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T.-L. Hsiung

National Cheng Kung University

L.-W. Wei

National Cheng Kung University

H.-L. Huang

National United University

H. Paul Wang (✉ wanghp@mail.ncku.edu.tw)

National Cheng Kung University <https://orcid.org/0000-0001-7272-8031>

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**Photocatalytic degradation of trace CHCl₃ in drinking water by nano
TiO₂**

T.-L. Hsiung¹, L.-W. Wei¹, H.-L. Huang², and H. Paul Wang^{1}*

¹ Department of Environmental Engineering, National Cheng Kung University, Tainan
70101, Taiwan

² Department of Safety, Health and Environmental Engineering, National United
University, Miaoli 36063, Taiwan

*Corresponding: Tel.: +886 6275 7575; fax: +886 6275 2790; E-mail address:
wanghp@mail.ncku.edu.tw (H. Paul Wang).

Abstract

Toxic disinfection byproducts such as trihalomethanes (CHCl_3) are frequently found after chlorination for drinking water. Nano TiO_2 which has been widely used for photocatalytic degradation of organic pollutants in wastewater, however, has relatively low effectiveness in the treatments of trace CHCl_3 . To engineer capable TiO_2 photocatalysts, an understanding of their photoactive sites is of great importance and interest. By *in situ* X-ray absorption near edge structure (XANES) spectroscopy, photoactive sites such as A_1 (4969 eV), A_2 (4971 eV) and A_3 (4972 eV) can be distinguished as four-, five-, and six- coordinated Ti species, respectively in the nano- TiO_2 (8.5 and 4.6 nm for TiO_2 on SBA-15), TiO_2 clusters ($\text{TiO}_2\text{-SiO}_2$), and highly atomic dispersed Ti (Ti-MCM-41) photocatalysts. It appears that the reactivity for the photocatalytic degradation of trace CHCl_3 in drinking water lacks an expected relationship with the crystalline phase, band gap absorption edge, nor the particle size of the TiO_2 -based photocatalysts. Notably, the A_2 sites being the main photocatalytic active species of the TiO_2 may be accountable for the main (about 95%) photocatalytic degradation of trace CHCl_3 in drinking water (7.2 ppm $\text{CHCl}_3/\text{gTiO}_2\cdot\text{hr}$). This work reveals that the A_2 active sites of a TiO_2 -based photocatalyst are responsible for the photocatalytic reactivity, especially in photocatalytic degradation of CHCl_3 in drinking water.

Keywords: Nano TiO_2 , photocatalysis, CHCl_3 , XANES, photoactive sites.

1 **Introduction**

2 In order to decrease the risk of water-borne diseases, chlorine is used in disinfection of
3 drinking water. However, toxic disinfection byproducts (DBPs) such as trihalomethanes
4 (THMs) are frequently formed in the drinking water chlorination processes. The U.S.
5 National Cancer Institute has suggested that chloroform (one of THMs) is carcinogenic
6 in rodents [1]. Lin and coworkers found that the level of THMs carcinogen exposure
7 could be as high as 47 µg/day by drinking or 30 µg/day by inhalation [2]. Conventional
8 methods for reduction of DBPs precursors include chemical coagulation, activated
9 carbon adsorption, membrane separation, ozonation, and combined ozonation/bio-
10 treatment [3-6]. Membrane separation as well as ozonation also has high efficiencies in
11 reduction of biological instability materials. However, those methods may not be
12 economically attractive in the engineering applications [4, 5].

13 TiO₂ possessing unique characteristics such as high photo-stabilities, effective band
14 gaps and easy availabilities has been widely applied in photocatalytic degradation of
15 toxic organics, splitting of H₂O, reduction of NO to N₂ and dye sensitized solar cells [7-
16 11]. Photocatalytic activities of TiO₂ can be enhanced with dispersed transition metal
17 promoters such as V, Cr, Fe, Cu, Ni, Mn, Ag, or Au [12-15]. Nanostructured TiO₂ which
18 has been considered a better photocatalyst may be associated with the fact of enlargement
19 of its surface-to-volume ratio [16, 17].

