Plasma functionalized MoSe₂ for efficient nonenzymatic sensing of hydrogen peroxide in ultra-wide pH range

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Abstract

Enzymatic sensors have inherent problems such as the low stability and limited pH range in industrial and biomedical applications and therefore, more efficient nonenzymatic sensors are highly desirable. Herein, plasma-functionalized defective MoSe₂ is prepared and studied as a highly efficient catalyst for electrochemical sensing of H₂O₂. Experiments and theoretical computations show that the plasma-induced Se multi-vacancies and nitrogen dopants generate new active sites, expose more edge active surfaces, narrow the bandgap, and strengthen binding with the ·OH intermediate, which imparts new fundamental knowledge about the roles of defects in catalysis. The defective MoSe₂-catalyzed sensor delivers competitive performance in hydrogen peroxide detection such as a low detection limit of 12.6 nmol/L, wide operational pH range of 1–13, good long-term stability, and high selectivity. The portable sensor produced by screen printing confirms the excellent commercial potential and in
addition, the results not only reveal a novel concept to design and fabricate high-performance sensors for H₂O₂ but also provide insights into the effectiveness of surface modification of diverse catalytic materials.

**KEYWORDS**
MoSe₂, plasma functionalization, electrochemical sensors, hydrogen peroxides, portable devices
not well understood, especially for electrocatalytic sensors. In this study, MoSe₂-catalyzed sensors are plasma-treated to achieve effective detection of H₂O₂. The hydrothermally synthesized MoSe₂ nanosheets are treated by an Ar plasma to create Se vacancies and a N₂ plasma is used to introduce nitrogen atoms to the vacancies as illustrated in Scheme 1. This defective structure has several advantages including new active sites around the vacancies, higher conductivity due to the smaller bandgap, better binding with -OH, and exposure of more edge active surfaces. The effects of etching and doping on electrochemical sensing are analyzed systematically by both experiments and theoretical calculations. Owing to the unique advantages, the defective MoSe₂-catalyzed sensor delivers competitive performance as manifested by a low detection limit of 12.6 nmol/L, wide pH operational range of 1–13, fast response, long-term stability, high selectivity, and applicability to real samples such as human serum, municipal wastewater, and milk. To demonstrate the commercial suitability, a portable sensor is prepared on a screen-printed substrate, and its convenient and real-time detection of H₂O₂ is clarified. The results provide insights into the effectiveness of surface modification of 2D catalytic materials and pave the way for the development of advanced electrochemical sensors for commercial applications.

2 | RESULTS AND DISCUSSION

2.1 | Plasma etching and doping effects

The treated MoSe₂ samples are denoted MoSe₂-Ex and MoSe₂-Ex-Dy, where x and y represent the plasma etching and doping times (min), respectively. As expected, the cyclic voltammetry (CV) curves in Figure 1A shows that the untreated MoSe₂ loaded on glassy carbon electrode (GCE) exhibits some electrocatalytic activity for H₂O₂ and plasma etching and doping further boost the electrocatalytic activity significantly. The optimal etching and doping times are 40 and 10 min, respectively, since a longer processing time causes deterioration. The Nyquist plots obtained by electrochemical impedance spectroscopy (EIS) impart information about the charge transfer resistance at the catalyst/solution interface as well as electrochemical kinetics. As shown in Figure 1B, the Nyquist plots of all of the samples show a semicircular shape. The smaller semicircle diameter represents enhanced electrochemical kinetics and the calculated charge-transfer resistance is shown in Figure S6 in accordance with the CV analysis. MoSe₂-E40-D10 with the highest catalytic activity is subsequently selected to evaluate H₂O₂ detection. After gradually increasing the H₂O₂ concentration in the electrolyte, the reductive peak current density (at about −0.30 V vs. saturated calomel electrode (SCE)) increases linearly with H₂O₂ concentration as shown in Figure S7, indicating that the electrical signals generated from the conversion from H₂O₂ to H₂O can be used in accurate sensing of H₂O₂.

