Mechanistic study of simultaneous arsenic and fluoride removal using granular TiO₂-La adsorbent

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HIGHLIGHTS

- Simultaneous As(III) and F removal is achieved by using granular TiO₂-La composite.
- LaCO₃OH showing orientated growth on TiO₂ {100} facet with matched lattice fringes.
- Molecular-level coadsorption mechanism is investigated by EXAFS and DFT calculation.
- The importance of crystal facet in material synthesis and adsorption is highlighted.

GRAPHICAL ABSTRACT

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ABSTRACT

Naturally co-occurring arsenic (As) and fluoride (F) in groundwater have caused increasing public concerns, and their simultaneous removal is still a challenge due to the lack of efficient adsorptive materials and their competition for adsorption sites. This study fabricated a novel TiO₂-La granular composite adsorbent with LaCO₃OH showing orientated growth on TiO₂ {100} facet. The material exhibited high As(III) (114 mg/g) and F (78.4 mg/g) adsorption capacities and a wide application pH, ranging 3–9, achieving a high percentage (>90%) of As(III) and F adsorption. Coadsorption experiment results demonstrated that high F concentrations inhibit As(III) adsorption, whereas the coexisting As(III) has no significant effect on F removal. The molecular-level mechanisms with EXAFS and DFT studies demonstrated that As(III) adsorption is favorable only on Ti sites as evidenced by an As-Ti distance of 3.36 Å when pH < 7, while La adsorption sites can also be occupied with an As-La distance at 3.42 Å when pH > 10. The F adsorption is pH-dependent and mainly occurred on La sites. The granular TiO₂-La with high As(III) and F adsorption capacities can be used to simultaneously remove As(III) and F. The insights gained from this study shed a new light on the interaction mechanism of As(III) and F with the TiO₂-La composite.

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1. Introduction

Elevated concentrations of co-existing arsenic (As) and fluoride (F) in groundwater have become a worldwide problem due to their

synergistic adverse health effects [1–3]. As the World Health Organization (WHO) suggests, the drinking water standards for As and F are 10 µg/L and 1.5 mg/L, respectively. However, reaching this WHO standard is still a great challenge, especially in low income and heavily contaminated areas, due to the lack of proper treatment [4,5]. Therefore, highly efficient simultaneous removal of As and F is of great urgency and high priority.

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Among various technologies for As and F removal, adsorption is considered suitable because of its high efficiency, cost-effectiveness, and feasible operation [6–9]. Therefore, the preparation and characterization of adsorptive media becomes the first and foremost step in water treatment using adsorption technology. TiO_2 has been successfully used as an adsorbent for As removal from drinking water and wastewater [5,10–12]. Activated alumina (AA) is an EPA standard and a widely used adsorbent for defluoridation. However, AA exhibits well-known limitations, including a reduced F removal efficiency at $\text{pH} > 6$, and the release of Al [2,13,14]. Recently, lanthanum (La) impregnated materials have been proven to be the most promising F adsorbent due to the specific affinity of La sites with F ions [15–18].

However, a limited number of studies have paid attention to developing effective adsorbents for the simultaneous removal of As(III) and F [19–21]. Recently, La-impregnated activated alumina (LAA) has been synthesized for As(III) (9.23 mg/g) and F (16.9 mg/g) adsorption, with both As(III) and F occupying the sites on La rather than on Al [15,22]. This result indicates that the impregnation of amorphous La oxide on AA may mask the Al sites, and thus As(III) and F have to compete for limited La sites. To take advantage of composite materials while avoiding the limitations of impregnation, we hypothesized that the orientated growth of La oxide on certain TiO_2 facets with matched lattice spacing would be a feasible approach to synthesizing hybrid materials with both exposed Ti and La sites. Although this TiO_2 -La hybrid material has not been examined before, the synergetic effects of coexisting Ti and La sites enable it as an efficient adsorbent for the simultaneous removal of As(III) and F.

