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How TiO₂ facets determine arsenic adsorption and photooxidation: spectroscopic and DFT studies†

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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 the {101} facets. In addition, the strong interaction of the {001} facets with molecular O₂ facilitates the transfer of photo-excited electrons to the adsorbed O₂ to generate a superoxide radical (O₂^{•−}), which is the primary As(III) oxidant as evidenced by our radical-trapping experiments. Meanwhile, the oxygen vacancies on the {001} facets could expedite the interfacial electron transfer and electron-hole separation, which promote the generation of O₂^{•−} and, ultimately, the catalytic efficiency. 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.

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1. Introduction

Adsorption and photooxidation on TiO₂ nanomaterials provide a promising technique for arsenic (As) removal.¹ Though the As adsorption mechanism is well-known to involve the formation of a bidentate binuclear surface complex,² even TiO₂ of the same anatase phase from different sources exhibit distinct adsorption and photocatalytic capacities.^{3–5} 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.

The adsorption and photocatalytic performance of anatase TiO₂ depend on its size, shape, and surface atomic structure.^{6–8} Meanwhile, the properties of surface acid sites including type, concentration, and strength also play an important role in the activity of TiO₂.^{9–12} In addition, the conduction band position¹³ and the transport mobility of charge carriers including photo-excited holes (h⁺) and electrons (e[−])¹⁴ may influence photoreactions on anatase TiO₂.

Mounting evidence over the past decade highlights the intrinsic complexity of the effects of structure on TiO₂ properties. However, the processes and associated molecular level mechanisms that influence As adsorption and photooxidation on anatase TiO₂ remain enigmatic.

Recent intriguing studies have shown that the adsorption and photocatalytic activity of TiO₂ largely depend on its surface atomic structure and the degree of exposed reactive crystal facets.^{15–17} The majority of exposed facets for most anatase are the less reactive and thermodynamically stable {101} facets (about 94%) with a minor portion of {001} facets.¹⁸ Conversely, water and dye molecules prefer to bind to anatase {001} rather than {101} facets.^{17,19–21} To the best of our knowledge, no publication has been reported on the effect of TiO₂ facets on As adsorption. Nevertheless, the molecular level knowledge on TiO₂ facets determining As adsorption is of paramount importance in the design and implementation of TiO₂ in As remediation.

The high photocatalytic performance for anatase {001} facets has been explained by the presence of the hydroxyl radical (•OH),²² which is proposed to be the main oxidant for As(III) photooxidation in the TiO₂/UV system.^{4,23} In contrast, Choi *et al.* propose that instead of •OH, the superoxide radical (O₂^{•−}) should play a dominant role,^{24,25} which is supported by other independent studies.^{26,27} The controversy in the As(III) photooxidation mechanism may stem from the knowledge gap concerning the effect of TiO₂ facets on the

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generation of reactive oxygen species (ROS). The generation of ROS such as $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ is mediated by the reaction of surface-adsorbed H_2O and O_2 molecules with photoexcited h^+ and e^- . Therefore, we hypothesize that anatase TiO_2 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 TiO_2 , 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 TiO_2 -based environmental technologies with high adsorption capacity and photocatalytic activity.

2. Experimental

Materials

Three different kinds of TiO_2 nanoparticles (NPs), including one homemade (HM) and two commercial samples, were used in this study. The HM anatase TiO_2 was prepared by hydrolysis of titanyl sulfate as detailed in our previous study.²⁸ Commercial JR05 and TG01 anatase were obtained from Xuancheng Jingrui New Material Co., Ltd. (Anhui, China). Terephthalic acid (TA), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), and superoxide dismutase (SOD) from bovine liver were purchased from Sigma-Aldrich (St. Louis, US). *p*-Benzoquinone was obtained from Acros Organics (Geel, Belgium). Dimethyl sulfoxide (DMSO) and isopropanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Stock solutions of arsenic were prepared using $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ and NaAsO_2 (Fisher Sci., US). Milli-Q water was used to prepare solutions.