The MoSe₂ samples are characterized to investigate the changes after plasma etching and doping. The X-ray diffraction (XRD) patterns in Figure S8a can be indexed to the 2H-MoSe₂ phase (JPCDS 29-0914), indicating that the phase of the samples is preserved after plasma etching and doping. The enlarged view of the (103) peak in Figure S8b discloses that the peak shifts to a smaller angle after N doping, possibly due to lattice distortion and larger basal plane spacing. Defects created by the plasma processes may alter the crystal lattice which can be detected by Raman scattering spectroscopy and the results are shown in Figure 1C. The characteristic peaks of 2H-MoSe₂, corresponding to the A₁g (237.3 cm⁻¹) and E₁²g (286.3 cm⁻¹) vibration modes are observed from all the samples. The A₁g peak shifts to smaller wavenumbers with increasing etching time. According to previous reports, this kind of Raman shift resulting from plasma etching can be attributed to the generation of Se vacancies which change the lattice vibrational frequencies because of stress and strain as well as adjacent interlayer forces. After N doping, the A₁g peak shifts to the opposite direction, implying that nitrogen atoms occupy some Se vacancies to alter the crystal structure. Figure S9
indicates that the full-width at half-maximum (FWHM) of the A1g peak widens after plasma etching and doping, further demonstrating that there are more defects (Se vacancies and heteroatom N) in the plasma-treated samples.

X-ray photoelectron spectroscopy (XPS) is performed to examine the surface chemistry. The Mo 3d spectra in Figure 1D reveal that the original MoSe2 exhibits two spin-orbit peaks of Mo 3d3/2 (231.9 eV) and Mo 3d5/2 (228.8 eV) arising from Mo4+ in MoSe2. In comparison with the pristine MoSe2, the Mo6+ peaks (235.9 and 232.7 eV) appear from the etched sample MoSe2-E40 and the intensity increases after doping (MoSe2-E40-D10). Dislodgment of Se atoms (Se vacancies and N heteroatoms) by the plasmas increases the number of dangling bonds on Mo atoms, which are oxidized to Mo6+ upon exposure to air. Se atoms can be dislodged or sputtered more easily than Mo atoms by ion bombardment because of the smaller surface energy. The existence of Se vacancies is confirmed by a comparison of the surface and bulk components shown in Figure S10a and S10b. As shown in Figure 1E, the peaks of Se 3d3/2 (54.4 eV) and Se 3d5/2 (53.6 eV) are attributed to Se2− and the valence of Se does not change after the plasma treatment, indicating that the remaining Se atoms are protected by excessive Mo. It can also be observed that the peaks of Se 3d3/2 and 3d5/2 shift to higher binding energy (by 0.8 and 0.7 eV, respectively) after Se loss and the peaks broaden after N doping, which is consistent with Se vacancy formation and heteroatom doping. Figure S10c presents the high-resolution spectrum in the binding energy range of 406–390 eV. The two peaks at 394.9 and 398.8 eV correspond to Mo 3p3/2 and N 1s for the Mo-N chemical bond, respectively, suggesting that N atoms are incorporated into the crystal lattice of MoSe2-E40-D10. The N dopant concentration is calculated to be 4.14 at% based on the XPS survey spectrum. Electron spin resonance (ESR) is a more effective means to assess Se
vacancies. Figure 1F shows the fingerprint paramagnetic peaks of Mo-Se dangling bonds (Se vacancies) at \( g \approx 2 \) and \( H \approx 324 \text{ mT} \) and the smaller intensity indicates more vacancies.\(^{37} \) The peak density decreases after Ar etching and then increases after N doping, suggesting sequential generation of Se vacancies in the first step and filling of Se vacancies by N atoms in the second step, as consistent with the Raman and XPS results. The magnetization curves in Figure S11a show that the magnetic hysteresis becomes more obvious after etching and doping because the defects (Se vacancies and N heteroatoms) promote the magnetic moment in the ferromagnetic MoSe\(_2\).\(^{34,38} \) The layer number of some typical ultra-thin nanosheets was measured to be 1 or 2 using atomic force microscope (AFM), as shown in Figure S11b and S11c.

