)	3.05 (±0.04) 3.24 (±0.03)	$5.2 (\pm 1.0)$ $3.2 (\pm 0.5)$	$0.00063 (\pm 0.0017) -0.0039 (\pm 0.0010)$	$3.6 imes 10^4$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{l} (6 \\ -0.0030 (\pm 0.0019) & 2.44 (\pm 0.03) \\ -0.0030 (\pm 0.0044) & \end{array}$	(d 2.44 (±0.03)	(q	l) S-Doped Me 0.2 (±0.2)	soporous TiO₂-583 Sample −0.0078 (±0.0008)	2.905 (±0.010) 3.177 (±0.006)	2.2 (±0.4) 7.3 (±0.6)	$-0.0064 (\pm 0.0012)$ $0.00015 (\pm 0.0011)$	$5.8 imes 10^{5}$
(e 6.2 (土0.3) 0.0095 (土0.0004) 2.40 (土0.03)	(e 0.0095 (土0.0004) 2.40 (土0.03)	(e 2.40 (±0.03)	e)) S-Doped Me 0.5 (土0.1)	soporous TiO₂-623 Sample 0.00009 (±0.0008)	3.07 (±0.05) 3.290 (±0.014)	5.5 (±1.3) 5.3 (±1.2)	$\begin{array}{c} 0.0043 \ (\pm 0.0045) \\ -0.0013 \ (\pm 0.022) \end{array}$	$2.9 imes 10^4$



Figure 1. Diffuse-reflectance UV-visible absorption spectra for mesoporous TiO₂ (spectrum a), N-doped mesoporous TiO₂ (spectrum b), SN-doped mesoporous TiO₂ (spectrum c), S-doped mesoporous TiO₂-583 (spectrum d), S-doped mesoporous TiO₂-623 (spectrum e), TiO₂ nanotube (spectrum f), TiO₂ nanotube-S (spectrum g), and anatase-type TiO₂ (spectrum h). (Inset) Tauc plots for mesoporous TiO₂ (curve a), SN-doped mesoporous TiO₂ (curve c), S-doped mesoporous TiO₂-583 (curve d), S-doped mesoporous TiO₂-623 (curve e), and anatase-type TiO₂ (curve h).

chosen and fixed to dehydrate catalyst surface for fair comparison of the dependence tests on a cutoff wavelength of 370-580 nm.

To the reaction system, 1.33 kPa of ethanol and 2.67 kPa of oxygen were introduced. The light exit of the xenon arc lamp house (Ushio, Model UI-502Q) was set 2 mm apart from the bottom of the quartz reaction cell. One of the UV-cut filters L37, L42 (>420 nm), Y48 (>480 nm), Y52 (>520 nm), and O58 (>580 nm) (Kenko) was set at the light exit. Products and reactants were analyzed using online GC using Porapak-Q and Active Carbon columns (GL Sciences).

Results

UV–Visible Spectra. Optical spectra were measured for doped/undoped mesoporous TiO₂, TiO₂ nanotubes, and anatase-type TiO₂ (see Figure 1). The spectrum for anatase-type TiO₂ (spectrum h) exhibited negligible absorption in the wavelength region of >400 nm. The E_g value was evaluated to 3.2 eV (see curve h in the inset of Figure 1), which was consistent with values given in the literature.¹ The absorption edge for mesoporous TiO₂ shifted toward greater wavelength (spectrum a) compared to anatase-type TiO₂. The E_g value was evaluated to 2.9 eV (see curve a in the inset of Figure 1, and Table 2A).

The spectrum for N-doped mesoporous TiO₂ (spectrum b in Figure 1) was similar to that for mesoporous TiO₂. The E_g value was evaluated to 2.8 eV (see Table 2A). The spectrum for SN-doped mesoporous TiO₂ exhibited significant absorption tailing in the wavelength region between 370 nm and 600 nm (see spectrum c in Figure 1). The E_g value decreased to 2.2 eV (see curve c in the inset of Figure 1, and Table 2A).

The tailing in the visible-light region for S-doped mesoporous TiO_2 -583 was similar/less than that for mesoporous TiO_2 (see spectrum d in Figure 1, and curve a in the inset of Figure 1). The E_g value was evaluated to 3.0 eV (see Table 2B). Extrapolation to the *x*-axis was also possible to 1.7 eV, because of the excitation from a separate impurity S 3p level to the CB (see curve d in the inset of Figure 1).⁶¹ As the CVD temperature with H₂S was elevated from 583 K to 623 K, the tailing in the visible-light region became significant, starting from 370 nm to as much as 900 nm (see spectrum e in Figure 1). Its associated E_g value was 0.8 eV (see curve e in the inset of Figure 1, and Table 2B).

