Low Overpotential in Vacancy-Rich Ultrathin CoSe$_2$ Nanosheets for Water Oxidation

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Supporting Information

ABSTRACT: According to Yang Shao-Horn’s principle, CoSe$_2$ is a promising candidate as an efficient, affordable, and sustainable alternative electrocatalyst for the oxygen evolution reaction, owing to its well-suited electronic configuration of Co ions. However, the catalytic efficiency of pure CoSe$_2$ is still far below what is expected, because of its poor active site exposure yield. Herein, we successfully overcome the disadvantage of insufficient active sites in bulk CoSe$_2$ by reducing its thickness into the atomic scale rather than any additional modification (such as doping or hybridizing with graphene or noble metals). The positron annihilation spectrometry and XAFS spectra provide clear evidence that a large number of VCo$^{2+}$ vacancies formed in the ultrathin nanosheets. The first-principles calculations reveal that these VCo$^{2+}$ vacancies can serve as active sites to efficiently catalyze the oxygen evolution reaction, manifesting an OER overpotential as low as 0.32 V at 10 mA cm$^{-2}$ in pH 13 medium, which is superior to the values for its bulk counterparts as well as those for the most reported Co-based electrocatalysts. Considering the outstanding performance of the simple, unmodified ultrathin CoSe$_2$ nanosheets as the only catalyst, further improvement of the catalytic activity is expected when various strategies of doping or hybridizing are used. These results not only demonstrate the potential of a notable, affordable, and earth-abundant water oxidation electrocatalyst based on ultrathin CoSe$_2$ nanosheets but also open up a promising avenue into the exploration of excellent active and durable catalysts toward replacing noble metals for oxygen electrocatalysis.

INTRODUCTION

As the key enabling process in various types of clean and sustainable energy technologies, electrochemical water oxidation, also known as the oxygen evolution reaction (OER), has stimulated extensive research in the societal pursuit of efficient energy storage and conversion.1–4 However, the kinetics of the OER are sluggish, which requires a high overpotential to experience a complex four-electron oxidation process.5,6 Although pioneering studies have revealed that some noble metal oxides, such as IrO$_2$ and RuO$_2$, can efficiently catalyze the OER process, their prohibitive cost and scarcity have seriously impeded their widespread application.7,8 Therefore, the exploration of highly efficient and economical water oxidation catalysts has become more significant in light of the dwindling global energy crisis and environmental challenges.

Recently, 3d transition metal (Ni, Co, Fe, and Mn) compounds have sparked worldwide interest owing to the fact that they are earth-abundant and environmentally benign; however, they underperform the state-of-the-art water oxidation catalysts.9–13 Yang Shao-Horn’s principle, which quantitatively describes that the ideal OER electrocatalyst can be obtained when the eg occupancy of surface transition-metal cations is close to unity, has been instrumental in designing highly active water oxidation catalysts.14 In this regard, cubic CoSe$_2$, with a t$_{2g}^6$e$_g^0$ electronic configuration near the optimal eg filling (Figure 1a,b), would be a terrific candidate. Meanwhile, theoretical calculations show the large local density of states (DOS) across the Fermi level (Figure 1c), which reveals the metallic behavior in CoSe$_2$. To confirm the theoretical investigations, the temperature dependence of the resistance was measured further. As shown in Figure 1d, the typical metallic behavior of CoSe$_2$ is reflected by the increased electrical resistance as the temperature increases, which ensures the efficient migration of electrons between the electrode and the surface of the catalysts to give high-performance OER.
catalysts. With these facts in mind, CoSe₂ would enable tremendous advances in high-performance OER. However, despite its optimal $e_g$ filling, pure CoSe₂ still exhibits relatively low catalytic activity, due to its poor active site exposure yield. Although a significant number of strategies, such as hybridizing with graphene or noble metals, have been used to improve the OER catalysis performance of CoSe₂, a systematic investigation of electrocatalysis of pure CoSe₂ has long been neglected, leading to the fact that its catalytic efficiency is still far below what is expected. Therefore, it is highly desirable and urgent to develop a new and convenient strategy to overcome these disadvantages to achieve the excellent intrinsic electrocatalytic activity of this promising compound.

