Micro-nanostructured δ -Bi₂O₃ with surface oxygen vacancies as superior adsorbents for SeO_x²⁻ ions

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GRAPHICAL ABSTRACT

Highlights First demonstration of promoting SeO_x^{2-} ions immobilization using oxygen vacancies

A high adsorptive capacity towards SeO_x^{2-} ions was reported

Intensively studied the adsorption mechanism of the oxygen vacancy-containing $\delta\text{-Bi}_2\text{O}_3$

The bonding mode between SeO_3^{2-} ions and (111) plane of $\delta\text{-Bi}_2\text{O}_3$ has been explored

Abstract

Removal of the toxic selenium compounds, selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}), from contaminated water is imperative for environmental protection in both developing and industrialized countries. Providing high selectivity adsorbents to the target ions is a big challenge. Here we report that micro sphere-like $\delta\text{-Bi}_2\text{O}_3$ (MS- $\delta\text{-Bi}_2\text{O}_3$) with surface oxygen vacancy defects can capture hypertoxic SeO_x^{2-} anions from aqueous solutions with superior capacity and fast uptake rate. High capture selectivity to SeO_3^{2-} anions is observed, since the O atoms of SeO_3^{2-} anions fill the oxygen vacancies on the (111) facet of $\delta\text{-Bi}_2\text{O}_3$ forming a stable complex structure. This mechanism is distinctly different from other known mechanisms for anion removal, and implies that we may utilize surface defects as highly efficient and selective sites to capture specific toxic species. Thus, we present a new route here to design superior adsorbents for toxic ions.

Keywords: $\delta\text{-Bi}_2\text{O}_3$; surface oxygen vacancies; selective adsorption; SeO_x^{2-} ions; bonding mode

GRAPHICAL ABSTRACT

1. Introduction

Selenium (Se) is believed to be an extremely important and necessary trace element for living organisms including humans [1, 2], mainly because the selenocysteine amino acid is necessary to keep the activity of a few vital antioxidant enzymes in our body. On the other hand, Se compounds become highly toxic at high doses [3], and the gap between toxic and prophylactic or therapeutic doses of Se is very narrow. Apart from that, ^{79}Se isotope is a long-lived fission product with a half-life of 3.27×10^5 years, which is chemically and radiologically toxic [4]. Thus, irreversible and selective immobilization of toxic and radioactive anions is an efficient way to avoid the secondary contamination. So far, the European Union (EU) and World Health Organization (WHO) have issued a regulation to control a maximum Se concentration in drinking water of 10 ppb, and the US Environmental Protection Agency (EPA) have also set a limit of 50 ppb [5]. Pollution of drinking water is mainly from thermal power stations, factories producing semiconductors, solar batteries, photoelectric cells, insecticides, fungicides, copper alloys, and glassware, industries related to mining of phosphates and metal ores or nuclear industry, which are all sources of Se contamination of the aquatic environment [6]. In the context of the disposal of this kind of pollutant, efficient separation processes are required prior to environmental discharge in order to limit contamination of drinking water resources in the geosphere.

Generally, the solubility and toxicity of Se species depend on the oxidation state of Se. For instance, in the tetravalent and hexavalent oxidation states, Se prevails as aqueous oxyanions, with selenite (SeO_3^{2-}) being more toxic than selenate (SeO_4^{2-}) [7]. Recently, adsorption technology has been widely investigated as an economical

alternative for the capture of Se anions from water. Adsorption technology is superior to other commonly used remediation technologies including precipitation–filtration [8-13], anion exchange [14-17], and membrane filtration [18, 19], in water treatment, in terms of low-cost operation, simplicity in design, and ease of operation. Mineral adsorbents, such as aluminum oxides [13, 20, 21], iron oxyhydroxides [7, 22-29], and layered double hydroxides (LDHs) [30, 31], have attracted considerable attention. However, the above adsorbents have three drawbacks: 1. relatively low adsorption capacities, particularly for the more toxic SeO_3^{2-} anions, 2. very slow uptake kinetics, and 3. poor adsorption selectivity to the Se species in the presence of competing anions because of low affinity to the Se species. Therefore, more efficient materials for this purpose have to be invented, which will work with novel mechanism leading to large capacity, fast uptake and high selectivity to the Se species. It is well-known that the adsorption capacity depends on the total number of adsorption sites in a sorbent, and the selectivity to the target species on the structure of the adsorption sites; while the particle morphology of the sorbent has crucial impact on the adsorption dynamics. Hence, the main challenge is to develop materials with numerous adsorption sites that can capture SeO_x^{2-} selectively. Usual adsorption sites with anion exchange or physisorption properties cannot meet the need because of poor selectivity to SeO_x^{2-} in the presence of other anions. We have to find the sites that have strong interaction with SeO_x^{2-} by a mechanism other than physisorption or anion exchange. Moreover, large quantity of such sites and ready access to the sites are necessary, which can be achieved by manipulating particle morphology of the sorbent, for instance, assemblies of lamella have a morphology with large surface area [32]. The adsorption sites on the surface need to be readily accessible, thus, the sorption will be efficient.