20 Valence and local structure (<1 nm) of select elements in a complicated solid matrix
21 can be studied by synchrotron X-ray absorption spectroscopy. Molecular structure
22 information such as coordination number (CN), bond distance, and oxidation state of
23 elements can be determined by X-ray absorption (extended X-ray absorption fine
24 structure (EXAFS) and X-ray absorption near edge structure (XANES)) spectroscopy.

1 By XANES and EXAFS, it was found that copper oxide clusters were very effective in
2 catalysis in mesopores (MCM-41), micropores (e.g., ZSM-5 and ZSM-48), and TiO₂-
3 based photocatalysts [18-20]. These molecular-scale data turn out to be very useful in
4 revealing nature of catalytic active species and reaction paths involved.

5 Photocatalytic degradation of trace THMs or DBPs by nanostructured TiO₂ was not
6 very effective [21, 22]. On the other hand, photocatalytic generation of H₂ (from H₂O) on
7 atomic dispersed Ti and Zr in the mesoporous molecular sieve (MCM-41) (Ti-MCM-41
8 and Zr-MCM-41) can be enhanced by 17 and 80 times, respectively (if compared with
9 their bulky states) [23]. It seems that nano cluster or even atomic dispersed TiO₂ may
10 lead to unique enhancements in photocatalytic reactions. However, speciation of
11 photocatalytic active sites in TiO₂ is not well characterized particularly during reactions
12 [25, 26]. In order to prepare effective TiO₂ photocatalysts, a molecule-scale
13 understanding of the photoactive sites is essential. Thus, the main objective of the present
14 work was to study chemical structure of photoactive species in nano, cluster and atomic
15 dispersed TiO₂ during the photocatalytic degradation of trace CHCl₃ in drinking water by
16 *in situ* XANES and EXAFS.

18 **Experimental**

19 The nanosize TiO₂-SiO₂ (Ti/Si atomic ratio = 3/7) photocatalyst was prepared by the
20 sol-gel method [24-26]. Typically, 12.8 g of titanium(IV) n-butoxide (ACROS, 99%) and
21 24.3 g of tetraethylorthosilicate (C₈H₂₀OSi, TEOS) (MERCK) were well mixed (at the
22 pH value of 7.0) in the ethanol and distilled water (1:2) solution (45 mL). The TiO₂-SiO₂
23 solution was heated slowly until the sol-gel became xerogel, and then separated and

1 calcined at 673 K for 1 h. The nano TiO₂ photocatalysts was synthesized in a similar
2 procedure.

3 The TiO₂ supported on SBA-15 that has a 2-D hexagonal mesoporous structure with
4 long and straight channels parallel to the silica skeletons photocatalyst were prepared by
5 co-condensation of silica, titanium oxide and neutral charge poly(ethylene oxide)-
6 poly(propylene oxide)-poly(ethylene oxide) (EO₂₀PO₇₀EO₂₀ (P123)) (Aldrich, 99%)
7 nonionic surfactant [27]. Briefly, 0.21 g of titanium n-butoxide (Ti(OBu)₄, Aldrich, 97%)
8 and 15 g of sulfuric acid (1.2 M, MERCK) were well mixed until the solution became
9 clear, a solution containing 2.75 g of sodium silica (14% NaOH and 27% SiO₂) (Aldrich),
10 1.25 g of P123 and 200 g of distilled water was added. The pH value of the solution was
11 adjusted to 5.0. After separation, the photocatalysts was calcined at 773 K for 6 h.

12 The Ti-inserted (framework) MCM-41 (Ti-MCM-41) photocatalysts were synthesized
13 by the liquid crystal templating method [23]. Fumed silica (Sigma) and sodium silicate
14 solution were used as silica sources for the preparation of MCM-41. Hexadecyltrimethyl
15 ammonium bromide (CTAB) (Sigma, >99%) and tetramethyl ammonium hydroxide
16 (TMAOH, 25%) (Sigma-Aldrich) were used as a template and mineralizer, respectively.
17 The mole ratio of H₂O, CTAB, TMAOH, and Si in the mixture was 86:0.27:0.58:1.
18 Titanium n-butoxide (ACRÖS, 99%) was added into the MCM-41 mother liquid for
19 synthesis of Ti-MCM-41. A diluted sulfuric acid solution was used to adjust the pH
20 values of the solution between 11 and 12. The mixture was then heated in a Teflon lined
21 autoclave at 375 K for 24 h. The as-synthesized MCM-41 was filtered, washed with
22 distilled water, dried and calcined at 773 K for 5 h.