Triggered by the great success of graphene, two-dimensional (2D) ultrathin nanosheets have attracted explosive attention due to a wealth of unprecedented functionalities, which benefit from their extremely high surface percentage (nearly 100%). Moreover, ultrathin nanosheets with 2D configurations enable intimate and large area contact with both the GC electrode and the electrolyte, which guarantee faster interfacial charge transfer to improve the electrocatalytic reactions. Most importantly, the more exposed interior atoms inevitably induce the formation of defects with structure disorder on their surface, which usually increases the density of states near the Fermi level to serve as highly active sites for catalytic reactions. Thus, 2D ultrathin nanosheets undoubtedly provide not only new opportunities to satisfy the requirements of highly efficient catalysts but also an ideal platform for a comprehensive understanding of the underlying correlations among atomic, defect, electronic structure, and intrinsic properties.

Herein, inspired by the above considerations, we show that the atomically thick CoSe₂ nanosheets can effectively catalyze the OER without any additional modification (such as doping or hybridizing with graphene or noble metals), manifesting an OER overpotential as low as 0.32 V at a current density of 10 mA cm⁻² in pH 13 medium, which is almost the best performance among the reported Co-based OER electrocatalysts. These ultrathin CoSe₂ nanosheets also show small Tafel slopes of 44 mV/dec and large turnover frequencies (TOFs) of 0.33 s⁻¹ at an overpotential of 0.5 V, which indicates that the ultrathin nanosheets should be promising candidates for highly active electrocatalysts. In combination with positron annihilation spectra, XAFS spectra, and theoretical calculations, we can unambiguously conclude that the formation of $V_{Co}^{0}$ vacancies in the two-dimensional plane should mainly contribute to the significantly improved OER catalytic performance. Our work undoubtedly provides prospective insights into the exploration of highly efficient and durable electrocatalysts for water oxidation.

**EXPERIMENTAL SECTION**

**Materials.** Co(AC)$_3$·H$_2$O, K$_2$SeO$_3$, diethylenetriamine (DETA), cobalt powder, selenium powder, ethanol, KOH, and Na$_2$CO$_3$ solution (5 wt %) were all analytical grade purity acquired from Sinopharm Chemical Reagent Co., Ltd. and were used without any further purification.

**Synthesis of Nanohybrids, CoSe₂ Ultrathin Nanosheets, and Bulk CoSe₂.** CoSe₂ ultrathin nanosheets were fabricated by exfoliating the CoSe₂-based inorganic–organic lamellar nanohybrids. The typical experiment was mainly divided into two steps: first, lamellar hybrid CoSe₂/DETA intermediates were synthesized in conformity to the existing literature. Herein, DETA in the intermediates CoSe₂/DETA stands for diethylenetriamine. Second, 10 mg of CoSe₂/DETA product was dispersed in 20 mL of ethanol and then ultrasonicated in ice-water for 12 h. After ultrasonic treatment, the resultant dispersions were centrifuged at 3000 rpm for 10 min to remove the unfomedated component. The bulk CoSe₂ was synthesized by solid-state reactions. Typically, the cobalt powder and selenium powder mixture in a stoichiometric ratio was ground and then collected in a fused silica tube under vacuum, which was heated to 500 °C for 2 h at a rate of 50 °C h⁻¹ and then heated at the same rate to 650 °C. After sintering at 650 °C for 12 h, the obtained samples were cooled to room temperature over 12 h.

**Characterization.** XRD patterns were recorded by using a Philips X’Pert Pro Super diffractometer with Cu Kα radiation (λ = 1.54178 Å). Raman spectra were detected by a Renishaw RM3000 Micro-Raman system. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VGESCALAB MK II X-ray photoelectron spectrometer with an excitation source of Mg Kα (1253.6 eV). Thermogravimetric analysis (TGA) was carried out on a Shimadzu TA-50 thermal analyzer from room temperature to 800 °C at a heating rate of 10 °C min⁻¹. The field emission scanning electron microscopy (FE-SEM) images were taken on a JEOL JSM-6700F SEM instrument. The TEM and HRTEM measurements were carried out on a JEM-2100F field emission electron microscope at an acceleration voltage of 200 kV. Atomic force microscopy (AFM) was performed by means of a DI Innova Multimode SPM platform. The electrical resistivity study in this work was corrected for a Keithley 4200 station with the computer-controlled four-probe technique. Co K-edge X-ray absorption fine structure spectroscopy (XAFS) was carried out at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF) China. The storage ring of the SSRF was operated at 3.5 GeV with a maximum current of 200 mA.