The absorption tailing for TiO_2 nanotube and TiO_2 nanotube-S was negligible and very weak, respectively, in the



Figure 2. High-resolution TEM image for titanate nanotube-S.

wavelength region of 400–600 nm (see spectra f and g in Figure 1). The E_g values were evaluated to 3.1 eV (see Table 2C). Predominant formation of anatase-type TiO₂ was reported^{46,47} at ~673 K, starting from titanate. The spectra f and g for TiO₂ nanotube and TiO₂ nanotube-S consisted of a major anatase phase and, therefore, exhibited negligible absorption at 400–600 nm, similar to that for anatase-type TiO₂ (see spectrum h in Figure 1).

Specific Surface Area, XRD, High-Resolution TEM, and S K-Edge XAFS. The Brunauer, Emmett, and Teller (BET) specific surface area (SA) obtained based on N₂ adsorption was greatest for mesoporous TiO₂ ($608 \text{ m}^2/\text{g}$). The specific SA decreased to 229 m²/g for the SN-doped mesoporous TiO₂ (see Table 2A). For S-doped mesoporous TiO₂ via CVD, the specific SA decreased to 1.9–2.6 m²/g (see Table 2B). The specific SA for titanate nanotubes was 110–334 m²/g on a level similar to SN-doped mesoporous TiO₂ (see Tables 2C and 2A).

Narrow pore size distribution centered at 2.7 nm ($2\theta_{\text{Bragg}} = 3.34^{\circ}$) for mesoporous TiO₂ was preserved for SN-doped mesoporous TiO₂ centered at 2.9 nm ($2\theta_{\text{Bragg}} = 3.09^{\circ}$; see Table 2A). The lower angle XRD peak disappeared for S-doped mesoporous TiO₂-583/623 (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 titanate nanotube changed to 3.9, 0.83, and 62 nm, respectively, for the thinner and longer titanate nanotube-S (see Figure 2). This is the first report of titanate/TiO₂ nanotube synthesis starting from TiS₂.

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 TiS₂: 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 preedge region for mesoporous TiO_2 , doped mesoporous TiO_2 , and titanate 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 FeTiO₃ (see spectrum c in Figure 3B), except that the peak at 4972.6 eV did not appear for FeTiO₃. 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



Figure 3. (A) Ti 1s-3d pre-edge region spectra for mesoporous TiO_2 (spectrum a), N-doped mesoporous TiO_2 (spectrum b), SN-doped mesoporous TiO_2 (spectrum c), S-doped mesoporous TiO_2 -583 (spectrum d), S-doped mesoporous TiO_2 -623 (spectrum e), titanate nanotube (spectrum f), and titanate nanotube-S (spectrum g). (B) Reference spectra for rutile-type TiO_2 (spectrum a), anatase-type TiO_2 (spectrum b), FeTiO₃ (spectrum c), and TiS_2 (spectrum d).

(see spectra b–e in Figure 3A) resembled that for mesoporous TiO_2 (spectrum a), suggesting a predominantly amorphous matrix structure (see Tables 2A and 2B). The weak peak at 4972.6 eV appeared for mesoporous TiO_2 -derivative samples (see spectra a–e in Figure 3A) shifted to 4972.3 eV for titanate nanotube and titanate nanotube-S (spectra f, g). The latter samples may consist of amorphous matrix structure distorted from titanate^{1,48,49} (see Table 2C).

Ti K-edge EXAFS. The k^3 -weighted EXAFS function measured for mesoporous TiO2 was depicted in spectrum a in panel (1) of Figure 4. In its associated Fourier transform (spectrum a in panel (2) of Figure 4), two intense peaks appeared at 1.2 and 1.7 Å (phase shift uncorrected), and those were assigned to Ti-O bonds. Two relatively weaker peaks appeared at 2.4 and 2.9 A (phase shift uncorrected). The data in region of 0.94-3.03 Å were fit with two Ti-O shells and two Ti(-O-)Ti shells. The best-fit result was Ti-O bonds at 1.75 and 2.00 Å with the total coordination number (N) 4.2 and Ti(-O-)Ti bonds at 2.918 and 3.191 Å with the total N = 9.5(see Table 4a and spectrum a in panels (3) and (4) of Figure 4). Note that site structure evaluated from EXAFS is the statistical average for all the element sites in the sample,^{63,64} and unsaturated and bulk saturated Ti sites were suggested. The weak shoulder feature at 2.1 Å was not fit as either Ti-O or Ti(-O)Ti (see spectrum a in panel (4) of Figure 4).