As a proof-of-concept study herein, the purpose of this study was to construct a composite adsorbent with La oxide exhibiting orientated growth on TiO_2 for simultaneous and effective removal of As(III) and F. The molecular level interaction mechanism on this novel granular adsorbent was explored using multiple complementary techniques including extended X-ray absorption fine structure (EXAFS) spectroscopy and density function theory (DFT) calculations. The insights gained from this study further our understanding of the simultaneous removal mechanisms of As(III) and F on hybrid TiO_2 -La materials.

2. Material and methods

2.1. Materials

All chemicals used in this study were of analytical grade. Stock solutions containing 5000 mg/L of As(III) and F were prepared by dissolving NaAsO_2 (Fisher Sci., US) and NaF in deionized (DI) water, respectively. A 1 M La stock solution was prepared by dissolving $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in DI water, and the pH was adjusted to 6.0 using $\text{NH}_3 \cdot \text{H}_2\text{O}$.

2.2. Synthesis of TiO_2 -La composite

TiO_2 with exposed {100} facets used in this study was prepared via the hydrolysis of titanyl sulfate, then treated with NaOH. The detailed procedures are presented in the [Supplementary Information \(SI\)](#). TiO_2 -La composite was prepared by orientated La growth on the obtained {100}-faceted TiO_2 . Specifically, a mixture of 150 mg TiO_2 and La stock solution was sonicated for 3 h, and then calcined for 4 h at 400 °C in the muffle. After the obtained granules were ground and sieved, the material was washed with DI water until the conductivity was below 100 $\mu\text{S}/\text{cm}$, and then dried in an oven at 60 °C. The 60–80 mesh (180–250 μm) granular TiO_2 -La material was used in the adsorption experiments.

2.3. Characterization

The BET specific surface area and Barrett-Joyner-Halenda (BJH) pore size distribution were determined from N_2 adsorption-desorption isotherms using an automated gas sorption instrument (Quantachrome Instruments, U.S.). The crystal structure was determined by XRD using an X'Pert PRO diffractometer (PANalytical, Netherlands) with $\text{Cu K}\alpha$ radiation. The surface morphology was examined using an FE-SEM with an Oxford energy dispersive X-ray spectroscopy (EDX) analyzer (SU-8000, Hitachi), and the acceleration voltage was set at 5.0 kV. The crystal morphology was characterized using an HRTEM (JEM-2100F, JEOL) with an acceleration voltage of 200 kV. FTIR spectra were collected on a Thermo Nicolet iS50 FTIR spectrometer with a deuterated triglycine sulfate (DTGS) detector. Raman spectra were obtained on a Horiba JY HR800 Raman spectrometer with an excitation wavelength at 532 nm. X-ray photoelectron spectroscopy (XPS) was analyzed on a Thermo SCIENTIFIC ESCALAB 250 spectrometer with Al $\text{K}\alpha$ X-ray radiation at 1486.8 eV. The XPS data processing and peak fitting were performed using the XPSpeak 4.0 software package. The granule strength was measured to be 45 N by a particle strength tester (Haibo, China). The pH_{pzc} of TiO_2 and TiO_2 -La were determined using a Zetasizer Nano ZS (Malvern Instrument Ltd., UK) with suspensions containing either 0.2 g/L TiO_2 or TiO_2 -La in 0.04 M NaCl.

2.4. Adsorption experiments

Batch adsorption experiments were performed to compare the adsorption effectiveness of TiO_2 -La impregnated with different concentrations of $\text{La}(\text{NO}_3)_3$. In a typical experiment, 80 mg TiO_2 -La composite for TiO_2 impregnated with different concentrations of $\text{La}(\text{NO}_3)_3$, 0, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 mmol, respectively, were mixed with 40 mL of either 1.5 mg/L As(III) or 2.0 mg/L F solution at pH 7. A background electrolyte of 0.04 M NaCl was used in the experiment. HCl and NaOH were used to adjust the pH. The results shown in [Fig. S1](#) demonstrate that TiO_2 -La material with 0.5 mmol $\text{La}(\text{NO}_3)_3$ exhibited high adsorption densities for As(III) and F, thus this material was used for further adsorption experiments.

