TiO₂ facet-dependent arsenic adsorption and photooxidation: Spectroscopic and DFT study

L. Yan & C.Y. Jing

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, P.R. China

ABSTRACT: Anatase TiO₂ nanomaterials have been widely used in arsenic (As) remediation, although reports on their adsorption and photocatalytic capacity have been controversial. The motivation for our study is to explore the As adsorption and photooxidation processes on different TiO₂ facets at the molecular level. Our results from multiple complementary characterization techniques suggest that anatase {001} facets have stronger Lewis acid sites than those on {101} facets, resulting in a higher As adsorption affinity. Density functional theory (DFT) calculations confirmed that the As surface complex is more energetically favorable on {001} than on {101} facets. In addition, the strong interaction of {001} facets with molecular O₂ facilitates the transfer of photo-excited electrons to the adsorbed O₂ to generate superoxide radical (O₂^{•−}), which is the primary As(III) oxidant as evidenced by our radical-trapping experiments. The insights gained from this study provide a firm basis for the proposition that As adsorption and photoactivity can be mediated by tailoring the exposed TiO₂ facets, which is of essence in the design and application of TiO₂-based environmental technologies.

1 INTRODUCTION

Adsorption and photooxidation on TiO₂ nanomaterials provide a promising technique for arsenic (As) removal. Though the As adsorption mechanism is well known to involve the formation of a bidentate binuclear surface complex (Hu *et al.*, 2015), even TiO₂ of the same anatase phase from different sources exhibit distinct adsorption and photo-catalytic capacities. The lack of conformity of many experimental observations with the general belief that particle size or surface area regulates TiO₂ adsorption and photocatalysis motivates our study.

Recent intriguing studies have shown that the adsorption and photocatalytic activity of TiO₂ largely depend on its surface atomic structure and the exposed crystal facets (Liu *et al.*, 2014). The majority of exposed facets for most anatase are less-reactive and thermodynamically stable {101} facets (about 94%) with a minor proportion of {001} facets. Conversely, water and dye molecules prefer to bind to anatase {001} rather than {101} facets. However, the molecular level knowledge on TiO₂ facets determining As adsorption is not fully understood.

The high photocatalytic performance for anatase {001} facets has been explained by hydroxyl radical (•OH), which is proposed to be the main oxidant for As(III) photooxidation in the TiO₂/UV system. In contrast, other studies suggested that superoxide radical (O₂^{•−}) should play a dominant role. The controversy in the As(III) photooxidation mechanism may stem from the knowledge gap concerning the TiO₂ facets effect on the generation of reactive oxygen species (ROS).

Therefore, we hypothesize that anatase TiO₂ facets may affect ROS generation and ultimately determine photocatalytic performance.

The objective of this study was to identify the primary factor influencing As adsorption and photocatalysis on anatase TiO₂, as well as its mechanism. Multiple complementary characterization methods and density functional theory (DFT) calculations were employed to explore the molecular-level processes on the {001} and {101} facets. The intrinsic facet-dependent mechanism obtained from this study would be fundamental in developing TiO₂-based environmental technologies with high adsorption capacity and photocatalytic activity.

2 METHODS/EXPERIMENTAL

2.1 As(III) and As(V) adsorption on TiO₂

Three different kinds of TiO₂ nanoparticles (NPs), including one homemade (HM) and two commercial samples (JR05 and TG01), were used in this study. Adsorption isotherm experiments were performed to determine As(III) and As(V) adsorption capacity on the three types of TiO₂ in 0.04 M NaCl solution at pH 7. Suspension samples containing 0.31–3450 mg L^{−1} As(III) or 0.32–4484 mg L^{−1} As(V) and 5 g L^{−1} TiO₂ were adjusted to pH 7 with NaOH and HCl. The samples were covered with aluminum foil to prevent light exposure and mixed on a rotator for 72 h. Then, the final pH was measured and the suspensions were filtered

through a 0.22 μm membrane filter for measurement of soluble As using a furnace atomic absorption spectrometer (FAAS, Perkin-Elmer AAS-800).

2.2 As(III) photooxidation

As(III) photooxidation were carried out in an Erlenmeyer flask with 14 mg-As(III) L^{-1} in a suspension containing 0.3 g L^{-1} TiO_2 and 0.04 M NaCl at pH 7. The sample was stirred in the dark for 2 h to achieve equilibrium before being illuminated by a tubular mercury UV lamp (CEL-WLPM10-254, wavelength 254 nm) with an incident light intensity of about 4000 $\mu\text{W cm}^{-2}$. The photocatalysis process was monitored as a function of illumination time by taking 1 mL aliquots from the suspension and filtering through a 0.22- μm membrane. The As concentration and speciation were determined using high performance liquid chromatography (HPLC) coupled with a hydride generation atomic fluorescence spectrometer (HG-AFS, Jitian, P.R. China).