Theoretically, oxygen vacancies (OVs) in oxide solids are positively charged and the OVs on the outer solid surface may act as traps for anions. We also know that the structure and quantity of OVs vary from solid to solid, and if large number of surface OVs with strong interaction with the toxic SeO_x^{2-} anions can be created on some solids, they could be potentially efficient sorbents for the removal of toxic anionic species. To verify our hypothesis, in the present work, microsphere-like- $\delta\text{-Bi}_2\text{O}_3$ (MS- $\delta\text{-Bi}_2\text{O}_3$) was synthesized and exploited in the selective removal of SeO_x^{2-} from water. The well-known feature of $\delta\text{-Bi}_2\text{O}_3$ is its high ionic conductivity arising from two OVs in one unit cell [33]. Batch experiments were

firstly conducted to investigate the adsorption equilibrium capacity and kinetics of SeO_x^{2-} uptake. Also, relevant factors that affect the adsorption, such as pH, ionic strength, and competitive anions were examined. It was found that MS- δ - Bi_2O_3 was able to simultaneously adsorb both SeO_3^{2-} and SeO_4^{2-} anions from aqueous solution in a larger amount, more effectively and selectively than any other metal oxides that were previously reported. In addition, the chemical bonding between SeO_x^{2-} and OV-rich δ - Bi_2O_3 and their configuration, which affect adsorption of SeO_x^{2-} at the solid-water interface, were thoroughly investigated and identified at the molecular level.

2. Material and methods

2.1. Materials.

All of the chemicals were purchased from Aladdin Chemicals Co. Ltd. (Beijing, China).

2.2. Prepare MS- δ - Bi_2O_3 and Selenium Solutions

The preparation process of MS- δ - Bi_2O_3 was described previously [32, 34]. A typical synthesis procedure is as follows. First, 4 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co., Ltd. $\geq 99.0\%$) and 20 mmol $\text{NH}_2\text{CH}_2\text{COOH}$ (Aladdin Chemistry Co. Ltd. $\geq 99.0\%$) were dissolved in 60 mL deionized water, followed by vigorous stirring for 5 min at room temperature. Subsequently, the mixture was sonicated for 30 min by an ultrasonic generator. The mixture was put into a Teflon-lined stainless steel autoclave with a capacity of 100 mL. The autoclave was sealed and heated at 140 °C for 24 h. Then, the autoclave was cooled to room temperature naturally. Finally, the products were washed with absolute ethanol and deionized water several times followed by drying under vacuum at 60 °C for 24 h.

2.3. Equilibrium adsorption test

The equilibrium adsorption tests were conducted through batch experiments using SeO_x^{2-} concentrations ranging from 1 ppm to 700 ppm (the amount of adsorbent = 1 g L^{-1} , pH = 6.5). For comparison, the same amount of δ - Bi_2O_3 (Aladdin Chemistry Co. Ltd. $\geq 99.0\%$, the mean grain size is below 1 μm) was used as

a control. The equilibrated sorption under magnetic stirring lasted for over 48 h at room temperature. Afterwards the supernatants were analyzed by the inductively coupled plasma (ICP, Varian Liberty 200 ICP-OES) to determine the remaining concentration of SeO_x^{2-} . The total Bi and Se concentrations in the supernatants were analyzed by the inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Liberty 200). The concentration test report shows that almost no Bi signal ($<0.01 \mu\text{g L}^{-1}$) were detected for the supernatants.

