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Site Structure Analyses of Visible-Light Responsive Sulfur-Doped Titanium Oxide

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Anion-doped TiO_2 have been investigated as photocatalysts that show excellent visible light response and delayed charge recombination. However, local site structure has not been reported yet. In this report, sulfur and/or nitrogen-doped TiO_2 with uniform mesopores (2.9 nm) were synthesized and doped sulfur and nitrogen sites were studied using Ti and S K-edge XAFS.

Mesoporous TiO_2 was synthesized via the hydrolysis of Ti(*i*-PrO)$_4$ in the presence of dodecylamine. Mesoporous S and/or N doped-TiO_2 were synthesized by adding water to the mixture of Ti(*i*-PrO)$_4$, dodecylamine, and urea/thiourea with molar ratio 2 : 1 : 1 (Meso N-TiO_2 and Meso SN-TiO_2) [1]. Separately, S-doped TiO_2 were synthesized via chemical vapor deposition method with hydrogen sulfide at 583 or 623 K (S/meso TiO_2-583 and -623). Ti and S K-edge XAFS spectra were measured at beamline 9C and 9A.

Based on Ti K-edge EXAFS analyses, the bond distances for Meso N-TiO_2 exhibited negligible change compared to those for Meso TiO_2 (Table 1). In contrast, total coordination number *N* for Ti–O (or Ti–N) bonds effectively increased. This suggests a transition from unsaturated TiO_4 to saturated octahedral $TiO_{6-x}N_x$. Similar saturation was also observed for S/meso TiO_2-623.

Ti–S bond distances were obtained at 2.40 – 2.44 Å for S/meso TiO_2-583 and -623 (Figure 1), based on Ti K-edge EXAFS curve-fit analyses. These distances were close to typical value 2.43 Å for TiS_2. The bond distance was shorter at 2.283 Å for Meso SN-TiO_2. The presence of substitutional S was demonstrated on the O sites of the TiO_2 matrix. The peak positions of S K-edge XANES spectra for S-TiO_2 in this report resembled those for TiS_2 [1].

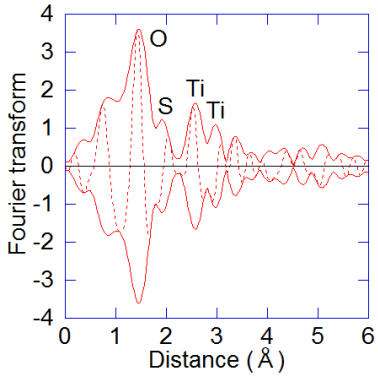

Figure 1. Fourier transform of Ti K-edge EXAFS oscillation for S/meso TiO_2-623. The solid line and dotted line represent the magnitude and the imaginary part, respectively.

Reference

[1] Y. Izumi, T. Itoi, S. Peng, K. Oka, Y. Shibata, *J. Phys. Chem. C* **113(16)**, 6706 – 6718 (2009).

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Table 1: Best Fit Results of Ti K-edge EXAFS Spectra for Mesoporous TiO_2 and Anion Doped Mesoporous TiO_2

	Ti–O [or Ti–N]			Ti–S			Ti(–O–)Ti [or Ti(–N–)Ti]		
sample	*R* (Å)		*N*	*R* (Å)		*N*	*R* (Å)		*N*
Meso TiO_2	1.75	(±0.02)	2.3 (±0.6)				2.918	(±0.011)	1.6 (±0.3)
	2.00	(±0.03)	1.9 (±0.5)				3.191	(±0.005)	7.1 (±0.9)
Meso N-TiO_2	1.73	(±0.02)	3.2 (±0.8)				2.89	(±0.02)	0.8 (±0.3)
	2.00	(±0.02)	3.0 (±0.6)				3.181	(±0.008)	8.8 (±0.8)
Meso SN-TiO_2	1.879	(±0.003)	4.4 (±0.5)	2.283	(±0.003)	0.7 (±0.04)	3.05	(±0.04)	5.2 (±1.0)
							3.24	(±0.03)	3.2 (±0.5)
S/meso TiO_2-583	1.74	(±0.02)	2.0 (±0.6)	2.44	(±0.03)	0.2 (±0.2)	2.905	(±0.010)	2.2 (±0.4)
	2.01	(±0.03)	2.2 (±0.9)				3.177	(±0.006)	7.3 (±0.6)
S/meso TiO_2-623	1.881	(±0.001)	6.2 (±0.3)	2.40	(±0.03)	0.5 (±0.1)	3.07	(±0.05)	5.5 (±1.3)
							3.290	(±0.014)	5.3 (±1.2)