Both the k^3 -weighted EXAFS function and its associated Fourier transform for S-doped mesoporous TiO₂-583 wellresembled the corresponding data for mesoporous TiO₂ (see spectra d and a in Figure 4). The fit result for data in the region of 0.93–3.00 Å with four waves [two Ti–O and two Ti(–O–)Ti] was Ti–O bonds at 1.74 and 2.01 Å with the total N = 4.2 and Ti(–O–)Ti bonds at 2.905 and 3.177 Å with the total N = 9.5(see entry d in Table 4 and spectrum d in panels (3) and (4) in Figure 4). When a Ti–S shell was added in the fit, the fit result for two Ti–O and two Ti(–O–)Ti shells negligibly changed and Ti–S bonds at 2.44 Å with the N = 0.2 were given (see spectrum d in Table 4). The goodness-of-fit value negligibly changed at 5.8 × 10⁵ with the addition of one Ti–S shell.

The amplitude of k^3 -weighted EXAFS function for N-doped mesoporous TiO₂ was suppressed to <1.5 in the *k*-region of >8

Å⁻¹ (see spectrum b in panel (1) of Figure 4). Accordingly, the peak appeared at 2.4 Å in its associated Fourier transform became weaker (see spectrum b in panel (2) of Figure 4) than the peaks appeared at similar bond distances for other samples. The data in the region of 0.90–3.00 Å were first fit with three shells [two Ti–O (or Ti–N) and one Ti(–O–)Ti {or Ti(–N–)Ti}], but the goodness-of-fit value dramatically decreased from 7.8×10^5 in the three-shell fit to 2.1×10^5 in four-shell fit (see spectrum b in panels (3) and (4) of Figure 4). The best fit with four shells was Ti–O (or Ti–N) bonds at 1.73 and 2.00 Å with the total N = 6.2 and Ti(–O–)Ti {or Ti(–N–)Ti} bonds at 2.89 and 3.181 Å with a total of N = 9.6 (see entry b in Table 4).

The k^3 -weighted EXAFS function for SN-doped mesoporous TiO₂ (see spectrum c in panel (1) of Figure 4) was apparently different from the data in spectrum a, b, or d in panel (1) of Figure 4 in the *k*-region of >8 Å. In its associated Fourier transform (spectrum c in panel (2) of Figure 4), two peaks due to Ti–O bonds centered between 1 and 2 Å merged into one centered at 1.5 Å and a new shoulder peak appeared at 1.9 Å. The new peak was not fit with parameters of Ti–O bond, but nicely fit with those of Ti–S bond. The best-fit result for data 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 TiO₂-623 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 1.03–3.18 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 TiO₂, acetaldehyde (2.1 μ mol h⁻¹ g_{cat}⁻¹) and water (3.4 μ 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 μ mol h⁻¹ g_{cat}⁻¹) was reported,^{65,66} but the water formation rate in the literature (16 μ mol h⁻¹ g_{cat}⁻¹) decreased to 21% (see entry a versus 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 TiO₂ may be critical for the photo-oxidation of O₂. Pretreated under the more-severe condition, the products were exclusively acetaldehyde and water and no CO₂, 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 TiO₂ (see spectra a-c in Table 5). 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 TiO₂. The acetaldehyde formation was not promoted, but the water formation rate was 11 times greater over S-doped mesoporous TiO₂-583 compared to over undoped one (see spectra d and a in Table 5). The promotion of acetaldehyde formation over S-doped mesoporous TiO₂-623 was 1.9 times on similar extent to SN-doped and N-doped ones (1.8–2.3 times). Water formation was dramatically promoted



Figure 4. Ti K-edge EXAFS spectra for mesoporous TiO₂ (spectrum a), N-doped mesoporous TiO₂ (spectrum b), SN-doped mesoporous TiO₂ (spectrum c), S-doped mesoporous TiO₂-583 (spectrum d), and S-doped mesoporous TiO₂-623 (spectrum e). Panel (1) shows the k^3 -weighted EXAFS χ -function, panel (2) shows its associated Fourier transform, and panels (3, 4) best-fit the results in *k*-space (3) and *R*-space (4). (The thin red line represents the experimental values, and the thick blue line represents calculated values). (The dashed line (---) represents the magnitude and the dotted line (++++) represents the imaginary part (in panels (2) and (4).)