2.4. Kinetic adsorption test

The kinetics of adsorption were determined by using SeO_3^{2-} (100 ppm) and SeO_4^{2-} (50 ppm) aqueous solutions. After appropriate time intervals, the supernatants were analyzed as described above. The pH value of suspension liquid during the adsorption process was well kept 6.5 ± 0.1 (the amount of adsorbent = 1 g L^{-1}).

2.5. Selective adsorption

The selective uptake of SeO_x^{2-} in the presence of high concentrations of Cl^- , NO_3^- , SO_4^{2-} , CO_3^{2-} and PO_4^{3-} anions was investigated. Briefly, 20 mg of adsorbent was dispersed into 20 ml aqueous solution mixture containing 20 ppm Na_2SeO_3 or Na_2SeO_4 and 2.0×10^4 ppm of Cl^- , NO_3^- , SO_4^{2-} , CO_3^{2-} or PO_4^{3-} anions (the amount of adsorbent = 1 g L^{-1} , pH = 6.5).

2.6. The influence of pH and ionic strength on SeO_x^{2-} immobilization

Uptake of SeO_x^{2-} in weak acid and base solution was done by adjusting the pH with CH_3COOH (0.001 M) and NH_4OH solutions with the initial concentration of SeO_x^{2-} set at 150 ppm (the amount of adsorbent = 1 g L^{-1}). To investigate the ionic strength on SeO_x^{2-} immobilization, we controlled the concentration of NO_3^- to affect the ionic strength of solution. The background electrolytes were obtained by adjusting the concentration of NO_3^- (0.001, 0.01 and 0.1 M).

2.7. Characterization

The morphology, composition and crystal phases of the samples before and after sorption of SeO_3^{2-} anions were obtained by a scanning electron microscope (SEM; Hitachi, S-4800) with energy-dispersive X-ray (EDX) spectroscopy, High-resolution transmission electron microscopy (HRTEM, JEM-2100F JEOL), X-ray photoelectron spectroscopy (XPS, ESCALab250 Thermo Scientific Corporation), Raman spectra (Renishaw 1000 NR) and powder X-ray diffraction (XRD, D8 Advance Bruker) analysis. Room temperature electron spin resonance (ESR) spectra were performed by using a JEOL JES-FA200 ESR spectrometer (300 K, 9.062 GHz). The Brunauer–Emmett–Teller (BET) specific surface area was measured on a Micromeritics TriStar Surface Area and Porosity Analyzer. Theoretical calculations were performed based on one spin-polarized density functional theory (DFT) package, CASTEP method. In our calculations, a slab of $\delta\text{-Bi}_2\text{O}_3$ (111) surface unit cell was used in our calculations, which is composed of 5 diatomic layers thick with one SeO_3^{2-} . To prevent interactions between periodic arrangements, the vacuum width of 15 Å was used in the direction perpendicular to the surface. The surface structures were optimized before adsorption. The adsorption energies for the SeO_3^{2-} adsorption on the $\delta\text{-Bi}_2\text{O}_3$ can be obtained by the Equation:

$$E_{\text{ads}} = E_{\text{slab} + \text{SeO}_3^{2-}} - E_{\text{slab}} - E_{\text{SeO}_3^{2-}}$$

Where the E_{slab} , $E_{\text{SeO}_3^{2-}}$ and $E_{\text{slab} + \text{SeO}_3^{2-}}$ represented the energy of the $\delta\text{-Bi}_2\text{O}_3$ (111) slab, a free SeO_3^{2-} and slab + SeO_3^{2-} . A larger negative value refers to the stronger adsorption ability.

3. Results and discussion

3.1. Morphology and Structural Characterization of Adsorbents

It is widely accepted that the lattice-cell of $\delta\text{-Bi}_2\text{O}_3$ is dominated by defect sites, particularly surface OV_s. These OV_s have a positive influence on the electronic properties, the steric properties, and the chemical reactivity of the adsorbent surfaces [35]. As shown in Figure 1a and 1b, the (111) plane of $\delta\text{-Bi}_2\text{O}_3$ contains a high density of OV_s. These OV_s make $\delta\text{-Bi}_2\text{O}_3$ one of the most technologically important oxide ion conductors, but its adsorption ability for toxic anions aroused little attention until its capture behavior of radioactive iodine was revealed by our group [32]. As is known to all, the existence of OV_s causes obvious changes