As(III) and As(V) adsorption

Adsorption isotherm experiments were performed to determine the As(III) and As(V) adsorption capacity on the three types of TiO_2 in 0.04 M NaCl solution. 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} TiO_2 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) with a detection limit of 0.7 $\mu\text{g L}^{-1}$.²⁹

As(III) photooxidation

As(III) photooxidation experiments were carried out in an Erlenmeyer flask with 14 mg of As(III) per L 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 $\mu\text{W cm}^{-2}$. A control experiment in the dark was also performed. 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 a high performance liquid chromatograph (HPLC) coupled with a hydride generation-atomic fluorescence spectrometer (HG-AFS, Jitian, P.R. China) with a detection limit of 0.7 $\mu\text{g L}^{-1}$ for As(III) and 1.7 $\mu\text{g L}^{-1}$ for As(V).³⁰

ROS species measurement

The $\cdot\text{OH}$ radical measurement followed the procedure described in a previous report.³¹ Terephthalic acid (TA) was used as a fluorescence probe because it can react with $\cdot\text{OH}$ to generate 2-hydroxy terephthalic acid (TAOH), which emits a unique fluorescence band at around 426 nm. TiO_2 samples (62.5 mg) were suspended in a 250 mL solution containing 3 mM TA, and the suspension was stirred in the dark for 2 h to reach equilibrium. Then, the sample was illuminated with UV light, and 2 mL aliquots were taken out every 15 min and immediately filtered through a 0.22 μm membrane for fluorescence measurement. The photoluminescence (PL) emission spectra were recorded using a spectrofluorometer (Hitachi F-4500, Japan) with an excitation wavelength at 312 nm.

The electron spin resonance (ESR) signal of the radicals spin-trapped by DMPO was recorded on a Bruker EMX plus spectrometer after 30 s of photoirradiation with a 100 W mercury lamp (LOT-Oriel GmbH&Co. KG). The settings were as follows: center field at 3503 G, microwave frequency at 9054.6 MHz, and power at 0.998 mW.

Zeta (ζ) potential measurement

To study the pHzpc of TiO_2 NPs, the ζ potential was measured using a Zetasizer Nano ZS (Malvern Instrument Ltd., UK). The pH of the suspension containing 0.2 g L^{-1} TiO_2 in 0.04 M NaCl was adjusted between 3 and 9 using NaOH and HCl. Suspension samples were placed on a rotating shaker for 24 h and the final pH was measured. The reported ζ potential value was the average of three measurements.

Characterization

The crystal structures of the three TiO_2 samples were determined by powder X-ray diffraction (XRD) using an X'Pert PRO diffractometer (PANalytical, Netherlands) with Cu K α radiation. The shape and morphology were characterized by a field-emission scanning electron microscope (FE-SEM, SU-8020, Hitachi) and a transmission electron microscope (TEM, JEM-2100 from Jeol Ltd.). The Brunauer-Emmet-Teller (BET) specific surface area and Barrett-Joyner-Halenda (BJH) pore size distribution were determined from N_2 adsorption-desorption isotherms measured at 77 K using an automated gas sorption instrument (Quantachrome Instruments U.S.

Autosorb-iQ) after the samples were degassed at 105 °C for 12 h. The amount of acid sites was estimated from NH_3 temperature programmed desorption (NH_3 -TPD) measurements performed by using a Quantachrome TPRWinV3.51 system (Quantachrome Instruments U.S. ChemBET Pulsar TPR/TPD). The acid properties were also examined by FTIR spectroscopy of pyridine adsorbed on samples using a Thermo-Nicolet Nexus 6700 FTIR spectrometer. Raman measurements were performed on a Horiba JY HR800 Raman spectrometer with an exciting wavelength at 633 nm. UV-vis diffuse reflectance spectra (DRS) were obtained using a scanning UV-vis spectrophotometer (DRS, UV-2450) equipped with an integrating sphere assembly, while BaSO_4 was used as a reference. The X-ray photoelectron spectra (XPS) and X-ray photoelectron valence-band (VB) spectra were recorded on a Thermo Scientific ESCALAB 250 spectrometer with Al K α X-ray radiation at 1486.8 eV.

