Nanometer effect promoting arsenic removal on α-MnO₂ nano-surface in aqueous solution: DFT+U research

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Abstract
The nanometer effect in the process of arsenic ions removal on α-MnO₂ nano-surface is studied by the first-principle method through microfacet models. Several parameters, such as adhesion energy, electrostatic potential, and Mulliken population were calculated to illuminate the internal mechanism. The results show that the adsorption energies of As(OH)₃ molecules on MnO₂[(100×110)] nanostructure are smaller than that on the bulk surface with the same concentration, which means the nanometer effect is beneficial to enhance the adsorption ability of MnO₂ nano-surface. In an aqueous solution, there exist two possible removal ways of As ions. One is the direct reaction of As(OH)₃ → As(OH)₆⁻, which occurs both in bulk surface and nano-surface. However, to nanomaterials, there exists another removal way of As(OH)₃ → As(OH)₄ → As(OH)₆⁻ through an intermediate As(OH)₄ molecule produced by nanometer effect. Furthermore, the smaller electrostatic potential of As ions on [(100×110)] nano-surface is beneficial to enhance the removal capability of As ions. Then the reason why MnO₂ nanomaterials have better catalytic activity than the bulk materials is originated from its much less adhesion energy, much more removal ways, and much smaller electrostatic potential. So this research provides a detailed understanding of the removal capability of toxic ions influenced by a nanometer effect.

Keywords Arsenic ions · MnO₂ nano-surface · Catalytic mechanism · Transitional product · DFT+U method

Introduction
The toxic arsenic ions entering the human body through drinking water will cause protein inactivation in the human body and lead to poisoning, which seriously threatens the safety of human life (Jomova et al. 2011; Chandra et al. 2010). Therefore, the removal of arsenic ions from an aqueous solution has become one of the hot spots in human society. However, the traditional coagulation filtration (Gupta and Ghosh 2009), ion exchange (Pessoa-Lopes et al. 2016), and other arsenic removal technologies (Xiao et al. 2015) have the disadvantages of a complex operation process and high operation cost, which limit their application scope. Thus, the adsorption technology, which is economical and efficient, becomes the prior choice (Mishra and Ramaprabhu 2011). Among the numerous adsorption materials, α-MnO₂ has the characteristics of large natural reserves, high safety, no pollution, low cost, good physical, and chemical properties, so it can effectively remove arsenic ions in water via adsorption and catalysis (Xiao et al. 2009; Li et al. 2014; Gheju et al. 2016) and has become an optimal candidate material for arsenic ion removal in aqueous solution.

In recent years, experts and scholars at home and abroad have done a lot of experimental or theoretical researches on the removal of arsenic ions in aqueous solution by α-MnO₂. Thanh et al. (2012) have synthesized some α-MnO₂ nanorods through ball-milling of a physical blend and an in situ formation of laterite. He finds that their adsorption capacities
(9.7mg/g) for arsenite (As(V)) are affected by highly pH-dependent and adsorption kinetics. Zhang and Sun (2013) have investigated the As removal capacity of α-MnO2 dandelion-like microspheres and point out that the arsenite (As(III)) species can be effectively oxidized by synthesized MnO2 nanomaterials followed by the adsorption of As(V) species. Their adsorption capacities for As(V) ions increase from 7.5mg/g to 14.5mg/g. Luo et al. (2018) have discussed the influence of pH and solvent (NaF, NaCl, Na2SO4) on the arsenic adsorption of α-MnO2 nanofibers and find that the adsorption capacity of As(III) and As(V) ions is enhanced to 117.72 mg/g and 60.19 mg/g, respectively. During the oxidation of As(III)→As(V) ions in the adsorption process, trace As(IV) ions appear in experimental research (Sun et al. 2015; Klaening et al. 1989). Some Mn(IV) ions are also reduced to Mn(III) ions and even Mn(II) ions to dissolve (Zhang and Sun 2013; Ge et al. 2016). So all of them find the MnO2 nanomaterials have excellent arsenic adsorption capacity. But the internal mechanism of a nanometer effect still keeps mysterious. To explore this problem, Luo et al. (2018) pointed out the As(III) and As(V) ions on MnO2(100) surface were more stable than that on MnO2(110) surface, and the strong As(III) removal ability of α-MnO2 nanofibers originated from its large adhesion energy by density functional theory (DFT) method. Zhang et al. (2015) have investigated the As(V) adsorption ability on TiO2(001) and TiO2(110) bulk surface and reveal that the TiO2(110) plane has a higher affinity toward arsenate than the TiO2(001). α-MnO2 nanomaterials may have many active sites such as steps, ledges, kinks, and vacancy. Such chemical active sites are much more vigorous than that of a bulk surface (Chen et al. 2017). Chen et al. (2017) have investigated the chemical property of α-MnO2 nanorod through a bulk surface and microfacet with nanostructure by DFT and find that the surface energy of microfacet is larger than that of the bulk surface. The junction of different Miller indexes in nanomaterials is the chemical active site. Then using the bulk surface model to investigate the chemical property of nanomaterial has its own limits (Jiao and Bruce 2007). Furthermore, the formation process of metastable valance state As(IV) ion keeps still mysterious right now. Using microfacet with nanostructure, the formation mechanism of Sb(OH)4− precursor product is illuminated in detail (Li et al. 2018). Thus, this paper is to explore the nanometer effect of α-MnO2 nano-surface influence on the adsorption/desorption processes of arsenic ions and to discover the catalytic mechanism of metastable As4+ by DFT + U method.