Adsorption isotherm experiments were performed to determine the As(III) and F adsorption capacities on the TiO_2 -La in a 0.04 M NaCl solution. Suspension samples containing either 0.1–2500 mg/L As(III) or 0.5–2830 mg/L F and 2 g/L TiO_2 -La were adjusted to pH 7 with NaOH and HCl. The adsorption kinetics on 2 g/L TiO_2 -La were studied at pH 7 in 1 L of 0.04 M NaCl solution with initial either 1.7 mg/L As(III) or 2.4 mg/L F. The adsorption envelope experiments with 2.5, 25, and 250 mg/L As(III) or F on 2 g/L TiO_2 -La were conducted as a function of the solution pH. The pH of the suspension in 0.04 M NaCl was adjusted to desired pH values in the range of 2–12 using NaOH and HCl. As(III) and F coadsorption experiments were conducted to determine the adsorption performance as a function of As(III), F concentrations, and pH conditions. The bottles for adsorption experiments were covered with aluminum foil to prevent light exposure. After the samples were mixed on a rotator for 24 h, the final pH was measured and the suspensions were filtered through a 0.22- μm membrane filter for analysis.

The measurement of soluble As was performed using a furnace atomic absorption spectrometer (FAAS, Perkin-Elmer AAS-800). The F concentration was measured using an F ion-selective electrode (Orion, Thermo Fisher Sci., US).

The adsorption isotherm was simulated with Langmuir model and expressed as Eq. (1):

$$\frac{C_e}{q_e} = \frac{1}{q_m \times K} + \frac{C_e}{q_m} \quad (1)$$

where q_m (mg/g) is the maximum adsorption capacity; q_e is the equilibrium adsorption density with certain equilibrium concentration of C_e (mg/L) for adsorbate in the solution; and K (L/mg) is the adsorption equilibrium constant.

The adsorption kinetics was modeled by pseudo-second order kinetics, and was calculated using Eq. (2):

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k \times q_e^2} \quad (2)$$

where q_t and q_e are the adsorption density (mg/g) at time t and at equilibrium, respectively; and k (g/(mg h)) is the rate constant.

2.5. Micro-beam X-ray fluorescence (μ -XRF) analysis

The μ -XRF sample was prepared with 100 mg/L As(III), 250 mg/L F, and 2 g/L TiO_2 -La in 0.04 M NaCl at pH 7. The spent media was freeze-dried and deposited onto Kapton tape. The μ -XRF maps were acquired on beamline 15U at Shanghai Synchrotron Radiation Facility (SSRF), China. The monochromator was set at 14 keV with the beam as $3 \times 3 \mu\text{m}^2$ and the dwell time per pixel was 0.3 s. The step size was $3 \mu\text{m}$. The peak intensities for As, Ti, and La were collected at each pixel of μ -XRF maps that were $67 \times 67 \mu\text{m}^2$ in size.

2.6. EXAFS study

The samples from coadsorption experiments were freeze-dried and ground to 200 mesh, and then sealed between two layers of Kapton tape. The As K-edge (11,867 eV) spectra were collected on beamline 01C1 at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The spectra were acquired with a standard Lytle detector at cryogenic temperature (77 K) using a helium cryostat to prevent beam-induced oxidation. An energy range of -200 to 1000 eV from the K-edge was used to acquire the spectra. To improve the signal-to-noise ratio, three to five scans were collected for each sample, inspected for overall quality, and averaged. The EXAFS data was analyzed using the Athena and Artemis programs in the Demeter computer package [23]. The analysis procedure was similar to that in our previous studies [11,24], and is detailed in the SI.

2.7. DFT calculations

The density function theory (DFT)-based geometry optimization and adsorption energy of As(III) and F surface complexes were calculated using the Castep package in Materials Studio 7.0 (Accelrys, San Diego, CA). The model building was detailed in the SI. A plane-wave cutoff energy of 340 eV was selected and the core electrons were treated using ultrasoft pseudopotentials. The generalized gradient approximation (GGA) approach of Perdew-Burke-Ernzerhof (PBE) was employed to calculate the exchange-correlation energy. The k -point over the Brillouin zone was set as a $2 \times 2 \times 1$ grid. The geometry optimization was calculated with the BFGS method until meeting the convergence criteria, 1.0×10^{-6} and 1.0×10^{-5} eV/atom, respectively, for SCF and energy tolerances [25]. All atoms were relaxed during calculations.