23 Chemical structure of the photocatalysts was characterized by X-ray powder
24 diffraction (XRD) spectroscopy (D8 advance, Bruker) with a Cu K α (1.542 Å) radiation.

1 Samples were scanned from 10 to 50° (2 θ) at a scan rate of 5°/min. Diffuse reflectance
2 ultraviolet/visible spectra (DR UV-Vis) of the photocatalysts were also determined
3 (between 200-700 nm) on an UV-Vis spectrophotometer (HITACHI U-3010) at a scan
4 speed of 120 nm/min.

5 The *in situ* Ti K-edge (4966 eV) XANES spectra of the photocatalysts were collected
6 at 298 K on the Wiggler beam line of the Taiwan National Synchrotron Radiation
7 Research Center. The absorption spectra were collected in ion chambers that were filled
8 with helium and nitrogen mixed gases. The beam energy was calibrated to the adsorption
9 edge of a Ti foil at the energy of 4966 eV. The electron storage ring was operated at
10 energy of 1.5 GeV (ring current = 120-200 A). The isolated EXAFS data were
11 normalized to the edge jump and converted to the wavenumber scale. Fitting of data to
12 model compounds was performed using the FEFFIT (UWXAFS 3.0) in combination
13 with the multiple scattering code FEFF 8.0 simulation programs [8, 28]. The FEFFIT
14 was used to determine the best fitting results with the minimum Debye-Waller factors
15 (<0.01 Å²). The Fourier transform was performed on k^3 -weighted EXAFS oscillations in
16 the range of 3.8-11.7 Å⁻¹.

17 Photocatalytic degradation of CHCl₃ (500 ppb) were performed on a home-made *in*
18 *situ* EXAFS cell [8]. Typically, 0.15 g of the TiO₂ photocatalyst was suspended in H₂O
19 containing trace CHCl₃ (500 ppb). A 300-Watt high-pressure Xe arc lamp (Newport,
20 Model 6258) was used as the light sources (250-800 nm) while the synchrotron X-ray
21 absorption spectra of the TiO₂ photocatalysts were determined. Concentrations of CHCl₃
22 were determined by a GC (Model 3400, Varian) equipped with an electrolytic
23 conductivity detector (Model 100, Tracor) and a purge/trap system (Model LCS-2000,
24 Tekmar).

1

2 **Results and discussion**

3 The XRD patterns of the TiO₂-based photocatalysts are shown in Fig. 1. The Ti-MCM-
4 41 and TiO₂-SiO₂ photocatalysts have broadened features between 17-31° (2θ),
5 suggesting the absence of TiO₂ crystalline, which may be associated with the existence of
6 very small TiO₂ nanoparticles or highly atomic dispersed Ti therein. For the TiO₂/SBA-
7 15 and nano TiO₂, anatase phases ((101), (004) and (200)) are observed with crystalline
8 sizes of about 4.6 and 8.5 nm, respectively (calculated using the Scherrer equation).

9 Figure 2 shows the DR UV-Vis spectra of the photocatalysts. The band gap absorption
10 edges for the TiO₂-SiO₂ and Ti-MCM-41 are 3.38 and 3.42 eV, respectively. Beck and
11 coworkers also found blue shifts for the band gap absorption edge with highly dispersed
12 Ti in the SiO₂ framework [24]. The absorption feature (<260 nm) for the Ti-MCM-41
13 can be attributed to the ligand-to-metal charge transfer between Ti(IV) and the
14 amorphous SiO₂ framework. It seems that Ti is well dispersed in the Ti-MCM-41
15 photocatalyst.