**Simulation Models and Method**

For α-MnO2 nanoparticles, its nano-surface is mainly composed of (110) and (100) Miller indexes (Reddy et al. 2009; Tompsett et al. 2014a). Then its corner nanostructure is simulated by [(100×110)] microfacet model. For comparison, the corresponding (100) and (110) bulk surfaces were also built as shown in Fig. 1. To investigate the adsorption/desorption ability of arsenic ions in the solution environment, different concentrations of As(OH)3 or As(OH)6− surrounded by several water molecules were constructed as shown in Fig. 1. It is obvious from Fig. 1 that the MnO2(100) bulk surface (Mn64O128) is composed of two {100} Miller index units, the MnO2(110) bulk surface (Mn48O96) is composed of two {110} Miller index units, and there is one chemical active site in each Miller index unit of MnO2(100) and MnO2(110) bulk surface, respectively. The MnO2[(100×110)] microfacet (Mn50O100) is composed of one {100} Miller index unit and two {110} Miller index units, so there are three chemical active sites. Therefore, these active sites are preferred as adsorption sites of As(OH)3 or As(OH)6− molecules and labeled with Roman numbers I, II, and III from right to left. In addition, the adsorption sites of As(OH)3 or As(OH)6− molecules above the {100} and {110} Miller planes are labeled with Roman numbers IV and V, respectively. To distinguish different concentration As(OH)3 or As(OH)6− molecules, Arabic numbers as 1, 2, 3, … represent the numbers of arsenic molecules. Finally, the concentration of As(OH)3 molecules is based on the ratio of the mass or number of As(OH)3 molecules absorbed via the MnO2 model under simulated conditions to the total mass or number of As(OH)3 molecules absorbed by MnO2 model under ideal conditions (each Mn atom adsorbs one As(OH)3 molecule). For example, (100)-3As(III) indicates that there exist three As(OH)3 molecules located at (I), (II), and (III) sites, respectively, and the concentration of As(OH)3 molecules is 46.8mg/g. The detailed adsorption/desorption models of As ions on the MnO2 surface are shown in Fig. S1.

The calculated models in this paper were optimized by DFT embedded in Cambridge Sequential Total Energy Package (CASTEP) code with plane waves and pseudopotentials (Luo et al. 2018; Song et al. 2018; Segall et al. 2002). A generalized gradient approximation (GGA) incorporated with Perdew, Burke, and Ernzerh with Hubbard U correction was used to treat their electronic structure to get a globally stable structure (Xin et al. 2015; Youmbi and Calvayrac 2014). The cut-off energy of all simulation models was set at 450 eV, and the K point was set as 1×2×1 in the Brillouin zone of supercell models. The Broydten-Fletcher-Goldfarb-Shanno (BFGS) scheme (Tompsett et al. 2014a) was used to adjust the convergence criteria as root-mean-square (RMS) force (0.1 eV/Å), stress of 0.2 GPa, and displacement of 0.005 Å (Chen et al. 2017). The energy tolerance was set to 5 × 10−4 eV/atom, and the convergence criteria of self-consistent field (SCF) was set to 1.0×10−4.

Previous work has shown that DFT+U can well describe the structural stability, band gap, and magnetic interaction.
when the fully localized limit (Chen et al. 2017), which is the reason for our application in this study. The Hubbard U value is set to 1.6 eV to correct the $3d$ orbital electronic structure of Mn atoms (Luo et al. 2018). The calculated lattice constants of $\alpha$-MnO$_2$ obtained from DFT + U are listed in Table S1. And these results are within 1.8% of the theoretical (Luo et al. 2018; Tompsett et al. 2014b) and experimental (Johnson et al. 1997; Li et al. 2011) determined lattice parameters, indicating that DFT + U is reliable to evaluate the unit cell volume. The lattice constants of the initial $\alpha$-MnO$_2$ cell are $a = b = 9.922$ Å and $c = 2.904$ Å. All of these surface models were constructed from the optimized globally $\alpha$-MnO$_2$ crystal.

Results and discussion

Removal ability of bulk surface

Luo et al. (2018) have pointed out the surface complexes of As(III) and As(V) on (100) are more stable than (110) and electrons transfer from As(III) on (100) is greater than that on (110). But he doesn’t consider the influence of As ions concentration. In this paper, the effect of As(OH)$_3$ concentration in an aqueous solution is considered further. In order to study the difference in arsenic adsorption between bulk surface and nano-surface, the adsorption energy ($E_{ad}$) of As ions with different concentrations was calculated as following equation (Li et al. 2018):