Computational details

DFT calculations were conducted to investigate the effect of TiO_2 facets on the As adsorption and photocatalysis. The plane-wave based calculations were performed using the CASTEP package in Materials Studio (Accelrys, San Diego, CA).³² The model-building procedures were similar to our previous study and detailed in the ESI.[†] A plane-wave cutoff energy of 340 eV was selected during the calculations. Ultrasoft pseudopotentials available with the package were used in the treatment of core electrons. The exchange–correlation energy was calculated with the generalized gradient approximation (GGA) approach of Perdew–Burke–Ernzerhof (PBE).³⁴ The k -point over the Brillouin zone was set as a $1 \times 2 \times 1$ grid due to the large size of the slab model. The BFGS method was employed for geometry optimization until the SCF and energy tolerances were less than the convergence criteria, 1.0×10^{-6} and 1.0×10^{-5} eV per atom, respectively.³³

3. Results and discussion

Characterization

The three types of TiO_2 NPs were in the anatase phase (Table 1 and Fig. S1[†]). The XRD-derived particle size was in reasonable agreement with that obtained from the BET surface area, S_{BET} (Fig. S2[†]), and the TEM analysis (Fig. S3[†]). All TiO_2 samples had comparable surface components in the same chemical states as evidenced by XPS (Fig. S4[†]). Detailed structural characterization and comparison of the three TiO_2 NPs are shown in Table S1.[†]

S_{BET} effect on adsorption capacity

The adsorption isotherms of As(III) and As(V) on the three TiO_2 NPs conformed to the Langmuir model (Fig. 1a and b), and the fitting parameters are shown in Table S2.[†] Unexpectedly, no linear dependence was observed for the maximum adsorption capacity (q_m) on S_{BET} or particle size (Fig. 1c and d). 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

Table 1 Summary of characterization of the three TiO_2 NPs

Sample	HM	JR05	TG01
Crystalline phase	Anatase	Anatase	Anatase
XRD crystal size (nm)	4.6	7.5	18.4
S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	336	167	71
Acid concentration (mmol g^{-1})	0.078	0.036	0.043
Exposed {001} facet (%)	4	17	7
pHzpc	5.3	6.5	6.1
As(III) adsorption capacity (mg g^{-1})	136	138	71
As(V) adsorption capacity (mg g^{-1})	140	144	106
As(III) surface coverage (molecules per nm^2)	3.2	6.6	8.0
As(V) surface coverage (molecules per nm^2)	3.3	6.9	12.0
As(III) loading (mol per mol acid)	23.2	51.1	22.0
As(V) loading (mol per mol acid)	23.9	53.3	32.9
As(III) photooxidation rate $k \times 10^{1000}$ (min^{-1})	60.0	213	225

140 mg g^{-1} , respectively, for As(III) and As(V)) (Table 1). Similarly, the adsorption density in the unit of molecules per nm^2 was not proportional to the particle size (Fig. 1d). Specifically, HM, with the smallest particle size (4.6 nm), resulted in the lowest As adsorption density (<3.5 molecules per nm^2). In contrast to the general belief that q_m depends on S_{BET} or particle size,⁸ our results suggest that S_{BET} or particle size may not be the key factor influencing the As adsorption capacity on TiO_2 NPs.

Effect of surface acid sites

The type and concentration of acid sites were determined by pyridine-adsorbed FTIR spectra and NH_3 -TPD analysis, respectively. Only the Lewis type of acid sites existed on the surfaces of the three TiO_2 NPs (Fig. 2a), and the acid site concentration was not proportional to the adsorption capacity (Table 1). For instance, JR05 exhibited the highest As(V) adsorption capacity (144 mg g^{-1}), while having the lowest acid concentration ($0.036 \text{ mmol g}^{-1}$) among all three TiO_2

Fig. 1 Adsorption isotherms of As(III) (a) and As(V) (b), the maximum adsorption capacity (c) and adsorption density (d) on the three TiO_2 NPs.