The adsorption energies (E_{ads}) of As(III) and F molecules was calculated according to the following Eq. (3):

$$E_{\text{ads}} = E_{\text{mol+surf}} - (E_{\text{surf}} + E_{\text{mol}}) \quad (3)$$

where $E_{\text{mol+surf}}$ is the total energy of the surface complexes; E_{surf} is the energy of the isolated TiO_2 {100} and LaCO_3OH {011} facets; and E_{mol} represents the energy of isolated As(III) and F molecules. Note that a negative value for E_{ads} suggests a stable adsorption configuration.

3. Results and discussion

3.1. Characterization of granular TiO_2 -La composite

The morphology and structural properties of the TiO_2 -La and control samples were characterized using SEM, TEM, and EDX (Fig. 1). The SEM and TEM images of TiO_2 (Fig. 1a–c) showed that the nanorod TiO_2 of ca. 750 nm was tetragonal spindle exposed mostly with high-energy {100} facets [26]. The thermodynamically stable {101} facets existed only on the tip of the spindle with a lattice spacing of 3.5 Å [27]. The images of TiO_2 -La (Fig. 1e–g) showed that LaCO_3OH had orientated growth on TiO_2 with their matched lattice spacing (1.9 Å) between the TiO_2 (2 0 0) plane and LaCO_3OH (0 3 3) plane [28]. Considering the same atomic coordination of the TiO_2 {1 0 0} facet and (2 0 0) plane, which is the same as the LaCO_3OH crystal (for {0 1 1} facet and (0 3 3) plane), we used unified facet to represent the crystal plane. The EDX spectra (Fig. 1h) confirmed that the sample is composed of Ti, La, C, and O elements. The control sample that was synthesized without addition of TiO_2 was nanorod $\text{La}(\text{OH})_3$, and composed of La and O elements with exposed {1 0 1} facets (Fig. 1i–l), which highlights the significance of TiO_2 facet for the synthesis of hybrid TiO_2 -La materials.

XPS was used to inspect the surface composition and chemical states of the TiO_2 -La material. Each of the binding energies obtained in the XPS analysis were calibrated using the C 1s peak at 284.60 eV from contamination as reference. The survey XPS spectrum of the prepared TiO_2 -La sample (Fig. 2a) indicates the presence of Ti, La, O, and C, in accord with the result of EDX (Fig. 1h). The XPS spectra of the Ti 2p core level region of the sample is shown in Fig. 2b. The two peaks at about 458.3 eV and 464.0 eV can be assigned to the Ti 2p_{3/2} and Ti 2p_{1/2} spin orbital splitting photoelectrons in the Ti^{4+} chemical state [25,29], respectively. Fig. 2c shows the La 3d XPS spectrum of the prepared sample. The electron binding energy values are observed at 835.1 eV and 851.7 eV, corresponding to the main peaks (3d⁹4f configuration) of La 3d_{5/2} and La 3d_{3/2} with the shake-up peaks (3d⁹4f¹ configuration) located at 838.8 eV and 855.6 eV, respectively, which correspond to the La(III) oxidation state [28,30]. The binding energies at 531.8 eV and 529.8 eV in O 1s spectra (Fig. 2d) are related to lattice oxygen in LaCO_3OH and TiO_2 [31,32], respectively. The C 1s spectrum (Fig. 2e) exhibits peaks at 289.8 eV and 284.60 eV, corresponding to the carbonate and carbon contamination as reference, respectively [28].

The XRD patterns of TiO_2 -La shown in Fig. S2 indicate that all diffraction peaks can be indexed to the tetragonal TiO_2 (JCPDS: 65-5714) and orthorhombic LaCO_3OH (JCPDS: 49-0981). FTIR and Raman characterizations suggest that the impregnation of La composite on TiO_2 had no change on the TiO_2 structure (Fig. S3). The BET surface specific area of TiO_2 -La was determined to be approximately 23.7 m²/g, and the BJH pore size distribution ranged from 35 to 42 nm with the peak located at ca. 38 nm (Fig. S4). TGA analysis indicated that the material exhibited high thermostability with 6.3% weight loss after heating at 400 °C (Fig. S5). Detailed descriptions of the characterization results are presented in the SI.