$$E_{ad} = E_{surface+As} - E_{surface} - nE_{As(OH)_3} - mE_{H_2O}$$

wherein $E_{surface+As}$ means that the total energy of MnO$_2$ bulk or microfacet models with some As molecules in aqueous solution. $E_{surface}$ presents that the total energy of MnO$_2$ bulk or microfacet models. $E_{As}$ and $E_{H_2O}$ represent the energies of the As molecule and H$_2$O molecule, which are equal to $-2187.203$ eV and $-469.78$ eV, respectively. A $10 \times 10 \times 10$ (Å$^3$) vacuum box was built with only one As(OH)$_3$ or H$_2$O molecule at the center of the box to calculate their energy at gas state. And $n$ and $m$ mean the number of H$_2$O and As(OH)$_3$ molecules in the simulated system. The results are shown in Table 1 and Fig. S2. It is found that the adsorption energy is negative, so the smaller the adsorption energy is, the stronger the adsorption capacity is. The adsorption energy of (100)-As(I) (concentration equal to 15.6 mg/g) is $E_{ad} = -2.641$ eV. The adsorption energy of (100)-2As(II) with two As(OH)$_3$ molecules (concentration equal to 31.2 mg/g) is $E_{ad} = -6.05$ eV, which is smaller than the adsorption energy of (100)-As(I). But the adsorption energy of (100)-3As(III) with three As(OH)$_3$ molecules is $E_{ad} = -6.396$ eV, which is greater than the three times adsorption energy of (100)-As(I). That is because the third As(OH)$_3$ molecule cannot be adsorbed on the surface layer of (100). Its little difference in adsorption energy compared with (100)-2As(II) comes from the mutual effect of As(OH)$_3$ molecules. Analyzed the Mn atoms along the surface layer of (100) bulk surface, it is found that there exist two adsorbed sites for As(OH)$_3$ molecules on each up layer and down layer as shown in Fig. 1. Considering the periodic symmetry of the bulk surface model, the maximum adsorption capacity of the (100) bulk surface is quadruple to that of the (100)-As(I), which is equal to 62.4 mg/g. The evolution of adsorption energies in the (110)-As(OH)$_3$ system is consistent with that in (100)-As(OH)$_3$. The adsorption energy of (110)-2As(II) ($E_{ad} = -4.892$ eV) with two As(OH)$_3$ molecules is smaller than the double adsorption energy of (110)-As(I) ($E_{ad} = -2.401$ eV). The adsorption energy of (110)-3As(III) ($E_{ad} = -5.113$ eV) with three As(OH)$_3$ molecules is greater than the three times adsorption energy of (110)-As(I) ($E_{ad} = -2.401$ eV) with one As(OH)$_3$ molecule. Averaged by the number of As(OH)$_3$ molecules in adsorption energy $E_{ad}$, it is found that the $E_{ad}$ of (100)-3As(III) or (110)-3As(III) is the largest one among them. So the saturated concentration is harmful to the As ions removal capability by MnO$_2$ bulk.
Considering the periodic symmetry, the maximum removal capacity of the (110) bulk surface is quadruple to that of the (110)-As(I), which is equal to 83.2 mg/g. Although their adsorption energies don’t strictly decrease exponentially, the $E_{\text{ad}}$ value first increases significantly and then slows down with the increase of As(OH)$_3$ molecules concentration. Therefore, the maximum adsorption capacity of (100) and (110) can be increased at lower As(OH)$_3$ molecules concentration. In short, the trend of adsorption energy for (100) or (100)-As(OH)$_3$ system, which becomes gentle along with the increased concentration of As ions, indicates that the As removal capacity of MnO$_2$ bulk materials has a maximum value. This point has been proved by the experimental (Zhang and Sun 2013; Ge et al. 2016; Camacho et al. 2011) and theoretical (Luo et al. 2018) results. Comparing the same concentration of As(OH)$_3$ on (100) or (110) bulk surface, the adsorption ability and capacity of As(OH)$_3$ molecules on (100) bulk surface is indeed stronger than that on (110) bulk surface, which is also consistent with previous reports (Luo et al. 2018; Selvakumar et al. 2014).

### Removal ability of nano-surface

As well known, the $\alpha$-MnO$_2$ bulk materials show limited adsorption capacity of toxic ions in water, which is originated from their small surface area (Zhang and Sun 2013). However, the $\alpha$-MnO$_2$ nanomaterials have excellent adsorption and oxidation properties for their large specific surface area and many active sites (Thanh et al. 2012). But the internal influence of a nanometer effect is still mysterious. In the next part, the effect of nano-surface on the adsorption performance of $\alpha$-MnO$_2$ nanomaterials to As ions is discussed deeply by the microfacet model. All of the MnO$_2$-As(OH)$_3$ microfacet models are shown in Fig. 1c and Fig. S1. The results are presented in Table 1. Compared with different adsorbed sites along $\alpha$-MnO$_2$ microfacet layer, an As(OH)$_3$ molecule adsorbed on (100) plane of [(100×110)] was labeled by No. I and No. II and on (110) plane by No. III. When an As(OH)$_3$ molecule is adsorbed on (100) plane in [(100×110)-As(III)], its adsorption energy $E_{\text{ad}}$ is equal to $-3.592$ eV, which is lower than that of (100)-As(I) ($E_{\text{ad}} = -2.641$ eV) bulk surface. The adsorption energies $E_{\text{ad}}$ are equal to $-2.446$ eV or $-2.659$ eV when an As(OH)$_3$ molecule is adsorbed on (100) plane in [(100×110)-As(II)] or [(100×110)-As(I)], which is larger than that of [(100×110)-As(III)]. Although their adsorption concentration of As(OH)$_3$ molecules is 20 mg/g, their different adsorption energies are mainly due to different active sites in MnO$_2$ nanostructure. Then the adsorption ability of As(OH)$_3$ molecules on MnO$_2$ nano-surface is better than that on MnO$_2$ bulk surface due to the nanometer effect, which is consistent with experimental results that the MnO$_2$ nanomaterials have better catalytic performance than the bulk materials (Luo et al. 2018; Selvakumar et al. 2014). Such conclusion verifies further that it is a good way to reveal the nanometer effect through the microfacet model.