in the surface chemical environment, so X-ray photoelectron spectroscopy (XPS) could be utilized to examine the existence of the OV. In particular, one of peaks at 531.7 eV in O 1s core level spectrum of MS- δ -Bi₂O₃ stands out, which is attributed to the OV in the matrix of metal oxide (Figure 2a) [36, 37]. However, no apparent shoulder peaks appear at the same position in α -Bi₂O₃ counterpart, suggesting that there is no OV in its lattice. Further proof is provided by the electron spin resonance (ESR) spectroscopy (Figure 2b). The MS- δ -Bi₂O₃ sample exhibits an ESR signal at $g = 2.004$, which is assigned to the electrons trapped in the OV [37, 38]. An image by scanning electron microscope (SEM) of MS- δ -Bi₂O₃ is presented in Figure 1c. The δ -Bi₂O₃ sample consists of fluffy flower-like microspheres with an average diameter of $\sim 1.5 \mu\text{m}$. These microspheres were formed by assembly of δ -Bi₂O₃ lamellae leading to a high specific surface area (SSA) of $\sim 24 \text{ m}^2 \text{ g}^{-1}$ (Figure S1). The hierarchical structure along with high dense of OV on its exposed planes allows the contaminants in the fluid to more effectively access surface adsorption sites on the crystal face (Figure 1d) and thus, leads to their better entrapment. These microspheres could also be easily dispersed into Se-rich water environment because the spheres do not aggregate severely unlike fine clays and zeolites [32]. Furthermore, the saturated adsorbents with smaller SSA ($19.2 \text{ m}^2 \text{ g}^{-1}$ for SeO₃- δ -Bi₂O₃ and $20.1 \text{ m}^2 \text{ g}^{-1}$ for SeO₄- δ -Bi₂O₃, Table S1) can be readily separated from a liquid by self-sedimentation process, since its microsphere morphology remained intact after SeO_x²⁻ adsorption as shown in Figures. 1e-f, and this is expected to significantly reduce the cost of the separation of the adsorbent from a liquid.

3.2. Adsorption of SeO_x²⁻

Figure 3 shows the adsorption of SeO_x²⁻ (IV, VI) species by MS- δ -Bi₂O₃ with various SeO_x²⁻ concentrations. As shown in Figure 3a, the adsorption equilibrium isotherm illustrates that the maximum adsorption capacity of SeO₃²⁻ anions reaches up to 160 mg g^{-1} and that of SeO₄²⁻ anions is 58 mg g^{-1} . These values are much higher than those of commercial OV-free α -Bi₂O₃ counterpart, which shows the uptake of only 10 mg g^{-1} for SeO₃²⁻ and 0.01 mg g^{-1} for SeO₄²⁻. The uptake capacity of this compound

is also much higher than that of other conventional metal oxides, even the oxides with very large SSAs. For instance, the maximum capacity of $\text{Al}_2\text{O}_3/\text{SiO}_2$ is 20 mg g^{-1} for Se (IV) and 2.4 mg g^{-1} for Se (VI) [10]; NU-1000 with a very high SSA of $1035 \text{ m}^2 \text{ cm}^{-3}$ can only reach the saturated adsorption of 102 mg g^{-1} for Se (IV) (Supplementary Table S1) [14].

As illustrated in Figure 3b, the anions can be completely removed by the MS- δ - Bi_2O_3 adsorbent when the SeO_3^{2-} anion concentration is below 100 ppm or SeO_4^{2-} anion concentration below 50 ppm. The adsorbent can adsorb about 78% of SeO_3^{2-} anions from a 200ppm solution. Furthermore, the distribution coefficient (K_d) of the MS- δ - Bi_2O_3 , which is defined as the ratio of the amount of SeO_x^{2-} adsorbed by one gram of the sorbent to the amount of Se remaining in solution (per milliliter)^{39, 40}, was derived from the system with the Se concentration of 100 ppm. The calculated K_d value for SeO_3^{2-} by MS- δ - Bi_2O_3 is over $1 \times 10^5 \text{ mL g}^{-1}$, and the value for SeO_4^{2-} was 200 mL g^{-1} , which are much higher than those of the commercial α - Bi_2O_3 (111 mL g^{-1} for SeO_3^{2-} and 1 mL g^{-1} for SeO_4^{2-}). Besides, the energy-dispersive X-ray (EDS) spectrum discloses uniform distribution of Bi, Se and O of the SeO_x^{2-} -MS- δ - Bi_2O_3 adsorbent (Figure S2).