3 RESULTS AND DISCUSSION

3.1 Facet dependence of As adsorption

The adsorption isotherms of As(III) and As(V) on the three TiO_2 NPs conformed to the Langmuir model. Unexpectedly, no linear dependence was observed for the maximum adsorption capacity (q_m) on S_{BET} . For example, the S_{BET} of JR05 (167 $\text{m}^2 \text{g}^{-1}$) was about half that of HM (336 $\text{m}^2 \text{g}^{-1}$); however, the q_m of JR05 for As(III) (138 mg g^{-1}) and As(V) (144 mg g^{-1}) were comparable to those of HM (136 and 140 mg g^{-1} , respectively, for As(III) and As(V)). The results suggest that S_{BET} may not be the key factor influencing the As adsorption capacity on TiO_2 NPs. Notably, the acid-site-normalized loadings of As(III) and As(V) on JR05, 51.1 and 53.3 mol per mol acid, respectively, were approximately twice as high as for the other two TiO_2 NPs, indicating that the acid sites on JR05 have a greater strength. The NH_3 -TPD characterization indicated that 46% strong acid sites existed on JR05 sample.

The distribution of acid sites is closely related to surface atomic coordination and arrangement, indicating that different crystal facets may endow the same Lewis acid sites with different strengths. This assumption was justified by our DFT calculations. The NH_3 adsorption energies were estimated to be -2.43 and -1.14 eV for {001} and {101} facets, respectively, indicating that {001} facets exhibit stronger acid sites than those on {101} facets. We then proposed that the high As adsorption capacity on JR05 should be related to its exposed facets and their relative proportions.

DFT calculations were performed to compare the As adsorption energies on TiO_2 {001} and {101} facets. The results indicated that the surface complexes are more energetically favorable on {001} than on {101} facets due to the 100% five coordinated ($\text{Ti}_{5\text{c}}$) sites on {001} facet.

3.2 As(III) oxidation on three types of TiO_2

As(III) oxidation on the surfaces of the three TiO_2 NPs follows first-order kinetics. The first-order rate constant, k , varied in the order TG01 (0.0225 min^{-1}) > JR05 (0.0213 min^{-1}) > HM (0.006 min^{-1}). The different As(III) photooxidation rate inspired our further study to characterize ROS effects. Our ESR and fluorescence experimental results show that both $\cdot\text{OH}$ and $\text{O}_2^{\bullet-}$ existed for all TiO_2 samples. The radical trapping experiments suggested that $\text{O}_2^{\bullet-}$ dominated As(III) photooxidation on TiO_2 . The $\text{O}_2^{\bullet-}$ formation is the result of the trapping photogenerated electrons by molecular O_2 adsorbed on the TiO_2 surface. Because different TiO_2 facets exhibit distinct adsorption affinities for NH_3 and As, a reasonable postulation is that the exposed TiO_2 facets would influence the adsorption of molecular O_2 , and as a result, affect the formation of $\text{O}_2^{\bullet-}$.

To understand the facet effect on $\text{O}_2^{\bullet-}$ generation, DFT calculations were performed. The results suggested a more negative adsorption energy (-2.48 eV) and shorter Ti-O bond distance (2.012 Å) on {001} compared to those on {101} facets (-1.79 eV and 2.033 Å). The strong interactions between O_2 and TiO_2 {001} facet may facilitate the electron transfer from the surface to O_2 , forming $\text{O}_2^{\bullet-}$.

4 CONCLUSIONS

This work exploited structural effects on the adsorption and photocatalytic performance of TiO_2 . We found the distribution of exposed crystal facets is the key factor. TiO_2 {001} facets, with stronger Lewis acid Ti^{4+} atoms, exhibit higher adsorption affinity than {101} facets. Furthermore, the strong interactions of {001} facets with oxygen molecules lead to more photoelectrons being transferred to the adsorbed O_2 to generate superoxide radical, which is the primary oxidant in the As(III) photooxidation. Our experimental and theoretical results provide new insights into the intrinsic origin of the facet-activity relationship. The mechanism of the facet dependence of adsorption and photocatalysis should be applicable to other pollutant molecules beyond arsenic.

ACKNOWLEDGEMENTS

We acknowledge the financial support of the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB14020201).

REFERENCES

- Hu, S., Yan, L., Chan, T.S. & Jing, C.Y. 2015. Molecular insights into ternary surface complexation of arsenite and cadmium on TiO_2 . *Environ. Sci. Technol.* 49(10): 5973–5979.
- Liu, G., Yang, H.G., Pan, J., Yang, Y.Q., Lu, G.Q. & Cheng, H.M. 2014. Titanium dioxide crystals with tailored facets. *Chem. Rev.* 114(19): 9559–9612.