When the concentration of As(OH)$_3$ molecules increases to double times as 40 mg/g, its adsorption energy of [(100×110)-2As(II)] is equal to $-5.479$ eV (Fig. 1c and Fig. S1), which is lower than the $E_{\text{ad}}$ of [(100×110)-As(III)]. When the concentration of As(OH)$_3$ molecules increase to triple times as 60 mg/g, its adsorption energy of [(100×110)-3As(III)] is equal to $-7.438$ eV, which is lower than that of the same adsorption sites on (100) ($E_{\text{ad}} = -6.396$ eV) or (110) ($E_{\text{ad}} = -5.113$ eV) bulk surface. These changes mean two or three As(OH)$_3$ molecules adsorbed on [(100×110)] microfacet enhance their common adsorptive

### Table 1 Adsorption energy $E_{\text{ad}}$ of As(OH)$_3$ molecules on (100), (110), and [(100×110)] models in aqueous solution

| Miller indexer | Models | $E_{\text{As+surface}}$(eV) | $E_{\text{surface}}$(eV) | $E_{\text{ad}}$(eV) |
|---------------|--------|-----------------------------|--------------------------|-------------------|
| (100)         | (100)-As(I) | $-97939.206$ | $-93870.230$ | $-2.641$ |
|               | (100)-2As(II) | $-101539.167$ | $-93870.230$ | $-6.050$ |
|               | (100)-3As(III) | $-103726.716$ | $-93870.230$ | $-6.396$ |
| (110)         | (110)-As(I) | $-74467.344$ | $-70398.608$ | $-2.401$ |
|               | (110)-2As(II) | $-78066.387$ | $-70398.608$ | $-4.892$ |
|               | (110)-3As(III) | $-80253.811$ | $-70398.608$ | $-5.113$ |
| [(100×110)]  | [(100×110)-As(I)] | $-75643.896$ | $-71574.902$ | $-2.659$ |
|               | [(100×110)-As(II)] | $-75643.683$ | $-71574.902$ | $-2.446$ |
|               | [(100×110)-As(III)] | $-75644.829$ | $-71574.902$ | $-3.592$ |
|               | [(100×110)-2As(I)-II)] | $-78772.601$ | $-71574.902$ | $-4.595$ |
|               | [(100×110)-2As(I)-III)] | $-78773.485$ | $-71574.902$ | $-5.479$ |
|               | [(100×110)-2As(II)-III)] | $-78773.765$ | $-71574.902$ | $-5.759$ |
|               | [(100×110)-3As(III)] | $-83311.562$ | $-71574.902$ | $-7.438$ |
|               | [(100×110)-4As(IV)] | $-85499.646$ | $-71574.902$ | $-8.323$ |
|               | [(100×110)-5As(V)] | $-87686.654$ | $-71574.902$ | $-8.129$ |
capacity. As the concentration of As(OH)$_3$ molecules increase four or five times, the $E_{\text{ad}}$ of [(100×110)]-4As(IV) or [(100×110)]-5As(V) decreases to $-8.323$ eV or $-8.129$ eV, respectively. Their small difference in adsorption energies ($\Delta E_{\text{ad}}=0.194$ eV) originates from the similar adsorbing sites for As(OH)$_3$ on MnO$_2$ surface layer in aqueous solution (Fig. 1c). Analyzed the Mn atoms along the surface layer of [(100×110)], it is found that there exist three adsorbed sites. Considering the periodic symmetry of the microfacet model, the maximum adsorption capacity of [(100×110)] is sextuple of [(100×110)]-As(I), which is equal to 120 mg/g. It is larger than the maximum experimental value of 117 mg/g (Luo et al. 2018). Their difference in maximum adsorption capacity comes from many factors, such as an aqueous solution environment, size of nanomaterials, pH, and so on.

Systematically analyzing the adsorption abilities of (100), (110) bulk surface, and [(100×110)] microfacet model in aqueous solution to arsenic ions, it is found that the adhesion energies increase significantly at first and then slow down along with the increased concentration. Such a trend is consistent with previous experimental studies (Thanh et al. 2012; Ge et al. 2016). This phenomenon is due to the saturation of adsorption sites and existence of undisturbed arsenic ions (Fig. 1). Supposing all of the active sites of Mn atoms bonding with As ions, the saturated adsorption capability of [(100×110)] nanostructure is 120 mg/g, which is larger than that of (100) and (110) bulk surface. And to the same concentration of As ions, the adsorption energy of [(100×110)]-As system is lower than the corresponding (100) or (110) bulk surface. Their difference is only in the corner nanostructure of [(100×110)] nano-surface, which did not appear in the bulk surface. So the nanometer effect plays a vital role in the removal process of As ions in an aqueous solution by nanomaterials.