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 mesporous 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 TiO₂-623 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 Blue²⁴ and 2-propanol²⁵ over S-doped TiO₂ as the cutoff wavelength progressively increased. These dependences were effectively less steep, compared to the ethanol oxidation over V-doped mesoporous TiO₂,⁶⁰ the Methylene Blue decomposition over TiO_{2-x}N_y,³ and the water decomposition over Ti-N-O-F³¹ and Ga-Zn-N-O.⁶⁷

Discussion

N-Doped Mesoporous TiO₂. Nitrogen was doped in/on TiO₂ 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 ,^{12,15,17,20,21} except for that synthesized from hexamethylenetetraamine and $TiCI_3$ 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 3A), 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_y ($y \approx 4$) to saturated TiO_{6-x}N_x octahedra. Thus, N atoms substituted on the O sites of the TiO₂ 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 TiO₂. Sulfur was doped in/on TiO₂ with uniform mesopores via co-doping or CVD. The absorption tailing in the visible-light region grew progressively in the following order: TiO₂ nanotube-S < S-doped mesoporous TiO₂-583 \approx mesoporous TiO₂ < SN-doped mesoporous TiO₂ < S-doped mesoporous TiO₂-623 (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 TiO₂ (see Table 1).^{22,28} The sulfur doping via CVD (see spectrum e in Figure 1) at 623 K may be excessive.



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.

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 TiO₂ 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 m²/g to 229 m²/g (SN-doped mesoporous TiO₂) (see Table 2A), similar to the progressive decrease of specific SA for vanadium-doped mesoporous TiO₂.^{39,68} 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 $(53.3-10.0 \text{ m}^2/\text{g})$, compared to that for undoped TiO₂.⁶⁹ 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 TiO₂. The specific SA decreased to $1.9-2.6 \text{ m}^2/\text{g}$ for S-doped mesoporous TiO₂-583 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 TiO₂, SN-doped mesoporous TiO₂, S-doped mesoporous TiO₂-583, and S-doped mesoporous TiO₂-623

TABLE 5: Products Formation Rates in the Ethanol Photo-oxidation (55 μ mol of Ethanol, 110 μ mol of O₂) over Mesoporous TiO₂, S and/or N-Doped Mesoporous TiO₂, TiO₂ Nanotube-S, Crystalline TiO₂, and V-Doped Mesoporous TiO₂ under Visible Light (> 420 nm)

		Formati (µmol h	on Ra	$(1)^{-1}$	
entry ^a	catalyst	CH ₃ CHO	H_2O	CO_2	reference(s)
a	mesoporous TiO ₂	2.1	3.4	0	this work
a'		2.3	16	0.3	65,66
b	SN-doped mesoporous TiO ₂	4.8	23	0	this work
с	N-doped mesoporous TiO2	3.7	3.8	0	this work
d	S-doped mesoporous TiO ₂ -583	2.2	39	0	this work
e	S-doped mesoporous TiO ₂ -623	3.9	42	0	this work
f	TiO ₂ nanotube-S	1.9	39	0	this work
g	TiO ₂ (P25)	19	4.9	0.2	65
ĥ	V-doped mesoporous TiO_2	23	16	0.3	60, 65, 66

^{*a*} 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).

(see spectra a, c, d, and e in Figure 3A). Amorphous TiO_2 matrix was retained below the crystallization temperature of TiO_2 (623–673 K)⁶² and probably also due to the bonding strain of solid originating from doped sulfur or nitrogen.⁶⁹

Based on the Ti K-edge EXAFS analyses, Ti–S bond distances were obtained at 2.40-2.44 Å for S-doped mesoporous TiO₂-583 and TiO₂-623 (see Table 4d, e). The distances were near the typical value for Ti⁴⁺-S²⁻ (2.43 Å for TiS₂; see Table 3). The Ti–S bond distance was smaller at 2.283 Å for SN-doped mesoporous TiO₂ (see Table 4c). The presence of substitutional S was demonstrated on the O sites of TiO₂ matrix for S-doped mesoporous TiO₂-583 and TiO₂-623. Besides, S K-edge near-edge spectral pattern for these S-doped mesoporous TiO₂ resembled that for TiS₂. Anionic S substitution was supported. The anionic S sites were more complex because nitrogen that has been derived from thiourea may compete with S to substitute on the O sites of TiO₂ matrix for SN-doped mesoporous TiO₂.