Fig. 2 Pyridine-adsorbed FTIR spectra (a) and NH₃-TPD profiles (b) of the three TiO₂ NPs.

NPs. This observation indicates that the concentration of total acid sites may not be the determining parameter in As adsorption on TiO₂.

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 TiO₂ NPs (Table 1). This observation suggests that the acid sites on JR05 have a greater strength. This premise was further confirmed by our NH₃-TPD results, where a distinctive peak in the NH₃ desorption curve of JR05 was observed at about 410 °C, corresponding to about 46% strong acid sites (Fig. 2b).³⁵ In contrast, the other two NPs exhibited a homogenous distribution of weaker acid sites on the surface.

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 for the adsorption of NH₃, a probe molecule, on the TiO₂ {001} and {101} facets (Fig. S5†). The NH₃ adsorption energies were estimated to be -2.43 and -1.14 eV for the {001} and {101} facets, respectively (Fig. 3), indicating that the {001} facets exhibit stronger acid sites than those on the {101} facets.⁹ We then proposed that the high As adsorption capacity on JR05 should be related to

Fig. 3 DFT calculated NH₃ (left), As(III) (middle), and As(V) (right) adsorption energies on anatase {001} and {101} facets with bidentate binuclear (blue triangles) and monodentate mononuclear (red circles) surface configurations. The structure parameters for the optimized adsorption complexes and the calculation of adsorption energies are detailed in the ESI.†

its exposed facets and their relative proportions, and this hypothesis was justified by the following quantum chemistry calculations.

Facet dependence of the As adsorption energy

To explore the effect of facets, DFT calculations were performed to compare the As adsorption energies for bidentate binuclear (BB) and monodentate mononuclear (MM) inner-sphere complexes on the TiO₂ {001} and {101} facets (Fig. S6 and S7†). The results are summarized in Fig. 3 and highlight two observations. First, BB complexes are more stable than MM on both facets as evidenced by their more negative adsorption energies (Table S4†), in agreement with previous reports.^{36,37} Second, both BB and MM complexes are more energetically favorable on {001} than on the {101} facets. In fact, the adsorption energy for the BB configuration on the {001} facets was 3.36 and 2.89 eV more negative than on the {101} facets for As(III) and As(V), respectively. The As adsorption mechanism on TiO₂ was further elucidated using partial density of state (PDOS). The overlap of PDOS in Fig. S8 and S9† indicated that the five-coordinated Ti_{5c} atoms on the facets could form chemical bonds with O atoms from As oxoanions, where the newly formed Ti–O bonds were mainly attributed to the electron sharing between the O 2p and Ti 3d orbitals.³³

The TiO₂ {001} and {101} facets, having different surface atomic structures, exhibited distinct abilities in anchoring As. Notably, the TiO₂ {001} facets provide 100% five coordinated (Ti_{5c}) sites compared to 50% Ti_{5c} on the {101} facets.^{17,38} The different densities of these highly reactive unsaturated Ti_{5c} sites contribute to the variation in adsorption capacity for the facets. Thus, the higher proportion of exposed {001} facets with strong Lewis acid sites on JR05 gave rise to its high As adsorption capacity. This conclusion was justified by our Raman analysis (Fig. 4a, Table S3†), which implied that JR05 exposed 17% of the {001} facets, much more than the other two TiO₂ samples (4–7%). The % values refer to the facet area and not the number of facets. The As adsorption behaviors on TiO₂ NPs can also be evidenced by their pH_{zpc} (Fig. 4b, Table 1), which showed that JR05, with a high proportion of {001} facets, exhibited the highest pH_{zpc} (6.5), leading to a high adsorption affinity, consistent with our DFT calculations (Fig. 3). Though As adsorption removal using TiO₂ is well-studied and applied, research investigating the effect of TiO₂ facets on As adsorption has been rare. However, our molecular level insights on how the {001} facets determine As adsorption should be of paramount importance in

Fig. 4 Raman spectra of the three TiO₂ NPs (a) and the zeta potential of 0.2 g L⁻¹ TiO₂ as a function of pH (b).

the design and implementation of TiO_2 in As remediation as well as in other environmental applications.