**Electrostatic potential**

The difference in adsorbability between MnO$_2$ bulk surface and nano-surface originates basically from their covalent electrons. Although experimental results have proved that the adsorption performance of MnO$_2$ nanomaterials is better than that of MnO$_2$ bulk materials (Thanh et al. 2012), a detailed nanometer effect acting on the catalytic process of As(OH)$_3$ on MnO$_2$ in aqueous solution still remains mysterious. Patwardhan et al. (2012) have proved that the electrostatic attraction contributes to the adsorption and bonding through experiments and simulation analysis. Thus, the electrostatic potential of arsenic adsorbed on (100), (110), and [(100×110)] was calculated carefully as showed in Fig. 2, Fig. 3, and Fig. S3, wherein the electrostatic potentials range from blue to white to red means that their values range from small to large. The average electrostatic potential of a unit cell along with the Z direction is shown in Fig. 2 and Fig. 3. In order to visually and systematically study the electrostatic attraction of all the MnO$_2$ bulk surface and nano-surface, the difference value ($\Delta V$) of electrostatic potential between MnO$_2$ surface layer and As(OH)$_3$ molecule is calculated in all simulated arsenic adsorption models. It is found that the electrostatic potential between the oxygen atom in As(OH)$_3$ molecule and the manganese atom in the MnO$_2$ surface layer is very large (electrostatic potential region is red), which means they are bonded strongly with each other (Fig. S3).

Furthermore, all of the electrostatic potentials of As, Mn, and H elements are positive and that of O$^2-$ is negative. So the As(OH)$_3$ molecules prefer to bond with OH$^-$ to form As(OH)$_4$. The electrostatic potential of H$_2$O is very small. From Fig. 3, it is found that all of the electrostatic potential of MnO$_2$ no matter in bulk surface or microfacet is larger than the arsenite molecule. So the ability of electrons gain for the Mn atom is much more powerful than that of As atom. Then Mn element performs oxidability and arsenic element performs reducibility. When the As(OH)$_3$ molecules are adsorbed on MnO$_2$, the Mn$^{4+}$ is reduced into Mn$^{2+}$, and As$^{3+}$ is oxidized into As$^{5+}$ or As$^{2+}$. Youmbi and Calvayrac (2014) have shown that large adsorption capacity comes from the large difference in electrostatic potential value $\Delta V$ of the terminal layer and adsorbent layers. The trend of $\Delta V$ in (100) and (110) bulk surface along with different arsenic concentration is as follows: $\Delta V_{((100)-3\text{As}(\text{III})]}=1.029$ eV $> \Delta V_{((100)-2\text{As}(\text{II})]}=1.015$ eV $> \Delta V_{((100)-\text{As}(\text{I})]}=0.844$ eV, $\Delta V_{((110)-3\text{As}(\text{III})]}=0.679$ eV $> \Delta V_{((110)-2\text{As}(\text{II})]}=0.586$ eV $> \Delta V_{((110)-\text{As}(\text{I})]}=0.489$ eV in Fig. 2. The trend of $\Delta V$ in [(100×110)] microfacet along with different arsenic concentration is $\Delta V_{((100×110)-5\text{As}(\text{V})]}=0.163$ eV $> \Delta V_{((100×110)-4\text{As}(\text{IV})]}=0.142$ eV $> \Delta V_{((100×110)-3\text{As}(\text{III})]}=0.121$ eV $> \Delta V_{((100×110)-2\text{As}(\text{II})]}=0.107$ eV $> \Delta V_{((100×110)-\text{As}(\text{I})]}=0.089$ eV. These phenomena show that the higher the concentration of As(OH)$_3$ molecule in aqueous solution leads to the stronger the electrostatic attraction of (100), (110), and [(100×110)] surface, which is basically consistent with the trend of their adsorption energy. Previous papers (Xin et al. 2015; Praveena et al. 2014) confirm that large electrostatic potential values can lead to a strong electrostatic attraction, which plays an important role in physicochemical properties. However such conclusion is only achieved by the bulk surface method, which doesn’t consider the nanometer effect. In this paper, it is found that the electrostatic potential values in the [(100×110)]-As nano-surface system is smaller than that in the (100) or (110)-As bulk surface system, which is contrary to their trend in adsorption energy at the same concentration of As ions. Their only difference is originated from their geometric configurations whether containing nanostructure. Then the reason for [(100×110)]-As system possessing large adsorption energy with small electrostatic potential values is only derived from the influence of
nanometer effect in [(100×110)] nano-surface. Small electrostatic potential values will be more beneficial to enhance the removal capability of As ions on MnO2 nanomaterials. That may be a reason why MnO2 nanomaterials have better catalytic activity than the bulk materials (Luo et al. 2018). Detaiely analyzed the product of As(OH)₄, which is only produced in [(100×110)] microfacet (Fig. 3е–g and Fig. S3k–m), it is found that their difference value (ΔV′) of electrostatic potential is smaller than the corresponding concentration of As(OH)₃, which means the adsoriblity of As(OH)₄ is weaker than that of As(OH)₃ on [(100×110)]. And the trend of ΔV′ for metastable As(OH)₄ molecule becomes more and more small along with the addition of As(OH)₃ concentration. So the increased concentration of As ions weakens the adsorption ability of As(OH)₄ molecules on α-MnO₂ nanostructure. And the nanometer effect can
promote the production of transitional product As(OH)$_4$ molecule, which is also beneficial to enhance the removal capability of As ions on MnO$_2$ nanomaterials.