16 The EXAFS spectra best-fitted by the Fourier transformation and k^3 -weighted for the
17 TiO₂-based photocatalysts in the ranges of 0-4 and 4-11 Å are shown in Fig. 3. The
18 speciation parameters for the Ti in those photocatalysts are also listed in Table 1. The
19 bond distances for the Ti-(O)-Si species (in the 2nd shells) in the Ti-MCM-41 and TiO₂-
20 SiO₂ photocatalysts are 3.13 and 3.31 Å, respectively. It is worth noting that the Ti-
21 MCM-41 has a greater coordination number (CN) for the Ti-(O)-Si bonding than that for
22 the TiO₂-SiO₂, representing that more Ti atoms are dispersed in the amorphous SiO₂
23 framework for the Ti-MCM-41, and differently the TiO₂-SiO₂ one has more TiO₂
24 aggregates on the SiO₂ surfaces with a metal-support interaction related to its relatively

low CN. It seems that the $\text{TiO}_2\text{-SiO}_2$ contains sub-nano TiO_2 (supported on the SiO_2) that is not observed by XRD, which may behavior like a TiO_2 cluster. The Ti-O-Si species are, on the contrary, not found in the $\text{TiO}_2\text{/SBA-15}$. It seems that the TiO_2 nanoparticles may be formed in the hexagonally ordered mesoporous channels (an opening of 5.7 nm) of the SBA-15. Note that the averaged diameter of the TiO_2 nanoparticles in the SBA-15 is 4.6 nm approximately (see Table 2).

Photocatalytic degradation of trace CHCl_3 (500 ppb in drinking water) by the nano, cluster, and atomic dispersed TiO_2 photocatalysts under the UV/Vis radiation (250-800 nm) is shown in Fig. 4. An enhanced photocatalytic degradation of trace CHCl_3 by the Ti-MCM-41 is observed. After a 4-h UV/Vis radiation, accumulated 28.8 ppm $\text{CHCl}_3\text{/gTiO}_2$ are photocatalytically degraded by Ti-MCM-41. The nano TiO_2 has a relatively low conversion for photocatalytic of degradant of CHCl_3 if compared with the Ti-MCM-41. Note that the $\text{TiO}_2\text{-SiO}_2$ containing a very small nanosize TiO_2 (i.e., clusters) also has a much less conversion during the photocatalytic degradation than the $\text{TiO}_2\text{/SBA-15}$ that has a larger TiO_2 nanoparticles (an average size of 4.6 nm). It appears that the reactivity for the photocatalytic degradation of trace CHCl_3 in drinking water is not related to the crystalline phase, band gap absorption edge, nor particle size of the TiO_2 -based photocatalysts.

To reveal the key factor that influences the photocatalytic degradation reactivity of the TiO_2 -based photocatalysts, Table 2 summarizes the characterization of the TiO_2 -based photocatalysts, the related photocatalytic degradation reactivity and the photoactive sites involved. It seems that the photocatalysts, i.e., Ti-MCM-41 and $\text{TiO}_2\text{/SBA-15}$ possessing meso-pore channel systems have greater photocatalytic degradation conversions than the other ones that have nano and cluster TiO_2 on SiO_2 . Apparently, the MCM-41 and SBA-

1 15 possessing meso-pores have a large enough pore opening for free diffusion of small
2 CHCl_3 molecules to the TiO_2 photoactive sites. Thus, there may exist other factors that
3 control the photocatalysis.

4 In Fig. 5, A_1 (4969 eV), A_2 (4971 eV) and A_3 (4972 eV) can be resolved in the pre-
5 edge XANES spectra (between the absorption threshold (4966 eV) and jump (4984 eV))
6 of the photocatalysts. The A_1 , A_2 and A_3 species in TiO_2 may be attributed to four-
7 (TiO_4), five- ($(\text{Ti}=\text{O})\text{O}_4$) and six- (TiO_6) coordinated Ti species, respectively [25, 26].
8 The B and C features (at 4974 and 4980 eV, respectively) are due to the interactions of
9 the central Ti 4p orbitals hybridized with the near Ti or O atoms. The Ti K edge post-
10 edge at 4980-5020 eV can be assigned to 3s-to-np dipole-allowed transitions. The
11 insertion of Ti atoms into the SiO_2 matrix may cause distortion of the Ti-O octahedron
12 structure. It is worth noting that the broadened white line absorption (4987 eV) for Ti-
13 MCM-41 and TiO_2 - SiO_2 is observed, suggesting the existence of highly dispersed Ti
14 atoms in the SiO_2 matrix.