The sorption kinetics of SeO_x^{2-} ions was plotted in order to better understand the role of MS- δ - Bi_2O_3 in efficient sewage treatment. As shown in Figure 4a, the removal percentage for SeO_x^{2-} reached 90% on MS- δ - Bi_2O_3 in the first 30 min, and the adsorption reached equilibrium within 1 h. To verify if the current EPA standards for SeO_x^{2-} in water can be satisfied by using MS- δ - Bi_2O_3 as a sorbent, uptake of SeO_x^{2-} at low concentrations (40°C , $\text{pH} = 6$) was also studied to simulate the remediation of recirculating cooling water in power plants [14]. When exposed to 20 mL of an aqueous solution of Na_2SeO_3 or Na_2SeO_4 at 1000 ppb, 20 mg of MS- δ - Bi_2O_3 adsorbed 99% of the SeO_3^{2-} or SeO_4^{2-} in solution in less than 1 min (Figure 4b). With a remnant concentration below 20 ppb Se in the solution even after the adsorbent remained in it for 3 hours, the use of MS- δ - Bi_2O_3 adsorbent can meet the EPA standards of Se for drinking water (<50 ppb). The above successful tests showed that MS- δ - Bi_2O_3 is a promising candidate for removal

of SeO_3^{2-} and SeO_4^{2-} under power plant operating conditions. The adsorption rate of MS- δ - Bi_2O_3 places it among the fastest adsorbing materials kinetically for SeO_3^{2-} and SeO_4^{2-} described to date (Table S1). The uptake time of < 1 min sets MS- δ - Bi_2O_3 apart from other materials such as Al_2O_3 and Fe_2O_3 derivatives as well as ion exchange and polymer resins, each of which requires much longer time to reach maximum adsorption capacity under equivalent conditions.

The influence of pH on the capture of SeO_x^{2-} anions by the MS- δ - Bi_2O_3 was investigated in a pH range of 4-10, which are totally cover the possibility of pH range in real recirculating cooling water [14]. As presented in Figure 5a, the uptake amounts of SeO_3^{2-} and SeO_4^{2-} were reduced by 15% and 23%, respectively, when the pH value was raised from 4 to 10. A slight decrease in adsorption capacity of SeO_x^{2-} in basic environment is due to the competition for adsorption sites between negatively charged SeO_x^{2-} and abundant OH^- ions. The slight increase in adsorption capacity of SeO_x^{2-} in acid media is owing to the fact that the electrostatic attraction occurred at lower pH between positively charged adsorbent surface and negative ion during the adsorption process that favor the sorption performance. To investigate the selective adsorption of SeO_x^{2-} anions by the MS- δ - Bi_2O_3 , the adsorption tests were carried out in the presence of a large excess of common Cl^- , SO_4^{2-} , CO_3^{2-} , NO_3^- or PO_4^{3-} anions. As illustrated in Figure 5b and 5c, the presence of high concentrations of NO_3^- , SO_4^{2-} or Cl^- ions (the concentration of which is 1000 times higher than that of SeO_x^{2-} ions) have limited or no influence on SeO_3^{2-} uptake. However, the excessive CO_3^{2-} or PO_4^{3-} anions can seriously reduce the adsorption capacity of SeO_3^{2-} . It is also found that the presence of the above five competitive anions seriously reduced the SeO_4^{2-} removal efficiency, especially in the presence of PO_4^{3-} . Obviously, MS- δ - Bi_2O_3 is more efficient and selective for SeO_3^{2-} ions removal.

3.3. Structural Evolution and Adsorption Mechanism

Profound structural changes can be observed from the wide-angle X-ray diffraction (WXR) patterns for MS- δ - Bi_2O_3 after adsorption of SeO_3^{2-} (Figure 6a). For instance, the most obvious changes are the