3.2. Heterostructure of TiO_2 -La

To further elucidate the significant role of TiO_2 {100} facet in synthesizing TiO_2 -La, we compared the hybrid materials by impregnating La on TiO_2 with three index facets of {100}, {001}, and {101} (Fig. S6). Our results clearly demonstrate that LaCO_3OH showed orientated growth only on {100}-faceted TiO_2 with La contents up to 26.4% (Fig. 1), which is an order of magnitude higher than that on {101}-faceted (3.9%) and {001}-faceted (6.9%) TiO_2

Fig. 1. SEM, TEM, and EDX characterization of {100}-faceted TiO₂ (a–d), TiO₂-La (e–h), and La(OH)₃ (i–l).

Fig. 2. XPS spectra of TiO₂-La sample (a), and of the core levels of Ti 2p (b), La 3d (c), O 1s (d), and C 1s (e).

(Fig. S6). This unique advantage of {100} facet can be attributed to two reasons. Firstly, the TiO_2 {100} facets favor CO_2 adsorption ($E_{\text{ads}} = -0.1$ eV) and subsequently the formation of CO_3^{2-} on the surface (Fig. 3a). Secondly, only the lattice spacing (1.9 Å) and parallel crystal orientation of {100} facet (Fig. 1g), not of {101} (3.5 Å) and {001} facets (perpendicular orientation with {100} facet), match that of LaCO_3OH {011} facets.

The formation of LaCO_3OH can be attributed to the following reaction Eqs. (4)–(6), where $\text{NH}_3 \cdot \text{H}_2\text{O}$ is used to adjust pH of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution:

The geometry-optimized TiO_2 -La heterostructure is presented in Fig. 3b. The results suggest that new Ti–O and La–O bonds were formed in the heterostructure interface. The formation of new bonds is a Lewis acid-base reaction because surface Ti^{4+} and La^{3+} atoms shared an electron pair of coordinated O^{2-} that existed on the surface to form Ti–O and La–O bonds, as elucidated by our partial density of states (PDOS) analysis. The overlap of PDOS in Fig. 3c and d indicates that the five-coordinated Ti atoms on the TiO_2 facets covalently bonded with O atoms from La oxides, as evidenced by the electron sharing between the O-2p and Ti-3d orbitals [25]. The newly formed La–O bond was mainly attributed to the electron sharing between the O-2p and La-5d orbitals.

The TiO_2 -La heterostructure provides more La adsorption sites than pristine TiO_2 for As(III) and F adsorption. The adsorption comparison between TiO_2 and hybrid TiO_2 -La with different facets is summarized in Fig. S7 and highlights two observations. First, As(III) adsorption on {100}-faceted TiO_2 -La was enhanced by 40.1% compared with TiO_2 , whereas it was reduced by 2% on other two-faceted TiO_2 -La materials. Though all three of the faceted TiO_2 -La hybrid materials enhanced F removal compared with

pristine TiO_2 , {100}-faceted TiO_2 -La (79.2% increase) exhibited a significant superiority to {001}-faceted (7.4%) and {101}-faceted (7.6%) TiO_2 -La (Fig. S7a). Second, the adsorption density of As(III) and F in the unit of molecules/ nm^2 on {100}-faceted TiO_2 -La (0.25 for As(III), 1.18 for F) was an order of magnitude higher than the other two faceted TiO_2 -La materials (0.016–0.029 for As(III), 0.021–0.029 for F, Fig. S7b). Due to its unique advantage, we focus our study on {100}-faceted TiO_2 -La hybrid material.