**Positron Annihilation Measurement.** Sandwiched samples of CoSe₂/Na source/CoSe₂ with a total count of 1 million were used for the positron lifetime experiments, which were carried out by a fast-slow coincidence ORTEC system with a time resolution of 230 ps full width at half-maximum. Positron lifetime calculations were performed using the ATSUP method, in which the electron density and the positron crystalline Coulomb potential are constructed by the non-

![Figure 1](image-url)
self-consistent superposition of free atom electron density and Coulomb potential in the absence of the positron.

Calculations. The first-principles calculations were carried out with the Vienna ab initio simulation package,\(^\text{27}\) in which the generalized gradient approximation augmented by a Hubbard U term (GGA+U) with the PBE functional is used.\(^\text{28}\) The energy cutoff was set to 400 e\(\text{V}\), and the atomic positions were allowed to relax until the energy and force were less than \(10^{-3}\) e\(\text{V}\) and \(5 \times 10^{-3}\) e\(\text{V/Å}\), respectively. The on-site repulsion was treated within Dudarev’s approach, where the on-site Coulomb repulsion (Hubbard U) and the atomic orbital intra-exchange energy (Hund’s parameter J) are simplified to the single parameter U\(_{\text{eff}}\) (U\(_{\text{eff}} = U - J = 2.0\) e\(\text{V}\)). The perfect (210)-oriented CoSe\(_2\) nanosheets were simulated by periodically repeating the three CoSe layers along the [210] direction of the unit cell with a vacuum region of 15 Å, whereas the V\(_{\text{Co}}\) vacancy rich CoSe\(_2\) nanosheets were simulated by removal of Co atoms from the surface of perfect (210)-oriented CoSe\(_2\). The concentration of V\(_{\text{Co}}\) vacancies for the DFT calculations is 5%. The bulk CoSe\(_2\) comparison was simulated by periodically repeating the 11 CoSe layers along the [210] direction of the unit cell.

Electrochemical Measurements. Electrocatalytic properties were studied with a standard three-electrode system controlled by a CHI660B electrochemical workstation. An Ag/AgCl (in 3 M KCl solution) electrode and a graphite rod (Alfa Aesar, 99.9995%) were used as the reference electrode and the counter electrode, respectively. To prepare the working electrode, 2 mg of catalyst and 30 \(\mu\text{L}\) of Nafion solution (5 wt %) were dispersed in 1 mL of ethanol–water mixed solvent with a volume ratio of 1:3 with sonication for at least 30 min to generate a homogeneous suspension. Then 5 \(\mu\text{L}\) of this solution (containing 20 \(\mu\text{g}\) of catalyst) was drop-casted onto a 3 mm diameter glassy-carbon electrode and then the solvent was evaporated at room temperature, yielding a catalyst loading of 0.142 mg cm\(^{-2}\). All electrochemical measurements were conducted in 0.1 M KOH solution with a scan rate of 5 mV s\(^{-1}\). The turnover frequency (TOF) was calculated on the basis of the reported methods,\(^\text{29,30}\) and calculation details are given in the Supporting Information.

## RESULTS AND DISCUSSION

The ultrathin CoSe\(_2\) nanosheets were synthesized by an integrated process of liquid exfoliation and evaporation of the lamellar CoSe\(_2\)/DETA (DETA represents diethylenetriamine) intermediate (Supporting Information, Figure S1). The crystallinity of as-obtained ultrathin CoSe\(_2\) nanosheets was determined by Raman spectra (Figure 2a), where the sharp peak at 190 cm\(^{-1}\) was assigned to the Se–Se stretching mode of cubic CoSe\(_2\).\(^\text{31}\) The XPS data in Figure 2b reveal the electron-binding energies of Co 2p\(_{1/2}\) at 778.3 e\(\text{V}\) and Co 2p\(_{3/2}\) at 793.4 e\(\text{V}\), which are consistent with Co\(^{2+}\) cations in CoSe\(_2\). Meanwhile, an obvious satellite at the higher energy side of the Co 2p signal indicates the antibonding orbital between the Co atom and Se atom.\(^\text{32}\) This result implies that the electronic structure of the obtained CoSe\(_2\) corresponds to \(d^4\) in the form of \(t_{2g}^3e_g^1\) near the optimal \(e_g\) filling of 1.2 for a high-activity paramagnetic configuration, which is desired for high-performance electrocatalysts. The TEM image in Figure 2c clearly reveals the 2D graphene-like morphology of the nanosheets, and its near-transparency indicates its ultrathin thickness. AFM images (Figure 2d) clearly show a smooth sheet with an average thickness of 1.4 nm. The X-ray diffraction pattern in Figure 2e clearly demonstrates a highly (210) preferred orientation in the ultrathin CoSe\(_2\) nanosheet, which is consistent with the corresponding high-resolution TEM image (Figure 2f). Therefore, all of the results mentioned above clearly demonstrate that CoSe\(_2\) ultrathin nanosheets were successfully fabricated.