As(III) photooxidation on the three types of TiO_2

In addition to its high adsorption capacity, TiO_2 also exhibits effective As(III) photocatalytic oxidation.^{4,24,39} The plot of As(III) to initial As(III) (C/C_0) versus irradiation time shown in Fig. 5 suggests that As(III) oxidation on the surfaces of the three TiO_2 NPs follows first-order kinetics.^{8,39} 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}) (Table 1). No oxidation of As(III) to As(V) was observed in the absence of TiO_2 (Fig. S10†) and the control experiment indicated that As(III) photooxidation is negligible under dark conditions. The different As(III) photooxidation rates on the three TiO_2 NPs inspired us to further study the characterization of the ROS effects.

Identification of ROS in the As(III)- TiO_2 /UV system

Reactive oxygen species (ROS), including $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$, are commonly accepted as the main oxidants in the TiO_2 /UV process.^{4,24,40,41} Our ESR and fluorescence experimental results show that both $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ existed for all TiO_2 samples (Fig. 6 and 7). The amount of $\cdot\text{OH}$ followed the order TG01 > JR05 > HM (Fig. 7 and S11†). By comparing the ESR signal after addition of 10% DMSO ($\cdot\text{OH}$ scavenger) and 0.05 g L^{-1} SOD ($\text{O}_2^{\cdot-}$ scavenger) to 0.1 g L^{-1} TiO_2 dispersions, the amount of $\text{O}_2^{\cdot-}$ present during photooxidation was found to follow the order JR05 > TG01 > HM (Fig. 6).

To compare the contributions of $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$, and photo-generated holes (h^+) to As(III) photooxidation, the photocatalytic reaction was investigated using the radical trapping technique with three selective radical scavengers and N_2 purging. The results in Fig. 5 show that the As(III) oxidation in TG01 was appreciably suppressed by 74% and 34%, respectively, after addition of isopropanol ($\cdot\text{OH}$ scavenger, 200 mM)^{42,43} and EDTA-2Na (h^+ scavenger, 40 mM).⁴⁴ In contrast, no discernable difference was observed in the As(III) oxidation upon the removal of $\cdot\text{OH}$ and h^+ in HM and JR05. Notably, 40 mM *p*-benzoquinone, an $\text{O}_2^{\cdot-}$ scavenger,⁴⁵ almost inhibited all As(III) photooxidation for the three types of TiO_2 NPs (Fig. 5, Table 2). This result strongly indicates that $\text{O}_2^{\cdot-}$ dominated As(III) photooxidation on TiO_2 ,^{24,27,41} and $\cdot\text{OH}$ and h^+ were involved for TG01, but not for HM and JR05.

Fig. 5 As(III) oxidation kinetics with the addition of different scavengers (isopropanol: $\cdot\text{OH}$ scavenger; EDTA-2Na: h^+ scavenger; *p*-benzoquinone: $\text{O}_2^{\cdot-}$ scavenger) for HM (a), JR05 (b), and TG01 (c). Initial As(III) = 14 mg L^{-1} ; TiO_2 = 0.3 g L^{-1} ; pH = 7.

Fig. 6 Electron spin resonance spectra of radical adducts trapped by DMPO in HM (a), JR05 (b), and TG01 (c) dispersions after 30 s of UV irradiation with the addition of different scavengers (DMSO: $\cdot\text{OH}$ scavenger; SOD: $\text{O}_2^{\cdot-}$ scavenger). DMPO- $\cdot\text{OH}$ radical and methyl radical are labeled by triangles and circles, respectively.