3.3. Adsorption experiments

The adsorption isotherms of As(III) and F on TiO_2 -La conformed to the Langmuir model, and the fitting parameters are shown in the inset of Fig. 4a. The results suggested that the maximum adsorption capacities (q_m) for As(III) and F followed the order of $q_m(\text{As})$ (114 mg/g) > $q_m(\text{F})$ (78.4 mg/g). This is because two sites (mixed Ti and La sites) were available for As(III) adsorption, whereas only La site was responsible for F adsorption (*vide infra*). The q_m for present studied TiO_2 -La composite is higher than other reported adsorbents with simultaneous As and F removal, such as E33P, Al_2O_3 , La- Al_2O_3 (LAA), Ti-La impregnated activated carbon (TLAC), Al/Fe-doped adsorbents, and modified cellulose fibers, with adsorption capacities in the range of 7.3–40 mg/g for As, and 2.3–100 mg/g for F [15,19–22].

The adsorption of As(III) and F on TiO_2 -La followed pseudo-second order kinetics ($R^2 > 0.98$, Fig. 4b), suggesting that chemical adsorption is the rate-controlling step, which is further evidenced by our EXAFS and DFT study. The rate constant, k , for F adsorption was 0.51 g/(mg h), which is slightly higher than that for As(III) (0.43 g/(mg h), Fig. 4b inset). The faster kinetics of F may result from its smaller molecular size. Furthermore, the La sites, which are attributable to F uptake, have a short distance to access F molecules due to their orientated growth on the outside of the TiO_2 surface. The q_e in Fig. 4b was the adsorption density with initial As(III) and F concentration of 1.7 and 2.4 mg/L, respectively. The equilibrium concentration after adsorption was 0.23 mg/L for As(III) and 0.14 mg/L for F, leading to $q_e(\text{As})$ (0.8 mg/g) < $q_e(\text{F})$ (1.2 mg/g). This

Fig. 3. (a) Optimized CO_2 adsorption configuration on TiO_2 {100} facet. (b) Geometry optimized TiO_2 -La heterostructure. PDOS analysis for TiO_2 -La with newly formed, (c) Ti–O and (d) La–O bond. O_{Ti} and O_{La} in (b) represent the O atoms on the TiO_2 and LaCO_3OH surfaces, respectively.

Fig. 4. Isotherms (a) and kinetics (b) for As(III) or F adsorption on 2 g/L TiO₂-La in 0.04 M NaCl solution at pH 7. Symbols are experimental data, and the solid lines represent the Langmuir model (a) and pseudo-second order kinetics model simulation (b). Inset table in a and b shows parameters of Langmuir model and pseudo-second order kinetics model. As(III) (c) and F (d) removal efficiency as a function of pH. The initial As(III) or F concentrations are 2.5 mg/L, 25 mg/L, and 250 mg/L, respectively.

Fig. 5. As(III) (a) and F (b) coadsorption density with As(III) concentrations at 10 mg/L (green), 100 mg/L (blue), and 1000 mg/L (red); F concentration at 25 mg/L, 250 mg/L, and 1000 mg/L (the color become deepened with F concentration increased); and pH at 2, 4, 7, and 10, respectively. The size of the ball on behalf of the adsorption quantity, and the value was listed nearby the ball. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

observation can be explained by lower initial As(III) concentration compared to that of F.

The As(III) and F adsorption envelope experiments determined the percentage of As(III) and F adsorbed as a function of equilibrium pH (Fig. 4c and d). TiO₂-La exhibited a wide pH

application range (3–9), removing >90% of As(III) and 95% of F with their initial concentrations at 2.5 mg/L. When the initial concentrations were increased to 25 mg/L and 250 mg/L, an M-shaped curve for As(III) adsorption was observed with two adsorption maxima at pH's of about 4.8 and 8.5 (Fig. 4c), indicating the existence of two

different adsorption sites on TiO₂-La. One site was TiO₂ that is responsible for As(III) adsorption at a low pH range from 3 to 7, as evidenced by its low pH_{pzc} at 3.7 (Fig. S8). The other site was on La-oxide that favorable at high pH range of 7–10 with its pH_{pzc} at 9.2 [22]. The F adsorption behaviors with increasing initial concentrations followed the characteristic of anion adsorption on single metal oxide (LaCO₃OH), which is decreasing with the increasing pH (Fig. 4d).