![Figure 2. Characterization of CoSe\(_2\) ultrathin nanosheets: (a) Raman spectra from bulk CoSe\(_2\) and CoSe\(_2\)/DETA ultrathin nanosheet; (b) XPS spectra of Co 2p; (c) TEM image; (d) AFM image; (e) XRD pattern for a CoSe\(_2\) SLB film fabricated by LbL assembly; (f) HRTEM image.](image)

In order to study the OER activity, electrochemical measurements of CoSe\(_2\) ultrathin nanosheets as well as the bulk CoSe\(_2\) were performed at a uniform loading of 0.142 mg cm\(^{-2}\) on a glassy-carbon (GC) electrode. The polarization curve for ultrathin CoSe\(_2\) nanosheets in linear sweep voltammetry (LSV) curves exhibits higher current and earlier onset of catalytic current in comparison with those of the bulk CoSe\(_2\) and CoSe\(_2\)/DETA (as shown in Figure 3a). It is simple and convenient to evaluate the electrocatalyst properties by comparing the overpotentials at the current density of 10 mA cm\(^{-2}\). Remarkably, ultrathin CoSe\(_2\) nanosheets can afford such current density at the small overpotential \(\eta\) of 0.32 V, significantly lower than 0.59 and 0.4 V for the bulk CoSe\(_2\) and CoSe\(_2\)/DETA, respectively (Supporting Information, Figure S2). Moreover, ultrathin CoSe\(_2\) nanosheets display the largest electrocatalytic reaction current, with 79.5 mA cm\(^{-2}\) at an overpotential of 500 mV, which is roughly 20 times larger than that of bulk CoSe\(_2\). Since the electrocatalytic reaction current is directly proportional to the oxygen yield, the higher current density here indicates prominent oxygen evolution behavior in ultrathin CoSe\(_2\) nanosheets. To obtain further insights into the oxygen evolution activity, Tafel plots of various catalysts were investigated. The resulting Tafel slope for the ultrathin CoSe\(_2\) nanosheet is 44 mV/dec (Figure 3b), smaller than those of bulk CoSe\(_2\) and CoSe\(_2\)/DETA, implying that the more rapid OER rate can be achieved in practical applications with ultrathin CoSe\(_2\) nanosheets as electrocatalysts. To further assess the OER catalytic ability of the obtained nanosheets, we assumed that all of the Co ions are catalytically active and calculated
To gain a comprehensive understanding of the high OER activity within the ultrathin CoSe₂ nanosheet, local atomic information (Figure S5), further verifying its excellent stability. Moreover, the stability of the electrocatalyst is another important criterion for practical applications. To probe the durability of the ultrathin CoSe₂ nanosheet in an alkaline environment, continuous potential cycling was performed. As shown in Figure 3d, an imperceptible variation in the curves even after 1000 CV cycle catalytic tests, CoSe₂ still almost completely retained its morphology and structure (Supporting Information, Table S1).}

Table 1. Position lifetime parameters of ultrathin CoSe₂ nanosheets and bulk CoSe₂.

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<th>Sample</th>
<th>τ₁ (ps)</th>
<th>τ₂ (ps)</th>
<th>τ₃ (ns)</th>
<th>I₁ (%)</th>
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<td>CoSe₂ nanosheet</td>
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<td>Bulk CoSe₂</td>
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Figure 4. Position lifetime spectra and XAFS measurements (a) K-edge absorption fine structure spectroscopy (XAFS) corresponding Fourier transforms (FT) of k²χ(k)(a) = wave vector and χ(k) oscillation as a function of photoelectron wavenumber; (b) schematic of the formation of VCo₂缺陷.