diffraction peaks located at 32.56° and 46.57° , corresponding to the planes (200) and (220) of the $\delta\text{-Bi}_2\text{O}_3$, shift $+0.9^\circ$ and $+1.35^\circ$ after the capture of SeO_3^{2-} . The interlayer spacing of $\delta\text{-Bi}_2\text{O}_3$ shrinks evidently (e.g. the shrinkage crystal plane was calculated: $\Delta d_{(111)} = -0.12 \text{ \AA}$ and $\Delta d_{(200)} = -0.07 \text{ \AA}$) when the adsorption sites in the microstructure were occupied by SeO_3^{2-} ions. Small-angle X-ray diffraction (SXRD) pattern reveals that the intensity of the diffraction peak at 0.9° , which is attributed to the ordered arrangement of $\delta\text{-Bi}_2\text{O}_3$ crystal cell, became weak after the capture of SeO_3^{2-} (Figure S3). This is probably owing to the partial structural deformation induced by the shrinkage of lattice plane after SeO_3^{2-} was adsorbed on the exposed planes. The adsorption induced lattice deformation indicates strong interaction of the SeO_3^{2-} with the adsorbent lattice which usually results in irreversible adsorptive ability [32, 39]. However, no obvious lattice deformation was detected from WXR (Figure 6b) and SXRD patterns after adsorption of SeO_4^{2-} . This means that the interaction of the larger SeO_4^{2-} anions with the surface of $\delta\text{-Bi}_2\text{O}_3$ is not strong enough to cause deformation of the adsorbent lattice. The SeO_4^{2-} anions adsorption does not involve the formation of chemical bond and is most likely physisorption. The structural change induced by the entrapment of SeO_x^{2-} was also investigated by selected-area electron diffraction (SAED) pattern and high-resolution transmission electron microscopy (HRTEM), the representative images are compared in Figure 7.

Apparently, SAED dot pattern of pristine MS- $\delta\text{-Bi}_2\text{O}_3$ (Figure 7a) becomes a blurry ring pattern after SeO_3^{2-} adsorption (Figure 7b). Remarkably, the fringe spacing of (111), (220), (311) and (200) planes shrinks after capture of SeO_3^{2-} (Figure 7e), which is in good agreement with the WXR results. However, the $\text{SeO}_4\text{-}\delta\text{-Bi}_2\text{O}_3$ exhibits mixed dot-ring pattern (Figure 7c) and same fringe spacing as that of MS- $\delta\text{-Bi}_2\text{O}_3$ adsorbent (Figure 7f). The analysis of SAED patterns and HRTEM images also indicates that the adsorption of SeO_4^{2-} anions on MS- $\delta\text{-Bi}_2\text{O}_3$ is distinctly different from the adsorption of SeO_3^{2-} anions. The different effects of SeO_x^{2-} adsorptions on the $\delta\text{-Bi}_2\text{O}_3$ lattice could provide key information on the adsorption selectivity of the adsorbent.

Moreover, the SeO_3^{2-} - δ - Bi_2O_3 was analyzed by Se K-edge X-ray Absorption Fine Structure (XAFS) spectroscopy (Note S1). The Se *K*-edge $k^3\chi(k)$ spectra for the SeO_3 -MS- δ - Bi_2O_3 is mostly dominated by a Se-O Extended X-ray Absorption Fine Structure (EXAFS) oscillation, especially for the low to middle *k* data range up to $\sim 10 \text{ \AA}^{-1}$ [40] (Figure 8a). Converted to R space, this Se-O oscillation component is presented correspondingly as the first shell nearest neighbor Fourier transform (FT) with its magnitude peak “A” centered at $\sim 1.3 \text{ \AA}$ (Figure 8b). Other relatively weak EXAFS features, e.g. shoulder peak “a” and asymmetry feature “b” for EXAFS oscillation are also revealed throughout middle to high *k* data range of 8-12 $\text{ \AA}^{-1}$ (Figure 8a). These high frequency EXAFS signals are displayed accordingly in R space as outer shells feature “B” to “C” around 3.2 $\text{ \AA}$ and 4.2 $\text{ \AA}$ R region, respectively (inset of Figure 8b). The R space curve fitting for the Se K edge EXAFS data from the SeO_3^{2-} -MS- δ - Bi_2O_3 reveals the existence of outer shell Se-O bonding between the SeO_3 first shell and the outer Se-Bi shell (Table S3). The results highlight that SeO_3^{2-} ions may attach to the surface oxygen of δ - Bi_2O_3 by Se-O-Bi bonding.