**Catalytic mechanism**

Until now, although the adsorbability of As ions on MnO$_2$ nanomaterials has been illuminated, the transformation process of As(OH)$_3$ ($\text{As}^{3+}$)→As(OH)$_6$ ($\text{As}^{5+}$) molecule, especially the formation of trace metastable As(OH)$_4$ molecule has not been discovered clearly. The detailed catalytic mechanism of As(OH)$_3$ molecules on (100), (110) bulk surface, and [(100×110)] nano-surface is analyzed systematically through the microscopic changes of geometry and electronic structure. For comparison, this paper only analyzes the same concentration of As ions adsorbed on MnO$_2$ models. And the original structure and electronic property of As(OH)$_3$, As(OH)$_6^-$, and H$_2$O molecules are calculated in Fig. 4a–c. Their electronic properties are revealed by Mulliken population analysis (detailed explanation is shown in Supplement Information). The results are shown in Fig. 4 and Fig. S4.

For the (100) and (110) bulk surface, it is found that their bond lengths of As(OH)$_3$ molecules have been changed significantly. The maximum bond length of As(OH)$_3$ molecule in its initial state is equal to 1.817 Å among three As-O bonds (Fig. 4a). However, it increases to 2.288 Å and 1.955 Å in the (100)-3As(III) and (110)-3As(III) system, respectively (Fig. 4d and e). Then their corresponding Mulliken populations are reduced from initial value 0.29 (Fig. S4a) to −0.04 (Fig. S4c) and 0.18 (Fig. S4d), which means a new bond is formed between Mn atom and OH$^-$ hydroxyl of As(OH)$_3$ molecule. Then these new bonds can weaken the structural stability of As(OH)$_3$ molecules on the α-MnO$_2$ bulk surface. This phenomenon confirms it as a chemisorption reaction between α-MnO$_2$ and As(OH)$_3$ molecules (Luo et al. 2018). And the transformation process (chemical reaction) of As(OH)$_3$→As(OH)$_6^-$ molecule can occur in the (100) or (110)-As system, which is verified by experimental study (Lafferty et al. 2011).

For [(100×110)]-3As(III), [(100×110)]-4As(IV), and [(100×110)]-5As(V) models (Fig. 4f–h), it is found that their geometric structures of As(OH)$_3$ molecules at site (I) are also changed obviously. At the same time, its environmental H$_2$O molecules are decomposed into OH$^-$ ion and H$^+$ ion clearly (Jung et al. 2005). That is because the bond lengths of H$_2$O molecules change from their initial state of 0.974 (Fig. 4c) to 1.799 Å (Fig. 4f), 1.844 Å (Fig. 4g), and 2.276 Å (Fig. 4f) (marked via red color). Then some As(OH)$_3$ molecules bond with OH$^-$ ions to form metastable As(OH)$_4$ molecules (labeled via (I) in Fig. 4f–h). And the H$^+$ ions will adsorb on the MnO$_2$ surface layer to form Mn-O-H clusters (Hasanpour and Saien 2019), whose bonds are equal to 1.002 Å (Fig. 4f), 1.005 Å (Fig. 4g), and 1.007 Å (Fig. 4h) (marked via blue color). Such phenomenon doesn’t appear in the (100) or (110)-As system. Analyzing the geometric structure of precursor As(OH)$_4$ molecules at site (I) in a series of [(100×110)] models, it is shown that their largest bond lengths are 2.383 Å (Fig. 4f), 2.288 Å (Fig. 4g), and 2.217 Å (Fig. 4h) and their Mulliken populations are −0.04 (Fig. S4e), −0.02 (Fig. S4f), and −0.02 (Fig. S4g), respectively. Then the new product As(OH)$_4$ molecule is very weak, which is consistent with the experimental reports.

![Fig. 4 Bond length of optimized model: (a) As(OH)$_3$, (b) As(OH)$_6^-$, (c) H$_2$O, (d) (100)-3As(III), (e) (110)-3As(III), (f) [(100×110)]-3As(III), (g) [(100×110)]-4As(IV), and (h) [(100×110)]-5As(V).](image-url)
phology of As(OH)₄ molecule with As(OH)₆ intermediate in As(OH)₃ (Sun et al. 2015; Klaening et al. 1989). Comparing the morphology of As(OH)₄ molecule with As(OH)₆ molecule (Fig. 4b and c), it can be found that their geometric configurations are very similar to each other, especially to their hydroxyl groups. Sun et al. have pointed out that the As⁺⁺ ion is a very crucial intermediate in the catalytic process of As⁺⁺→As⁵⁺ (Sun et al. 2015; Klaening et al. 1989). Therefore, we can infer that the As(OH)₄ molecule is the intermediate transition state oxide in the process of As(OH)₃→As(OH)₆ molecule. And the As(OH)₄ molecule intermediate appearing above [(100×110)] nano-surface is beneficial to As removal by MnO₂ nanomaterials. In other words, the nanometer effect promotes the As removal ability of MnO₂ nanomaterials through a new way of producing much more intermediates.

