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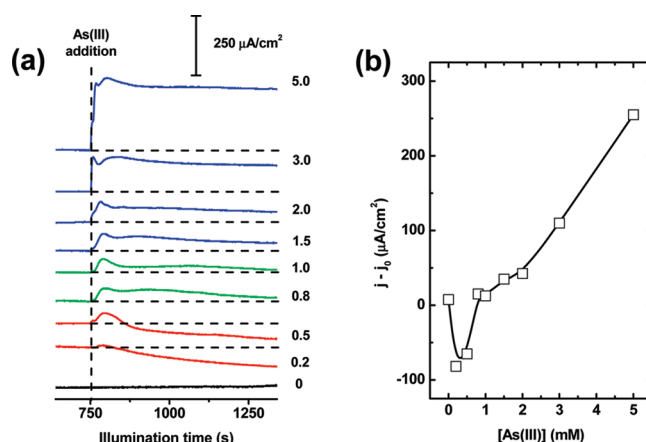
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## Response to Comment on “Photocatalytic Oxidation Mechanism of As(III) on TiO<sub>2</sub>: Unique Role of As(III) as a Charge Recombinant Species”

We write in response to the comments from Leng et al.<sup>1</sup> on our paper concerning the role of arsenite as a charge recombinant species in TiO<sub>2</sub> photocatalytic oxidation process.<sup>2</sup> They raised three major issues and our replies are as follows:

First, concerning the TDR spectroscopy measurements, they questioned if the laser light intensity was the same. We must state the transient absorption intensity was measured under the same experimental condition. In general, the sample dispersion property may affect the number of absorbed photons in the diffuse reflectance spectroscopy. However, we can assume such difference is negligible in the present experiments. The laser photolysis experiments were repeated three times with using different TiO<sub>2</sub> samples and the transient absorption intensity was reproducible. For example, the time profile of the transient absorption for the TiO<sub>2</sub> slurry sample with 10 mM As(V) (*reacting with neither electron nor hole*) was almost the same to that for pure TiO<sub>2</sub> slurry (see Figure 2 in ref 2). This indicates that the charge generation rate and the intrinsic recombination rate in the laser-irradiated TiO<sub>2</sub> slurry samples were unchanged throughout the measurements.

Second, Leng et al. carried out photoelectrochemical experiments (similar to ref 3) and found that the relative change of the photoanodic current was opposite. That is, they observed the increase of photocurrent upon spiking As(III), while we reported the decrease of the photocurrent.<sup>3</sup> This is the repetition of their previous comment<sup>4</sup> to which we have already replied.<sup>5</sup> We are repeating the answer with more clear experimental data. Figure 1 shows how the change in the photoanodic current upon spiking As(III) varies as a function of [As(III)]<sub>spike</sub>. We successively increased the concentration of added As(III) to check out the effect of concentration on the photocurrent density. The initial addition (0.2 mM) lowered the photocurrent from its initial value (*j*<sub>0</sub>), and the degree of photocurrent reduction decreased with increasing As(III) concentration. The change of photocurrent was reversed at >0.8 mM. Our previous report<sup>3</sup> showed a decrease in photocurrent upon spiking 0.5 mM of arsenite. As we explained previously,<sup>5</sup> the photocatalytic oxidation mechanism of As(III) also depends on the concentration of arsenite. This photocurrent experiment shows that its concentration dependence has a nonmonotonous behavior, clearly defining two regions: (i) below 0.8 mM where the photocurrent is reduced because of a predominant charge recombination of electrons with photogenerated As(IV) species ( $\text{As}^{\text{IV}} + e_{\text{cb}}^- \rightarrow \text{As}^{\text{III}}$ ) and (ii) above 0.8 mM where the photocurrent increases because of a predominant electron injection from excess As(IV) (*current-doubling* through  $\text{As}^{\text{IV}} \rightarrow \text{As}^{\text{V}} + e_{\text{cb}}^-$ ). The reason why Leng et al.<sup>1</sup> observed the opposite result is because they added much higher concentration of As(III) in the millimolar range. However, this current-doubling path has little practical significance since the environmentally relevant concentrations of As(III) in the



**Figure 1.** (a) Photocurrent density vs time profiles measured at +0.1 V (vs SCE) with varying [As(III)]<sub>spike</sub> (from 0 to 5 mM). The response of the photocurrent depended on [As(III)]<sub>spike</sub>. (b) Photocurrent density (stabilized after As(III) spike) as a function of [As(III)]<sub>spike</sub>. The photocurrent density values (*j*) were taken after 10 min and subtracted by the initial photocurrent density prior to As(III) addition (*j*<sub>0</sub>). Working electrode: P25 TiO<sub>2</sub> deposited on 4 cm<sup>2</sup> FTO. Counter electrode: Pt flag, Reference electrode: SCE. Electrolyte: air-equilibrated 0.5 M NaClO<sub>4</sub> solution at pH 3.

contaminated groundwater are much lower (typically a few micromolar range).

Third, the trapped electron lifetime mentioned as “>20  $\mu\text{s}$ ” seems to be misunderstood by Leng et al. We noted the electron lifetime as >20  $\mu\text{s}$  simply because we showed the transient time profiles only up to 20  $\mu\text{s}$ . It does not mean that the lifetime of trapped electrons is around 20  $\mu\text{s}$ . The actual lifetime of trapped electrons in the presence of O<sub>2</sub> has been reported to be about 0.33 ms.<sup>6</sup> This value can be compared with the even longer lifetime ( $\sim\text{ms}$ ) of trapped holes in TiO<sub>2</sub>. After the fast recombination process (intrinsic recombination + As(III)-mediated recombination), the trapped electrons are first scavenged by O<sub>2</sub> and then the remaining trapped holes slowly react with water or hydroxyl groups.

Leng et al. repeatedly raised questions regarding our proposed mechanism mainly in relation with the specific photoelectrochemical measurements.<sup>1,4</sup> However, they remain silent about the strong and obvious evidence against the role of holes and OH radicals.<sup>2</sup> To take a couple of examples, why is the photocatalytic oxidation rate of As(III) not reduced at all even in the presence of excess hole scavengers like methanol and *t*-butyl alcohol (0.2 M)? How is As(III) oxidized in the visible light-sensitized system

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where holes and OH radicals cannot be generated? If they support the hole-mediated mechanism, they should provide explanations for those basic questions.

**Damián Monllor-Satoca,<sup>†</sup> Takashi Tachikawa,<sup>‡</sup>  
Tetsuro Majima,<sup>‡</sup> and Wonyong Choi<sup>\*,†</sup>**

<sup>†</sup>School of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea

<sup>‡</sup>The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

## AUTHOR INFORMATION

### Corresponding Author

\*Fax: +82-54-279-8299; e-mail: wchoi@postech.edu.

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