Facet effect on $\text{O}_2^{\cdot-}$ formation

$\text{O}_2^{\cdot-}$ formation is the result of the trapping of photogenerated electrons by molecular O_2 adsorbed on the TiO_2 surface under UV irradiation.¹⁴ Our results in Fig. 5 show that the removal of dissolved O_2 by purging with N_2 led to the same level of suppression on As(III) photooxidation for the three TiO_2 NPs as *p*-benzoquinone, which confirmed that adsorbed O_2 could act as a photogenerated electron scavenger to produce $\text{O}_2^{\cdot-}$ and subsequently oxidize As(III). Because different TiO_2 facets exhibit distinct adsorption affinities for NH_3 and As (Fig. 3), 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 $\text{O}_2^{\cdot-}$.

To understand the facet effect on $\text{O}_2^{\cdot-}$ generation, DFT calculations were performed with molecular O_2 associated with a Ti_{5c} atom on the {001} and {101} facets. The optimized structure in Fig. 8 shows a significant structural disorder on the {001} facets, resulting in a more negative adsorption energy (-2.48 eV) and a shorter Ti-O bond distance ($2.012 \text{ \AA}$) compared to those on the {101} facets (-1.79 eV and $2.033 \text{ \AA}$, respectively).

The strong interactions between O_2 and the TiO_2 {001} facet may facilitate the electron transfer from the surface to O_2 , forming $\text{O}_2^{\cdot-}$. Analysis of the Mulliken charge shows that the {001} facets could donate a 0.39 charge to an adsorbed O_2 molecule. This charge transfer process would expedite the consumption of photoelectrons and thus prevent their immediate electron-hole recombination, which is beneficial to the photocatalytic activity.⁶

It should be noticed that according to a previous study,⁴⁶ the photogenerated electrons are mainly located in the sub-surface atomic layer of the {001} facets. Thus, an energy

Fig. 7 Fluorescence spectra of the UV irradiated TiO_2 suspensions in 3 mM terephthalic acid at different irradiation times: (a) HM, (b) JR05, and (c) TG01.

Table 2 As(III) photooxidation rate constants on the three TiO₂ NPs with the addition of different scavengers

First-order constant: $k \times 10\,000\ (\text{min}^{-1})$					
TiO ₂ samples	Control	•OH scavenger (isopropanol)	h ⁺ scavenger (EDTA-2Na)	O ₂ ^{•-} scavenger (<i>p</i> -benzoquinone)	N ₂
HM	60.0	53.0	67.2	0	0
JR05	213	228	200	0	0
TG01	225	58.0	149	3.39	5.61

Fig. 8 Optimized geometries of an O₂^{•-} molecule adsorbed at the Ti_{5c} site on the anatase {001} facets (a) and {101} facets (b). CT: charge transfer from TiO₂ facets to the adsorbed O₂ molecule, which is calculated by subtracting the Mulliken charge of isolated O₂ from that of O₂ after adsorption on TiO₂ facets. Note: a superoxide O₂^{•-} anion is added from the beginning by adding an extra electron to the system. The optimized geometric parameters and the calculation of the adsorption energies are detailed in the ESI.†

barrier should prevent the transfer of electrons from subsurface Ti_{6c} sites to surface Ti_{5c} sites. We hypothesize that the surface distortion after O₂ adsorption could promote the transfer of electrons from the subsurface atomic layer (the initial electron trapping sites) to the outermost atomic layer (where photocatalytic reactions generally occur). Therefore, we compared the surface distortion of the {001} and {101} facets after adsorption.