Removing process

The purpose of removing As³⁺ in fact is to make it be oxidized into nontoxic As⁵⁺ (Luo et al. 2012). Then the formation rate of As(OH)₆⁻ molecule plays a vital role in the application of MnO₂ nanomaterials. Experimental studies also show that some Mn³⁺ ions are resolved from the matrix MnO₂ surface layer in the removing reaction of arsenic ions (Ge et al. 2016), which will lead to the weight loss of MnO₂ nanomaterials. In this paper, we have proved the As(OH)₄ and Mn(OH)²⁺ (Mn-O-H) molecules will only appear in MnO₂ nano-surface, wherein the As(OH)₄ molecule is an important transitional intermediate in As(OH)₃→As(OH)₆⁻ process. As well known, there exist many hydroxyl groups in the aqueous solution. Then the reduction process of As(OH)₃→As(OH)₆⁻ molecule will exist in two steps as As(OH)₃→As(OH)₆⁻ or As(OH)₃→As(OH)₄→As(OH)₆⁻. In the next part, the desorption process of arsenic ion in [(100×110)]-3As(III), [(100×110)]-4As(IV), and [(100×110)]-5As(V) system will be investigated by climbing image-nudged elastic band (CI-NEB) way as shown in Fig.S5, which has been successfully applied to study desorption thermodynamics (Li et al. 2018; Zheng et al. 2017). The results are shown in Fig. 5. It is found the activation energies (ΔEₐ) of As(OH)₄ molecules in the desorption process of [(100×110)]-3As(III), [(100×110)]-4As(IV), and [(100×110)]-5As(V) system are equal to 2.332 eV, 2.732 eV, and 4.733 eV, respectively. This result clearly shows that the desorption reaction of As(OH)₄ molecules in [(100×110)]-3As(III) and [(100×110)]-4As(IV) is not hard due to their small activation energy, which may help us to have a deeper understanding of As(IV) ions in the experiment (Sun et al. 2015). As shown in Figs. 5d–f, the desorption energies of As(OH)₆⁻ molecules in [(100×110)]-3As(III)⁴⁻, [(100×110)]-4As(IV)⁴⁻, and [(100×110)]-5As(V)⁴⁻ system are equal to 3.138 eV, 3.936 eV, and 5.084 eV, respectively, which is close to the activation energy of the corresponding As(OH)₄ molecule in desorption process. This phenomenon not only shows that the desorption ability of As(OH)₆⁻ molecule is not very hard but also shows it has a similar desorption ability with As(OH)₄ molecule, which is a stronger proof that As(OH)₄ molecule is the precursor state of As(OH)₆⁻ molecule. No matter to As(OH)₄ or As(OH)₆⁻ molecule, their desorption activation energy increases along with the increased concentration of As ions, which means the free As(OH)₃ molecules can hinder the desorption reaction of As(OH)₆⁻ or As(OH)₆⁻ molecule.

In order to explore the dissolution ability of Mn³⁺ molecule influenced by the As ions, this paper takes [(100×110)]-3As(III)⁵⁻ system as an example to study the desorption process of Mn(OH)²⁺ molecule (Fig. S6). It is found that the dissolution process of single Mn(OH)²⁺ molecular (ΔEₐ=11.479eV) in [(100×110)]-3As(III) is much more difficult than the complex As(OH)₃⁻-Mn³⁺ molecular (ΔEₐ=5.447eV), which means the dissolution ability of Mn³⁺ molecule becomes easy after As(OH)₃ adsorbed on the surface of MnO₂. Furthermore, in the chemical reaction of As(OH)₃→As(OH)₄, the dissolution process of complex As(OH)₃⁻-Mn(OH)²⁺ has the smallest activation energy (ΔEₐ=4.602eV) among them. So the catalytic reaction of As(OH)₃→As(OH)₆⁻ may promote the dissolution ability of Mn³⁺ molecule, which is consistent with the experimental results (Ge et al. 2016). In the next paper, we will investigate the dissolution mechanism of Mn³⁺ molecule in the chemical reaction of MnO₂ nanomaterials. According to their activation energy, it can be inferred that there exist two possible desorption ways of As(OH)₃ molecule in aqueous solution: one is the catalytic reaction As(OH)₃→As(OH)₆⁻ molecule at the low concentration, and another is the catalytic reaction As(OH)₃→As(OH)₆⁻ accompanying with derivative reduction reaction of MnO₂→Mn(OH)²⁺. Nevertheless, the As(OH)₄ and Mn(OH)²⁺ molecules don’t have a stable structure, so the desorption process of As(OH)₄ molecule and Mn(OH)²⁺ molecule in this state exhibits As(OH)₄→As(OH)₆⁻ and MnO₂→Mn(OH)²⁺→Mn(OH)₂ criteria, respectively. So far the product of As(OH)₄ molecule and the dissolution of Mn³⁺ ions are only found in [(100×110)] nano-surface, which almost cannot be observed in MnO₂ bulk surface. Then the nanometer effect although benefits to enhance the removal capability of As ions through MnO₂ nanomaterials, it has bad influence to bring mass loss of nanomaterials. So the nanostructure of catalytic materials needs to be optimized further.

