Photocatalytic Oxidation of As(III) in TiO_2 Nanotubes

Tung-Li Hsiung (熊東澧)[1] and H. Paul Wang (王鴻博)[1,2]

[1]Department of Environmental Engineering, National Cheng Kung University, Tainan, Taiwan
[2]Sustainable Environment Research Center, National Cheng Kung University, Tainan, Taiwan

Photocatalytic oxidation of As(III) to the less toxicity and mobility As(V) effected by TiO_2 nanotubes (TNTs) have been studied by in-situ X-ray absorption (X-ray absorption near edge structure (XANES) and extend X-ray absorption fine structure (EXAFS)) spectroscopy. The component-fitted XANES spectra of arsenics show that As(III) is oxidized with two electron transfer during photocatalysis. The apparent first-order rate constant for the photocatalytic interconversion of As(III) to As(V) is 0.0148 min^{-1}. The in-situ EXAFS spectra indicate a decrease of the 1st shell bond distance (As-O) (1.77 to 1.67 Å) and an increase of its coordination number (CN) (3.9 to 5.3) during photocatalysis. The final pH values of the solution after photocatalytic oxidation of arsenic in air and high-purity N_2 are 9.26 and 10.43, respectively. It seems that the arsenic species (As(III) and As(V)) act as electron acceptor (about 28% of As(0) is found) during photocatalysis of As(III) on the TNT in high-purity N_2. About 28% of As(III) covered to form As(V) during photocatlaytic oxidation of copper dispersed TNT for 210 min. Note that the electrode potential of copper are higher than those of oxygen, the photo-excited electrons are trapped onto copper species (6% Cu(I) and 3% Cu(0) are found) on the copper dispersed/TNT. Thus, it is very likely that the 28% of As(III) oxidized to form As(V) via direct photo-excited hole transfer on the TNT surface. This work also exemplifies the utilization of in-situ synchrotron X-ray absorption spectroscopy for a better understanding of photocatalysis especially occurring in TiO_2 nanotubes.

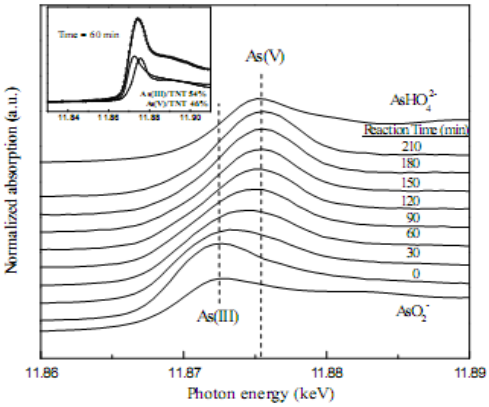

Fig. 1: In-situ XANES spectra of As(III) photocatalyzed by TNT

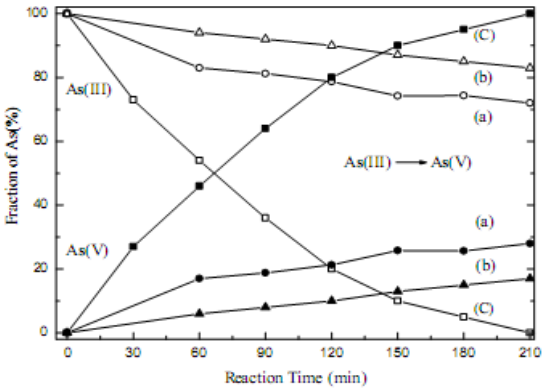

Fig. 2: Photocatalytic oxidation of As(III) (10 mM) (empty symbols) to As(V) (filled symbols) effected by 100g/L of (a) nanosize TiO_2 (triangle), (b) copper dispersed/TNT (circle), and (c) TNT (square).

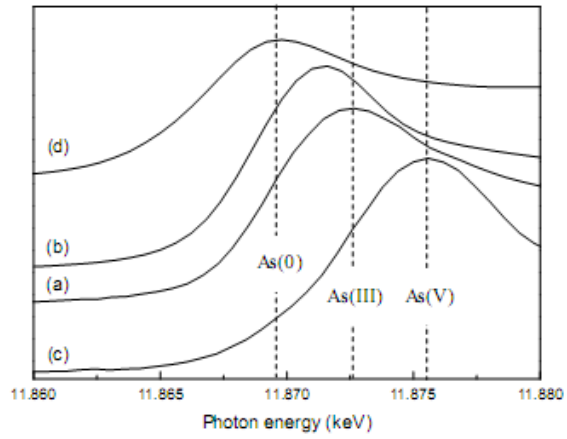

Fig. 3: XANES spectra of (a) As(III) on TNT, (b) in the absence and (c) presence of O_2 after photocatalysis for 210 min and (d) As(0).

Table 1 Structural parameters of arsenic during photocatalytic oxidation effected by TiO_2 nanotubes

Reaction time (min)	shell	R(Å)	CN	σ^2(Å^2)
0	As-O	1.77	3.9	0.006
30	As-O	1.76	4.3	0.006
60	As-O	1.72	4.6	0.008
90	As-O	1.72	4.9	0.006
120	As-O	1.70	5.5	0.009
150	As-O	1.70	5.7	0.008
180	As-O	1.69	5.8	0.007
210	As-O	1.67	5.3	0.005
Model compounds				
$NaAsO_2$ (As(III))	As-O	1.76	2.8	0.008
$AsHNa_2O_4$ (As(V))	As-O	1.67	4.8	0.004

R: bond distance
CN: coordination number
σ^2: Debye-Waller factor