The substitutional S²⁻ sites should be formed at the surface in the reductive CVD condition in H₂S for S-doped mesoporous TiO₂-583 and TiO₂-623. In the synthesis of SN-doped mesoporous TiO₂, thiourea was used as a sulfur source, which normally resulted in substitutional S⁴⁺ or S⁶⁺ sites after calcination of the catalyst.^{22,24–27} Because the SN-doped sample was not calcined in this work, (at least a part of) the sulfur in the sample was anionic substitutional sulfur. The relatively shorter Ti-S bond distance may be due to the strain effect of heteroatomic sulfur inside the TiO₂ matrix or due to co-doped nitrogen.

Photocatalytic Role of Doped S. The promotion of acetaldehyde formation by doping sulfur was in the order of TiO₂ nanotube-S \approx S-doped mesoporous TiO₂-583 (0.48 wt % S) < S-doped mesoporous TiO₂-623 (0.77 wt % S) < SN-doped mesoporous TiO₂ (1.7 wt % S) in ethanol + O₂ 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 TiO₂ (6.8) < TiO₂ nanotube-S (11) \approx S-doped mesoporous TiO₂-583 (11) < S-doped mesoporous TiO₂-623 (12), which is much greater SCHEME 1: Energy Diagram of Anionic S-Doped Mesoporous TiO₂ versus Cationic V-Doped Mesoporous TiO₂ and of Reductive and Oxidative Reactions under Visible Light



than the ratio of 1.1 observed for N-doped mesoporous TiO₂ (see Table 5). The sulfur contents and the N values for Ti-Sbonds (0.7, 0.2, and 0.5 for SN-doped mesoporous TiO₂, S-doped mesoporous TiO₂-583, 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 TiO₂.^{3,12,13,16,20,21} 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 TiO₂ (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).^{60,65,66} 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 vacuum⁶⁵ 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 μ mol h⁻¹ g_{cat}⁻¹) occurred only in the initial hour of reaction, and the rate gradually decreased in repeated catalytic tests.⁶⁰ Under visible light (>420 nm), reaction 5 (one-to-one formation of acetaldehyde and water) proceeded over V-doped mesoporous TiO₂.⁶⁵ Reductive reaction 4 of O₂, with the excited electrons formed when the doped cation impurity level was below the CB minimum of TiO₂ (see Scheme 1), should be less effective, compared to reaction 4' or 4" proceeding at the CB of S-doped TiO₂, based on water formation rates in Table 5. Actually, the four electron-reduction reaction 4, 4', or 4''

Over S-doped TiO₂:

consists of several elementary steps, probably including the formation of reactive hydroxyl radicals.^{2,14,60,72–75} 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-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 O₂ 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–)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 TiO₂ samples (see Table 4). Therefore, it is consistent that adsorbed ethoxyl group in reaction 2' or 2 has a tendency to remain stable on the surface⁶³ and only O₂ 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 TiO₂-623 (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 O₂ was enabled under visible light. In contrast, the sufficiently high potential of the S level(s) than VB of mesoporous TiO₂ was disadvantageous to receive electron (directly or indirectly) from ethanol/ethoxyl. Thus, the reduction of O₂ to water (and oxidation from ethanol to adsorbed ethoxyl species) proceeded 6.8–12 times faster than mesoporous TiO₂. The high potential nature of S-doped mesoporous TiO₂ 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 O₂ and proton reduction to H₂ (water splitting).⁷⁶

Conclusions

SN-doped TiO₂ with uniform mesopores centered at 2.9 nm was synthesized using thiourea. The specific surface area (SA) decreased from 608 m²/g (mesoporous TiO₂) to 229 m^2/g , because of bonding strain at the doped sulfur and nitrogen in the solid. S-doped TiO₂ was also synthesized via chemical vapor deposition (CVD) of H₂S over mesoporous TiO₂ at 583 or 623 K. The specific SA seriously decreased to $1.9-2.6 \text{ m}^2/\text{g}$, in accord with the loss of uniform mesopores of TiO₂. The absorption tailing in the visible-light region was ranked in the following order: S-doped mesoporous TiO2-583 \approx mesoporous TiO₂ < SN-doped mesoporous TiO₂ < S-doped mesoporous TiO₂-623. The ultraviolet-visible (UV-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 TiO₂. 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 O_2 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/ethoxyl 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 TiO₂-583. Even in the presence of a small amount of anionic sulfur on/in TiO₂, the O₂ reduction to water was promoted.

Acknowledgment. The X-ray absorption experiments were conducted under the approval of the Photon Factory Proposal Review Committee (No. 2007G576). The authors are thankful for financial support from the Grant-in-Aid for Scientific Research C (19550134) from JSPS and the Grant-in-Aid in the priority area "Molecular Nano-dynamics" (No. 432-17034013) from MEXT.

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JP810817Y