3.4. As(III) and F coadsorption experiments

As(III) and F coadsorption experiments were performed to determine the effect of pH and As(III) and F concentrations. The results summarized in Fig. 5a indicate that with a low coexisting F (25 mg/L) and As(III) (10 mg/L) at pH 7, the adsorption density

Fig. 6. As and F adsorption with different dosage of TiO₂-La, ranging from 0 to 50 g/L.

of As(III) was 5.2 mg/g. The density was significantly increased to 89.2 mg/g with the increase of initial As(III) concentration up to 1000 mg/L (Fig. 5a, yellow panel). However, the As(III) adsorption density decreased from 89.2 to 48.8 mg/g with the increase in F, albeit the initial As(III) concentration was increased as high as 1000 mg/L (Fig. 5a, purple panel). This result indicates that high concentrations of coexisting F can significantly influence As(III) adsorption in the presence of high initial As(III) concentrations. With initial As(III) concentrations decreased to 100 mg/L, the F influence on As(III) adsorption was negligible (Fig. 5a, green panel), which can be attributed to the hybrid adsorption sites of Ti and La for As(III) adsorption (Fig. 4c). The observed trend agrees with the logic that F adsorption on La sites may exaggerate the steric hindrance for the access of H₃AsO₃ to the TiO₂-La surface. As(III) adsorption in the pH range of 4–7 exhibited a higher adsorption density than that at pH 2 and 10, which is consistent with the results of pH edge (Fig. 4c).

The F adsorption density was about 11.0 mg/g with an initial F concentration of 25 mg/L at pH 7, and the increase in the coexisting As(III) concentration from 10 to 1000 mg/L had no effect on F adsorption (Fig. 5b, yellow panel). When initial F concentration was increased to 1000 mg/L, the F adsorption density significantly increased from 11.0 to 65.7 mg/g. The coexisting As(III) had no effect on F adsorption (Fig. 5b, purple and green panels). F adsorption is pH-dependent that the increase in pH decreases the F adsorption (Fig. 4d).

The hybrid TiO₂-La material was used to remediate a real groundwater sample taken from Shanxi, China, with a concentration of 342 µg/L As(III), 16 µg/L As(V), and 1.9 mg/L F at pH 8.2. Our results demonstrate an effective simultaneous removal of As and F using granular TiO₂-La composite, where a dosage of 5 g/L can provide As/F-safe drinking water (Fig. 6), which highlighted the environmental application of this TiO₂-La composite.

Adsorption experiments showed a macroscopic picture of As(III) and F behaviors on the materials, mechanistic information,

Fig. 7. Observed (red circles) and fitted (black lines) k^3 -weighted As K-edge EXAFS spectra (a) and their corresponding Fourier transform magnitudes (b) and real parts (c). The samples were prepared by reacting 100 mg/L As(III) and 25 mg/L F at pH 2, 4, 7, and 10 in 0.04 M NaCl. The fitting parameters are shown in Table S5 and the F -test results are shown in Table S9. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

however, cannot be explicitly derived from the above observations. Therefore, spectroscopic techniques were used to decipher the molecular-level mechanisms of As(III) and F adsorption on TiO_2 -La.

3.5. Distribution of elements on TiO_2 -La

The distribution of As on nanomaterials has been studied by synchrotron-based μ -XRF, and the results suggested that As was associated with Ti and La oxides (Fig. S9). The highly correlated Ti and La demonstrated that LaCO_3OH was evenly distributed on TiO_2 in μm -size resolution provided by μ -XRF. To further investigate the adsorption mechanism of As(III) and F on hybrid TiO_2 -La material, a molecular-level study including EXAFS and DFT was necessary.

3.6. EXAFS study

To explore the role of Ti and La sites on As(III) removal, we employed EXAFS to characterize the local coordination environment. The k^3 -weighted As K -edge EXAFS spectra and corresponding Fourier transforms (FT) for As(III) and F coadsorption samples are presented in Figs. S10–12, and their fitting parameters are shown

in Tables S1–4. For all samples, a strong FT signal at 1.78–1.79 Å was resolved corresponding to three As–O single scattering (SS) paths in the first shell. An As–O–O multiple scattering path within the AsO_3 pyramid was included in the fitting without adding extra variables [24].