As shown in Fig. 8, a substantial surface distortion was obtained for O₂ adsorption on the {001} facets compared with that on the {101} facets. The energy obtained from surface distortion on the {001} facets was 0.92 eV (Table S5†), which was capable of overcoming the electron trapping energy barrier on the {001} facets (0.38 eV).⁴⁶ Such an energy difference could facilitate the electron transfer from subsurface Ti_{6c} sites to surface Ti_{5c} sites.⁴⁷ These results suggest that the strong affinity of O₂ on the {001} facets and the significant surface distortion can synergistically enhance the separation of photogenerated electrons and holes.

The surface distortion induced by As(III) adsorption may also facilitate the electron transfer and lead to the change in the local potential. The energy obtained from surface distortion upon As(III) adsorption on the {001} facets was 1.27 eV and 3.42 eV for the MM and BB surface complexes (Table S5†), respectively, which is sufficiently high to overcome the energy barrier for the electron transfer from bulk to surface. Further understanding of the change in the local potential for the outermost and inner atomic layers with surface distortion was obtained by examining the projected densities of states (PDOS) on Ti atoms in different atomic layers on the {001} and {101} facets.

As shown in Fig. S12a and b,† the PDOS for Ti atoms in the first (Ti1), second (Ti2), and third (Ti3) layers on the {001} facets almost overlap (top half in each panel), indicating that almost no energy gradient exists to drive the flow of photogenerated electrons from the bulk to the surface layer. On the other hand, upon As(III) adsorption and surface distortion, the energy levels of the three Ti atoms were appreciably decreased by approximately 1.7 eV. The states of Ti1 and Ti2 became the lowest-lying one (−7.1 eV) for both MM and BB surface complexes (bottom half), whereas Ti3 resulted in a higher state at −6.7 eV. The energy difference between surface and bulk Ti atoms (0.4 eV) enables the flow of electrons from the bulk region to the surface layer.⁴⁷ However, such a change in the local potential was negligible on the {101} facets (Fig. S12c and d†), indicating the insignificant effect of As(III) adsorption on {101} surface distortion and electron transfer.

Surface electronic structure effect on photoactivity

The electronic band structure was analyzed to examine the effect of the transport mobility of charge carriers on photoactivity, and the results are shown in Fig. 9. The UV-vis absorption spectra (Fig. 9a) demonstrated that HM and JR05 resulted in comparable absorbance with nearly overlapping absorption edges, whereas the absorption edge of TG01 exhibited a red-shift of about 6 nm with respect to those of

Fig. 9 (a) UV-vis absorption spectra of HM, JR05, and TG01 and the inset showing their transformed Kubelka-Munk functions as a function of energy. (b) X-ray photoelectron valence-band (VB) spectra of the three TiO₂ NPs. (c) Valence-band and conduction-band edges of HM, JR05, and TG01 determined from the spectra.

HM and JR05. Thus, the band gaps followed the order $HM \approx JR05 > TG01$. The X-ray photoelectron valence-band (VB) spectra (Fig. 9b) revealed that the VB maxima of the three TiO_2 samples were at about 2.87 eV, in line with a previous report (2.93 eV).⁴⁰

The resolved band structures of the three TiO_2 NPs are illustrated in Fig. 9c. The nearly identical widths of valence bands for HM and TG01 (about 6.61 eV) indicated that the charge carriers (photo-excited electrons and holes) of these two TiO_2 had similar mobility.¹³ On the other hand, JR05 exhibited a wider valence band with an additional peak at about 11.3 eV (Fig. 9b), indicating the existence of oxygen vacancies as the result of exposed {001} facets.^{13,48,49} Because the high-energy {001} facets are characterized by unsaturated five-coordinated Ti_{5c} atoms and large Ti–O–Ti bond angles (144.9° compared to 101.9° for the {101} facets), substantial oxygen deficiency may occur.^{16,50,51} Such an oxygen vacancy can increase the transport mobility of charge carriers and thus reduce the possibility of recombination of electron–hole pairs.⁵²

