## **Electronic Supplementary Information**

# XANES Analysis of Spectral Properties and Structures of Arsenate Adsorption on TiO<sub>2</sub> Surfaces

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1. Selection of model plane

2. Identification of dominant complexes

#### 1. Selection of model plane

The geometries of bidentate binuclear (BB) surface complex formed on (101) and (100) surface, which is the most commonly reported inner-sphere adsorption geometry of arsenate on metal-(hydr)oxide surfaces, were compared (Figure S1). The good agreement of calculated As-Ti distances with experimental EXAFS results ( $3.20\pm0.05$ ) (He *et al.*, 2011; He *et al.*, 2009) (Table S1) implied that (100) surface was dominant in the TiO<sub>2</sub> powder used in this adsorption experiment. The Ti-Ti distance (3.78 Å) in anatase TiO<sub>2</sub> (101) surface is larger than that in (100) surface (3.04 Å). This resulted in the large As-O-Ti bond angles ( $145.0^{\circ}$ ) on (101) surface, and hence the larger As-Ti distance (3.38 Å) that was not observed in our EXAFS measurement.

#### 2. Identification of dominant complexes

In our previous study (He *et al.*, 2011), we calculated the structures of corner-sharing and edge-sharing Ti-AsO<sub>4</sub> surface complexes on (100) plane. Comparison between DFT calculated and EXAFS measured structural parameters are presented in Table S1. The calculated As-O distances for the four surface complexes (1.70~1.71 Å) agreed well with the EXAFS values (1.69 Å). The two experimentally measured As-Ti distances were close to DFT calculated values of bidentate binuclear (3.25 Å) and monodentate mononuclear (3.50 Å) complexes. The bidentate mononuclear (BM) edge-sharing modes would yield an As-Ti distance near 2.76 Å, much smaller than the distance obtained from EXAFS analysis (Table S1). This result indicated that the Ti-AsO<sub>4</sub> surface complexes consisted predominantly of the BB and MM complexation modes in this experiment. This phenomenon was also observed in the adsorption of arsenate on Fe-(hydr)oxides (Sherman & Randall, 2003). Therefore, the BM adsorption modes were excluded in the XANES analysis and calculation in the manuscript.

In the manuscript, to build the XANES model clusters, the arsenate structure was left to relax on the  $TiO_2$  surface, while the  $TiO_2$  substrate was kept frozen as the bulk structure of the anatase during the DFT calculation.



**Figure S1.** Calculated bidentate binuclear Ti-AsO<sub>4</sub> surface complexes using density functional theory: (a) (101) plane; (b) (100) plane. Purple, red, big gray, small gray circles denote As, O, Ti, H atoms, respectively. Distances are shown in angstroms.

**Table S1.** Comparison of DFT calculated and EXAFS measured structural parameters of arsenate adsorption on Ti(hydr)-oxides.

Calculated values	As-O		As-Ti				
	CN	R(Å)		CN R(Å)			
BB	4.0	1.70		2.0	3.26		
MM	4.0	1.70		1.0	3.50		
BM-A	4.0	1.71		2.0	2.75		
BM-B	4.0	1.70		2.0	2.88		
EXAFS values	As-O		As-Ti				
	CN	R(Å)	$CN_1$	$R_1(Å)$	$CN_2$	$R_2(Å)$	
Adsorption samples	4.1	1.69	2.0±0.4	3.20±0.05	1.0 <b>±</b> 0.4	3.60±0.02	

CN: coordination number; R: atomic distance. This table was taken from our previous studies, detailed description of the EXAFS analysis and DFT calculation were presented in them (He *et al.*, 2011; He *et al.*, 2009).

### References

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