15 The photoactive species (A_1 , A_2 and A_3) in the photocatalysts can be distinguished (in
16 the XANES spectra). As shown in Table 2, the well dispersed Ti in Ti-MCM-41 has a
17 much better performance for photocatalytic degradation of trace CHCl_3 in drinking water.
18 The A_2 species (five-fold coordinated Ti (IV)) possess a square pyramid structure
19 consisted of a double bond ($\text{Ti}=\text{O}$) and four Ti-O bonds which is predominant generally
20 on the surfaces for the very small (<10 nm) TiO_2 nanoparticles. Fractions of the TiO_2
21 active species for photocatalytic degradation of CHCl_3 have been determined by the
22 linear regression analysis. The A_2 species possess a major contribution (75%
23 approximately) to the photocatalytic degradation of trace CHCl_3 in H_2O . Interestingly,

about 95% of the photocatalytic conversion ($7.2 \text{ ppmCHCl}_3/\text{gTiO}_2\cdot\text{hr}$) is associated with the A_2 active species in Ti-MCM-41.

Conclusions

The photocatalytic degradation of trace CHCl_3 in drinking water was found to be associated insignificantly with the crystalline phase, band gap absorption edge and particle sizes of the TiO_2 photocatalysts. The A_1 (TiO_4), A_2 ($(\text{Ti}=\text{O})\text{O}_4$) and A_3 (TiO_6) species in TiO_2 were observed and distinguished by component fitted pre-edge XANES spectra of the bulky TiO_2 ($\text{TiO}_2/\text{SBA-15}$), nano TiO_2 , and highly atomic dispersed Ti ($\text{TiO}_2\text{-SiO}_2$ and Ti-MCM-41) photocatalysts. It appears that the conversion for the photocatalytic degradation of trace CHCl_3 in drinking water may not be related to the crystalline phase, band gap absorption edge, nor the particle size of the TiO_2 -based photocatalysts. Nevertheless, the A_2 photo-active species in the TiO_2 -based photocatalysts may have a major contribution (75% approximately) to the overall photocatalytic performance. In the photocatalytic degradation of trace CHCl_3 , for example, the A_2 active species in the atomic dispersed Ti (Ti-MCM-41) may account for 95% of the accumulated photocatalytic conversion. This work reveals that the A_2 active sites of a TiO_2 -based photocatalyst are associated significantly with its photocatalytic reactivity, especially in photocatalytic degradation of CHCl_3 .

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Table 1. Speciation parameters of Ti in the photocatalysts for degradation of trace CHCl_3 in drinking water.

	Sells	Bond distances (Å)	Coordination numbers	Debye-Waller factor (Å ²)
Ti-MCM-41	Ti-O _{eq.}	1.75	0.9	0.0058
	Ti-O _{ax.}	1.99	2.6	0.0029
	Ti-(O)-Si	3.13	2.9	0.0103
TiO ₂ -SiO ₂	Ti-O _{eq.}	1.77	1.9	0.0023
	Ti-O _{ax.}	2.32	2.5	0.0030
	Ti-(O)-Si	3.31	1.1	0.0027
Nano TiO ₂	Ti-O _{eq.}	1.92	1.5	0.0004
	Ti-O _{ax.}	2.03	3.1	0.0045
	Ti-(O)-Ti	3.03	3.5	0.0049
TiO ₂ /SBA-15	Ti-O _{eq.}	1.90	2.0	0.0038
	Ti-O _{ax.}	1.99	3.3	0.0044
	Ti-(O)-Ti	3.03	2.1	0.0043

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Table 2. Characterization and reactivity of the photocatalysts for degradation of trace CHCl₃ in drinking water.