Our molecular level insights indicate that As(III) photooxidation on TiO_2 can be simultaneously tuned through the synergistic effects of the surface atomic structure and the surface electronic structure. The {001} facets with 100% Ti_{5c} atoms exhibited stronger interactions with molecular O_2 as evidenced by the shorter Ti–O bond distance (2.012 Å) than that on the {101} facets (2.033 Å). Its unique surface atomic structure resulted in a more negative adsorption energy (−2.48 eV) compared with that on the {101} facets (−1.79 eV) (Fig. 8), which could facilitate the charge transfer (CT = 0.39) from the {001} facets to adsorbed O_2 to generate $O_2^{\cdot-}$. In addition, the electronic structure of the {001} facets with abundant oxygen vacancies facilitated the mobility of the charge carriers (Fig. 9b), which should expedite the interfacial electron transfer and electron–hole separation, and subsequently promote $O_2^{\cdot-}$ generation and As(III) oxidation. This synergistic effect could explain the higher photoreactivity of JR05 (0.0213 min^{−1}) with 17% of the {001} facets compared with HM (0.006 min^{−1}) with only 4% of the {001} facets.

Notably, our conclusion on the preference of $O_2^{\cdot-}$ generation on the {001} facets is in apparent contradiction with previous studies which propose that $O_2^{\cdot-}$ generation on the {101} facets is favorable due to their reductive properties.^{53,54} Though reductive {101} facets with more photoelectrons are favorable for the formation of $O_2^{\cdot-}$, we believe the adsorption of molecular O_2 should be the main factor in $O_2^{\cdot-}$ generation. The O_2 adsorption on the {001} facets had a higher affinity than on the {101} facets (Fig. 8). Furthermore, the photoelectrons anchored on the subsurface atomic layers on the {001} facets can be transferred to the outermost atomic layer to reduce O_2 and generate $O_2^{\cdot-}$ (Fig. 8 and Table S5†). Meanwhile, the synergistic effect of facet-derived oxygen deficiency on photocatalytic performance should be considered in addressing $O_2^{\cdot-}$ generation on different facets.

JR05 and HM were the two TiO_2 NPs involving only $O_2^{\cdot-}$ in the photocatalysis, and the generation of more $O_2^{\cdot-}$ on JR05 can be evidenced indirectly by the amount of As(III) adsorbed

under a N_2 environment. In fact, the As(III) adsorption density was increased to 21.6% under a N_2 environment compared to that of the control sample (Fig. 5). This pronounced increase could be ascribed to the greater number of available Ti_{5c} sites to adsorb As(III) under the N_2 condition because N_2 is inert toward the TiO_2 surface. On the contrary, O_2 molecules can occupy the Ti_{5c} sites to generate $O_2^{\cdot-}$, which reduces the As(III) adsorption density on the surface.

It should be noticed that though JR05 exposed a higher proportion of {001} facets (17%) than TG01 (7%) and generated more $O_2^{\cdot-}$ as evidenced by ESR results (Fig. 6), the photocatalytic rate of JR05 (0.0213 min^{−1}) was slightly lower than that of TG01 (0.0225 min^{−1}). The high photoactivity of TG01 could be attributed to the contribution of 'OH and h^+ as evidenced by our radical trapping experiments, and the reason for different ROS involved in TiO_2 photocatalysis is worth a further study.

4. Conclusions

This work exploited the structural effects on the adsorption and photocatalytic performance of TiO_2 . Contrary to the traditional concept that particle size or specific surface area is the main factor influencing As adsorption on TiO_2 NPs, we found that 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 the {101} facets. Furthermore, the strong interactions of the {001} facets with oxygen molecules lead to more photoelectrons being transferred to the adsorbed O_2 to generate a 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 results obtained from this study highlight the importance of crystal facets in adsorption and photocatalysis, which is of essence in the design and application of TiO_2 NPs with high adsorption ability and photocatalytic activity. In addition, the mechanism of the facet dependence of adsorption and photocatalysis should be applicable to other pollutant molecules beyond arsenic.

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