The second FT peak was ascribed to 1.8–2.1 Ti atoms at 3.35–3.39 Å (Table S1), which is in agreement with As(III) bidentate binuclear configurations on TiO_2 [24]. Conversely, the As–La SS path for the second shell fitting resulted in unsatisfactory R-factors (0.018–0.031, Fig. S11, Table S2). The idea that Ti was in the second shell of As was further justified by the F-test. The confidence level of including the As–Ti path is 74.1–97.3% (Table S4), higher than the required significance level of 67% [24]. In contrast, the confidence level with the inclusion of the As–La path was only 0–42.2% (Table S4), confirming that La atoms do not exist in the second shell of As. This analysis showed that As(III) mainly adsorbs on Ti sites of TiO_2 -La, and the coexisting F ions have no impact on the As(III) surface configuration.

The EXAFS results for As(III) and F co-adsorption samples at different pH's are shown in Figs. 7 and S13–15, and Tables S5–9. Interestingly, the sample at pH = 10 resulted in a second shell with mixed As–Ti and As–La paths, as evidenced by their high F-test

Fig. 8. Optimized As(III) and F adsorption configurations on TiO_2 {100} facet (a–c) and LaCO_3OH {011} facet (d–f).

values (69.9% for As-Ti, 79.1% for As-La). EXAFS analysis resolved 1.8 Ti atoms at a distance of 3.36 Å and 0.7 La atoms at 3.42 Å (Fig. 7, Table S5), indicating that As(III) adsorbed in bidentate configuration on Ti sites and in monodentate configuration on La sites [22,24]. The contribution of La sites for As(III) adsorption at pH 10 can be attributed to the fact that less electronic repulsion exists between the negatively charged As(III) species, H_2AsO_3^- , and La-oxide surfaces ($\text{pHpzc} = 9.2$) [22], compared with TiO_2 surfaces ($\text{pHpzc} = 3.7$).

3.7. DFT calculations

The DFT-optimized configurations of As(III) and F on TiO_2 {100} and LaCO_3OH {011} facets are shown in Fig. 8, and the calculated adsorption energy (E_{ads}) is listed in Table S10. The results clearly show that a bidentate As(III) structure on TiO_2 {100} and monodentate on LaCO_3OH {011} are energetically stable, as evidenced by their negative E_{ads} of -0.51 eV and -1.34 eV, respectively, which is consistent with EXAFS results that As(III) adsorption was favorable on both Ti and La sites (see Fig. 7).

Notably, the adsorption of both anionic F^- and HF molecule on TiO_2 {100} facet was unstable, as suggested by their positive E_{ads} of 0.70 eV and 4.21 eV, respectively (Fig. 8b and c). The even more unstable HF adsorption than F^- on the TiO_2 surface can be ascribed to the dissociation of HF when it reacts with H_2O molecules (Fig. 8c), and after the dissociation, the remaining F^- ions cannot form stable complexes on the TiO_2 surface. In contrast, the adsorption of anionic F^- on LaCO_3OH {011} is favorable as evidenced by its negative E_{ads} of -0.28 eV. Furthermore, in acidic conditions where F exists as HF molecules ($\text{pH} < 3$), its adsorption on LaCO_3OH {011} is more favorable ($E_{\text{ads}} = -0.52$ eV), in accordance with our pH edge observation that F adsorption is favorable at a low pH (Fig. 4d). Our DFT calculation confirms that TiO_2 has no affinity for F, whereas La oxides are responsible for F removal with $-\text{OH}$ exchange from surfaces [33,34]. This is our original intention for synthesizing hybrid materials for simultaneous As(III) and F removal.

4. Conclusions

Simultaneous removal of As(III) and F on granular TiO_2 -La was investigated by water chemistry experiments, multiple complementary spectroscopic techniques, and DFT calculations. The results uncover the molecular level mechanism for As(III) and F adsorption at a heterostructure interface. Furthermore, this comprehensive study provides new insights into the intrinsic origin of the facet-dependent hybrid materials synthesis with orientated growth of La oxide on {100}-faceted TiO_2 with matched lattice spacing. The results obtained from this study highlight the importance of crystal facets in the materials synthesis and adsorption, which is of essence in the design and application of TiO_2 -based materials.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2016.10.142>.

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