Photocatalyst	TiO ₂ chemical structure ^a	Crystalline size ^b (nm)	Band gap absorption edge ^c (eV)	Photocatalytic degradation of CHCl ₃ ^d (ppm/gTiO ₂ ·hr)	Photoactive species ^e (%)		
					A ₁	A ₂	A ₃
Ti-MCM-41	amorphous	-	3.42	7.2	7	49	44
TiO ₂ -SiO ₂	amorphous	-	3.38	0.9	25	33	42
Nano TiO ₂	anatase	8.5	3.25	0.7	22	32	46
TiO ₂ /SBA-15	anatase	4.6	3.30	5.6	19	40	41

^a: determined by XRD.
^b: calculated using the Scherrer equation [26].
^c: determined by DR UV/Vis.
^d: determined in a total UV/Vis reflectance system under UV/Vis irradiation for 4 h (initial CHCl₃ concentration = 500 ppb (in H₂O)).
^e: determined by XANES (A₁: TiO₄; A₂: (Ti=O)O₄; A₃: TiO₆).

Figure 1. X-ray diffraction patterns of (a) Ti-MCM-41, (b) $\text{TiO}_2\text{-SiO}_2$, (c) $\text{TiO}_2/\text{SBA-15}$, and (d) nano TiO_2 .

Figure 2. DR UV/Vis spectra of (a) Ti-MCM-41, (b) $\text{TiO}_2\text{-SiO}_2$, (c) nano TiO_2 , and (d) $\text{TiO}_2\text{/SBA-15}$.

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Figure 3. Ti K-edge XANES spectra of (a) $\text{TiO}_2\text{-SiO}_2$, (b) nano TiO_2 , (c) $\text{TiO}_2/\text{SBA-15}$, and (d) Ti-MCM-41 .

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Figure 4. Time dependence for photocatalytic degradation of trace CHCl_3 in H_2O effected by (a) Ti-MCM-41, (b) $\text{TiO}_2/\text{SBA-15}$, (c) $\text{TiO}_2\text{-SiO}_2$, and (d) nano TiO_2 .

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Figure 5. Ti K-edge XANES spectra of (a) $\text{TiO}_2\text{-SiO}_2$, (b) nano TiO_2 , (c) $\text{TiO}_2/\text{SBA-15}$, and (d) Ti-MCM-41 .

Declarations

■ Availability of data and materials

The datasets used and analyzed during the study are available from the corresponding author on reasonable request.

■ Competing interests

The authors declare that they have no competing interests.

■ Funding

No funding was associated with this manuscript.

■ Authors' contributions

TLH designed the concept and drafted the manuscript. LWW provided support of the literature search and some revision. HLH provided professional advice. WHP contributed to the writing of the final version of the manuscript.

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■ Author information

Corresponding Author

Tel: +886-6275-7575 ext 65832; fax: +886-6275-2790.

E-mail address: wanghp@mail.ncku.edu.tw (H. Paul Wang).

Figures

Figure 1

X-ray diffraction patterns of (a) Ti-MCM-41, (b) TiO₂-SiO₂, (c) TiO₂/SBA-15, and (d) nano TiO₂.

Figure 2

DR UV/Vis spectra of (a) Ti-MCM-41, (b) TiO₂-SiO₂, (c) nano TiO₂, and (d) TiO₂/SBA-15.

Figure 3

Ti K-edge XANES spectra of (a) TiO₂-SiO₂, (b) nano TiO₂, (c) TiO₂/SBA-15, and (d) Ti-MCM-41.

Figure 4

Time dependence for photocatalytic degradation of trace CHCl_3 in H_2O effected by (a) Ti-MCM-41, (b) $\text{TiO}_2/\text{SBA-15}$, (c) $\text{TiO}_2\text{-SiO}_2$, and (d) nano TiO_2 .

Figure 5

Ti K-edge XANES spectra of (a) $\text{TiO}_2\text{-SiO}_2$, (b) nano TiO_2 , (c) $\text{TiO}_2/\text{SBA-15, 6}$ and (d) Ti-MCM-41 .