Figure 8c displays that there are three possible forms for SeO_3^{2-} anions to attach to the exposed (111) facet of δ - Bi_2O_3 : Bi-O-Se single bonding-form (B1 model), Bi-O-Se double bonding-form (B2 model), and Bi-O-Se triple bonding-form (B3 model). Since OV's of the adsorbent are positively charged, the OV's at MS- δ - Bi_2O_3 surface should be the anion trapping sites. When the anions occupy the exposed OV's sites the adsorption is optimal in terms of adsorption energy. The optimal structures for SeO_3^{2-} anion adsorbed on the (111) plane in Figure 4c are obtained from calculation (Figure S4). All these structures are thermodynamically feasible. However, B1 model structure (red curve) is not supported by X-ray Absorption Near Edge Structure (XANES) modeling owing to the obvious disappearance of characteristic peak at 12663 eV (Figure 8d), which corresponds to both the 1st shell Se-O and the 2nd shell Se-Bi scattering [41]. So comparing the results of model simulation with experimental data (Figure 8d), we find that B3 model (pink line) almost coincides with experimental data (black line) especially at 12673 eV, which refers mainly to the 1st shell Se-O coordination. This means that B3 structure is more supported by

XANES results. For further verification, the Fourier transform infrared spectra (FTIR) clearly reveals that the Se-O stretches in SeO_3^{2-} is in the region of 747 cm^{-1} (Figures 9a-b). Particularly, the peak of Se-O stretches of SeO_3^{2-} -MS- δ - Bi_2O_3 obviously shifts to 700 cm^{-1} , which is ascribed to the formation of Bi-O-Se [42]. And Raman spectra also verify existence of Se-O-Bi bonding type rather than Bi-Se bond (Figure S5) [43]. Herein, the OV's on the (111) facet of δ - Bi_2O_3 are filled by the O atoms of SeO_3^{2-} anions achieving a stable structure. In accordance with the result of XANES modeling, the O 1s spectra reveal that the peak position of OV's at 531.7 eV are significantly reduced and slightly shift to a higher binding energy (532.3 eV) for SeO_3 -MS- δ - Bi_2O_3 , which refer to the Se-O bond on the surface of δ - Bi_2O_3 (Figure 9c). Nevertheless, the OV's are still remained in SeO_4 -MS- δ - Bi_2O_3 , and this is why MS- δ - Bi_2O_3 is complained for the low attractive force to SeO_4^{2-} ions. After sorption of SeO_3^{2-} ions, two tiny shoulder peaks can be observed in Bi 4f spectra, which refer to the four valence of Se in B3 mode (Figure 9d and Figures S6-7). The anion occupation in B3 model results in a slight lattice deformation as discussed above in SXRD. Surface charge effects, which might be distinct for each facet, could be another possibility to explain the lattice shrinkage in WXR, SAED and HRTEM [39].

4. Conclusions

SeO_3^{2-} anions occupation of the OV's on δ - Bi_2O_3 surface in B3 model results in strong affinity of SeO_3^{2-} anions to MS- δ - Bi_2O_3 adsorbent, and this is the reason for the difference in adsorption properties between SeO_3^{2-} and SeO_4^{2-} anions and the high selectivity to SeO_3^{2-} adsorption. SeO_4^{2-} anions can access the OV's on δ - Bi_2O_3 surface but cannot well fit with the OV's to form strong bonding so that SeO_4^{2-} adsorption is much weaker compared to SeO_3^{2-} adsorption. This theory can also be applied to explain influence of the presence of the common anions on the SeO_3^{2-} adsorption. Cl^- , SO_4^{2-} and NO_3^- cannot well fit with the OV's having limited influence while CO_3^{2-} and PO_4^{3-} anions can bond to the surface OV sites better and seriously reduce SeO_3^{2-} adsorption capacity. In contrast, the uptake capacity of SeO_4^{2-} was reduced significantly in the presence of the common anions (Figure S8) because of weak interaction between SeO_4^{2-} and the surface OV sites. Besides, the

OVs (sites) of MS- δ -Bi₂O₃ are adequately exposed because of the morphology of assembled lamellas, facilitating rapid and effective SeO_x²⁻ adsorption.

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Figures

Figure 1. The structure and morphology of OV-rich MS- δ -Bi $_2$ O $_3$. (a) Schematic representation of the crystalline structure and (b) the main plane (111) with high density of OV. (c) Typical SEM images of the as-obtained MS- δ -Bi $_2$ O $_3$ adsorbent. (d) Representation of the bonding effect of OV on δ -Bi $_2$ O $_3$ plane with SeO_x^{2-} ions and the SEM images of (e) the adsorbent after Se^{VI} adsorption (Se^{VI} -MS- δ -Bi $_2$ O $_3$) and (f) the adsorbents after Se^{IV} adsorption (Se^{IV} -MS- δ -Bi $_2$ O $_3$).