Figure 3. Water oxidation properties: (a) LSV curves and (b) Tafel plots in 0.1 M KOH medium with bulk CoSe₂, CoSe₂/DETA, and ultrathin CoSe₂ nanosheet as the electrocatalysts; (c) TOFs with respect to Co atoms of bulk CoSe₂, CoSe₂/DETA, and ultrathin CoSe₂ nanosheet at different overpotentials; (d) LSV curves obtained with as-prepared ultrathin CoSe₂ nanosheets before and after 1000 cycles of an accelerated stability test.
Co-Se peak is due to the significantly shortened Co-Se bond length that is exposed on the surface of the ultrathin nanosheet. Combining the above PAS and XAFS characterizations above, we can unhesitatingly validate that $V_{Co}^{\alpha}$ vacancies are confined on the surface of the CoSe$_2$ ultrathin nanosheets. The underlying mechanism of $V_{Co}^{\alpha}$ vacancy formation is, in fact, closely related to the synthetic process (Figure 4e). Taking into account the structure of the lamellar hybrid intermediate CoSe$_2$/DETA, since the Co atoms and DETA are combined together by coordinate bonds, the ultrasonic treatment enables the DETA to drag the Co atoms detached from the lattice, resulting in the formation of the predominant VCo vacancy for the ultrathin nanosheets.

In general, it has been proposed that H$_2$O molecules are initially adsorbed on the surface of catalysts during the electrocatalytic OER. That is to say, the adsorption energy of H$_2$O molecules plays a crucial role in the OER activity. We conducted a series of DFT calculations to study the H$_2$O adsorption on different cobalt sites of bulk CoSe$_2$ and ultrathin CoSe$_2$ nanosheets. Figure5a,b displays the binding energies ($E_b$) of H$_2$O molecules on cobalt sites. It is clear that the surface cobalt sites and $V_{Co}^{\alpha}$ vacancy sites of ultrathin CoSe$_2$ nanosheets possess adsorption energies (absolute value) of 0.63 and 0.85 eV, respectively, obviously larger than that 0.38 eV of cobalt sites in bulk CoSe$_2$, indicating that the $V_{Co}^{\alpha}$ vacancies in the ultrathin structure were more favorable for adsorbing H$_2$O molecules. Accordingly, the ultrathin CoSe$_2$ nanosheets outperforms the bulk in intrinsic OER catalytic activity. The optimized electronic structures of ultrathin CoSe$_2$ nanosheets definitely determine their remarkably enhanced oxygen evolution activity. Moreover, the remarkably enhanced adsorption ability of H$_2$O molecules benefited from the $V_{Co}^{\alpha}$ vacancies as the thickness was reduced to atomic scale; the ultrathin CoSe$_2$ nanosheets also show OER activity much better than that of most reported Co-based electrocatalysts, indicating that ultrathin CoSe$_2$ nanosheets should be promising candidates to serve in the design of effective OER electrocatalysts and be more competitive in practical applications of sustainable energy technologies.

**CONCLUSION**

In conclusion, we successfully overcame the disadvantage of insufficient active sites in bulk CoSe$_2$ through reducing the thickness into the atomic scale. Our developed CoSe$_2$ ultrathin nanosheets with atomic thickness can effectively catalyze the oxygen evolution reaction with low overpotential, small Tafel slopes, and large turnover frequencies, which are all superior to those of its bulk counterparts and most reported Co-based electrocatalysts. Positron annihilation spectrometry, XAFS spectra, and first-principles calculations provide clear evidence that a number of $V_{Co}^{\alpha}$ vacancies are formed in the ultrathin CoSe$_2$ nanosheets, which can serve as active sites to effectively adsorb H$_2$O molecules, resulting in the significantly improved OER catalytic performance. Considering the outstanding performance for these simple, unmodified ultrathin CoSe$_2$ nanosheets as the only catalyst, further improvement of the catalytic activity is expected when various strategies of doping or hybridizing are used. These results not only demonstrate the potential of a notable, affordable, and earth-abundant water oxidation electrocatalyst based on ultrathin CoSe$_2$ nanosheets but also open up a promising avenue into the exploration of excellent active and durable catalysts that can replace noble metals for oxygen electrocatalysis.

**ASSOCIATED CONTENT**

Supporting Information

Figures, tables, and text giving characterization data for the CoSe$_2$/DETA hybrid and CoSe$_2$ bulk, TGA, FT-IR, elemental mapping, and stability for ultrathin CoSe$_2$ nanosheets, EXAFS curve-fitting and structural parameters of bulk CoSe$_2$ and ultrathin CoSe$_2$ nanosheets, OER parameters, and calculation details of TOF. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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REFERENCES

(18) Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Nat. Nanotechnol. 2011, 6, 147.
(39) Tiysu, H.; Huang, Y. J.; Khan, S. B.; Asiri, A. M.; Yang, P. Nano Res. 2012, 6, 47.