Discussion

The nanometer effect acting on the catalytic mechanism of arsenic ions adsorbed on α-MnO₂ nanomaterials can be extracted clearly. To simulate the performance of nanomaterials, this paper uses the microfacet model representing the geometric configuration of nano-surface compared with bulk surface concurrently. It is
found that the trend of negative adsorption energies for As(OH)$_3$ molecules in bulk surface and microfacet system is basically decreased following the increasing concentration of As ions, which shows that the adsorption process is an exothermic reaction. The adsorption capacity of MnO$_2$ microfacet is larger than that of MnO$_2$ bulk surface, which is due to its much more active sites and less adsorption energy. A large difference in electrostatic potential of As(OH)$_3$ and MnO$_2$ layer attracts the adsorption process much easier. The nanometer effect provides a small electrostatic potential of [(100×110)] nano-surface with large adsorption energy compared with a bulk surface at the same concentration of As ions. Then in an aqueous solution, there exist two possible desorption ways of As(OH)$_3$ molecule in aqueous solution. One is the direct reaction As(OH)$_3$→ As(OH)$_6$$^-$$^-$ at the low concentration. In this process, the H$_2$O is separated into H$^+$ and OH$^-$. The H$^+$ bond with Mn-O to form Mn(OH)$_2$$^{2+}$ along with the surface layer of MnO$_2$, which has small desorbed activation energy. And the As(OH)$_3$, which is catalyzed into As(OH)$_3$$^{2+}$, adsorbs hydroxyl OH$^-$ to form As(OH)$_6$$^-$$^-$ molecule originated from their large electrostatic potential. Such catalytic reaction can be observed both in the bulk surface and nano-surface system. The other is the indirect process of As(OH)$_3$→As(OH)$_4$→ As(OH)$_6$$^-$$^-$. At some active sites, the As(OH)$_3$ molecule is catalyzed into metastable precursor As(OH)$_4$ molecule to form As(OH)$_6$$^-$$^-$. Although the desorbed activation energy of As(OH)$_4$ molecule is smaller than that of As(OH)$_6$$^-$$^-$ molecule, the As(OH)$_4$ molecule is metastable, and it is only produced at some special active sites. However, such catalytic reaction can easily occur in the nano-surface system. Compared with bulk materials, the nanomaterials have much more removal processes of As ions originated from a nanometer effect. Then the removal mechanism of As(OH)$_3$ on MnO$_2$ nanomaterials can be extracted as shown in Fig. 6.

**Conclusions**

In summary, based on the theoretical analysis, the results showed that:

1. The $E_{ad}$ of As(OH)$_3$ molecules on the $\alpha$-MnO$_2$ bulk surface and microfacet are negative. These phenomena show the adsorbing reaction of As(OH)$_3$ molecules on $\alpha$-MnO$_2$ nanomaterials is a spontaneous and chemical reaction. With
the augment of As(OH)$_3$ molecule concentration in aqueous solution, the adsorption energy increases significantly at first and then slows down. The maximum adsorption capacity of (100), (110), and [(100×110)] is equal to 62.4 mg/g, 83.2 mg/g, and 120 mg/g, respectively.

(2) Electrostatic potential between the oxygen atom of As(OH)$_3$ molecule and the manganese atom of MnO$_2$ is very large, which means that they are bonded strongly with each other. The electrostatic potential of MnO$_2$ no matter in bulk surface or microfacet is larger than the arsenite molecule. Then Mn elements perform oxidability and arsenic elements perform reducibility. The difference in electrostatic potential value $\Delta V$ shows that the higher the concentration of As(OH)$_3$ molecule in aqueous solution leads to the stronger the electrostatic attraction of (100), (110), and [(100×110)] surface.

(3) Bond lengths of As(OH)$_3$ molecules on the (100) and (110) bulk surface model have been changed from their initial state (1.817 Å) to 2.288 Å and 1.955 Å, respectively. Their corresponding Mulliken population is reduced from an initial value of 0.29 to $-0.04$ and 0.18. The As(OH)$_3$ molecule is adsorbed at site (I$'$) of [(100×110)] microfacet, and a new bond is formed between an OH$^-$ ion and an As(OH)$_3$ molecule to form a metastable As(OH)$_4$ structure. An H$^+$ ion is also adsorbed on MnO$_2$ to form Mn-O-H. Such phenomenon is due to the bond length of H$_2$O molecule changes from the initial state of 0.974 Å to a maximum value of 2.276 Å.

(4) The activation energies in the desorption reaction of As(OH)$_4$ molecule on [(100 × 110)] are equal to 2.332 eV, 2.732 eV, and 4.733 eV, respectively, and that of As(OH)$_6$ molecule are equal to 3.138 eV, 3.936 eV and 5.084 eV, respectively. Then the removal of arsenic from aqueous solution via $\alpha$-MnO$_2$ nanomaterials follows As(OH)$_3$ → As(OH)$_4$ → As(OH)$_6$ and MnO$_2$ → Mn(OH)$_2$ $\rightleftharpoons$ Mn(OH)$_3$. The activation energy of Mn(OH)$_2$ $\rightarrow$ Mn(OH)$_3$ molecule in the dissolution process of [(100×110)] is 4.602 eV. These phenomena indicate that the desorption reaction of arsenic will induce the manganese ions to dissolve.

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Author contribution Guifa Li and Pengsen Zhao conceived and conducted experimental research, analyzed experimental data, and drafted manuscripts. Lixia Yang, Yongxiang Geng, and Ping Peng provide expertise in adsorption catalysis. Haizhong Zheng initiated, conceived the experiment, and wrote the manuscript; all the authors participated in the revision of the manuscript.

Data availability and materials All the materials and data in this study can be found in this paper.

Declarations

Consent to participate All the authors volunteered to participate in this study.

Consent to publication All the authors agreed to publish the manuscript.

Conflict of interest The authors declare no competing interests.

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