Figure 2. Characterizations of the MS- δ -Bi $_2$ O $_3$ and α -Bi $_2$ O $_3$ samples: (a) O 1s core level XPS spectra and (b) ESR spectra.

Figure 3. The sorption property of OV-rich $\text{MS-}\delta\text{-Bi}_2\text{O}_3$ for hypertoxic SeO_x^{2-} ions. (a) The adsorption isotherms curves (dashed lines) of SeO_x^{2-} adsorption by $\text{MS-}\delta\text{-Bi}_2\text{O}_3$ and $\alpha\text{-Bi}_2\text{O}_3$ over 48 hours. (b) Removal of SeO_x^{2-} from solutions of different concentrations by $\text{MS-}\delta\text{-Bi}_2\text{O}_3$ and $\alpha\text{-Bi}_2\text{O}_3$ (the adsorbent mass to volume ratio = 1 g L^{-1} , 25°C , $\text{pH} = 6.5$). All data are the average of three measurements.

Figure 4. The sorption kinetics of OV-rich $\text{MS-}\delta\text{-Bi}_2\text{O}_3$. (a) SeO_x^{2-} adsorption dynamics of $\text{MS-}\delta\text{-Bi}_2\text{O}_3$. (b) Residual concentration of SeO_x^{2-} vs. time at low concentration (the adsorbent mass to volume ratio = 1 g L^{-1} , 40°C , $\text{pH}=6$). SeO_x^{2-} starting concentration of 1000 ppb.

Figure 5. The selective sorption properties of OV-rich MS- δ -Bi₂O₃. (a) Immobilization percentage of SeO_x²⁻ ions in the aqueous solution with a wide pH range. (b) and (c) Effect of high concentration of competitive anions on the removal of SeO_x²⁻ by MS- δ -Bi₂O₃ (the adsorbent mass to volume ratio = 1 g L⁻¹).

Figure 6. Crystalline structure evolution of OV-rich MS- δ -Bi₂O₃. X-ray diffraction (WXRD) patterns before and after adsorption of (a) SeO₃²⁻ and (b) SeO₄²⁻ ions.

Figure 7. Microstructure evolution of OV-rich MS- δ - Bi_2O_3 . The SAED patterns and HRTEM images of (a, d) δ - Bi_2O_3 , (b, e) SeO_3 - δ - Bi_2O_3 , and (c, f) SeO_4 - δ - Bi_2O_3 , respectively.

Figure 8. The mechanism bonding form of SeO_3^{2-} -MS- δ - Bi_2O_3 . (a) Comparison of $k^3(k)$ from the experimental data (black) and from the Feff modeling based on the result of R space curve fitting of SeO_3^{2-} -MS- δ - Bi_2O_3 (red). (b) the contrast between experimental data and those by the counterpart Feff modeling (Black, red, blue, and pink lines refer to experiment data, magnitude of Fourier transform (ExpData-Mag), experiment data, imaginary part of Fourier transform (ExpData-Im), R space curve fitting to the experiment data, based on Feff modeling, magnitude of Fourier transform (Feff fit-Mag), and R space curve fitting to the experiment data, based on Feff modeling, imaginary of Fourier transform (Feff fit-Im), respectively). (c) The schematic illustration of potential bonding modes of SeO_3^{2-} anion on the (111) plane via theoretical calculation results (Se-O molecular configuration in blue dotted box). (d) The XANES spectra of SeO_3 - δ - Bi_2O_3 from the experimental data and modeling data.

Figure 9. The spectral characterization of OV-rich MS- δ -Bi₂O₃ before and after sorption of SeO_x²⁻.

(a) FTIR patterns of MS- δ -Bi₂O₃, SeO₄²⁻, SeO₃²⁻, SeO₄²⁻-MS- δ -Bi₂O₃ and SeO₃²⁻-MS- δ -Bi₂O₃ and (b) its enlarged patterns. XPS spectra of (c) O 1s, (d) Bi 4f of MS- δ -Bi₂O₃, SeO₃²⁻-MS- δ -Bi₂O₃ and SeO₄²⁻-MS- δ -Bi₂O₃.

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