The Mott-Schottky curves are obtained to determine the semiconductor properties of the MoSe\(_2\) samples (Figure 1G). The positive slope in the curves reveals n-type characteristics and the flatter slope after etching and doping reflects enhanced electron transfer. The charge carrier density is calculated to increase by 2.07 times after etching and 5.81 times after doping according to the Mott-Schottky equation. The flat band potentials (\( E_{\text{fb}} \)) are estimated to be \(-0.48 \text{ V}, -0.66 \text{ V}, \) and \(-0.98 \text{ V} \) versus normal hydrogen electrode (NHE) for the untreated MoSe\(_2\), MoSe\(_2\)-E40, and MoSe\(_2\)-E40-D10, respectively, based on the intersecting points by the linear extension method. The negative shift of \( E_{\text{fb}} \) after plasma processing suggests a shift of the Fermi level towards the conduction band minimum (CBM), thus favoring electron transfer in MoSe\(_2\).\(^{39} \) It is well known that the CBM of n-type semiconductors is about 0.1 V more negative than \( E_{\text{fb}} \) and the estimated CBM values are \(-0.58 \text{ V}, -0.76 \text{ V}, \) and \(-1.08 \text{ V} \) versus NHE for the untreated MoSe\(_2\), MoSe\(_2\)-E40, and MoSe\(_2\)-E40-D10, respectively.\(^{40} \)

UV-vis absorption spectroscopy (Figure 1H) is carried out to identify the band energy change. The bandgap decreases from 1.27 eV (original MoSe\(_2\)) to 1.11 eV (MoSe\(_2\)-E40) after Ar etching and then to 0.87 eV (MoSe\(_2\)-E40-D10) after N doping indicative of better conductivity. Based on the above analysis, the change in the band structure after plasma processing is illustrated in Figure 1I. The down-shift in the energy band and bandgap narrowing improve the electron mobility and catalytic activity. The \( I-V \) curves acquired from the MoSe\(_2\) samples without an electrolyte by a probing system are shown in Figure S12a and the corresponding calculation results in Figure S12b disclose that the intrinsic conductivity is elevated significantly after plasma etching and doping.

The morphological evolution is monitored by scanning electron microscopy (SEM). The original MoSe\(_2\) is composed of two-dimensional nano-sheets with an average diameter of \(-60 \text{ nm} \) and smooth surface, as shown in Figure 2A. Compared with the original MoSe\(_2\), the etched MoSe\(_2\) nano-sheets have a rough surface and mutilated edges due to collisional effects of the Ar plasma, as shown in Figure 2B. However, no marked change is observed after plasma doping (Figure 2C). The morphology of MoSe\(_2\)-E40-D10 shown by the transmission electron microscopy (TEM) image (Figure 2D) confirms the SEM results, and more morphological details are shown in the top and side views in Figure S13a and S13b. Figure S13c displays the corresponding selected-area electron diffraction (SAED) pattern showing the (110), (103), (100), and (004) planes of 2H-type MoSe\(_2\).\(^{33} \) The HR-TEM image in Figure 2E indicates that the partial loss of Se atoms does not break the stability of the 2H-type hexagonal symmetry atomic configuration. To better clarify the plasma etching effect, the atomic-level images from spherical-aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) are presented in Figure 2F–H. The comparison before and after the etching clearly shows that a number of Se atoms are sputtered by plasma bombardment leaving Se vacancies. The uniformity of the N dopants in the crystal structure of MoSe\(_2\) is corroborated by the energy-dispersive spectroscopy (EDS) maps and line scans in Figure 2F and Figure S14. Figure S15 presents the specific surface area and porosity of the MoSe\(_2\) samples. The specific surface area increases after the plasma treatments, that is, 23.79 m\(^2\)/g for the original MoSe\(_2\), 40.99 m\(^2\)/g for MoSe\(_2\)-E40, and 47.06 m\(^2\)/g for MoSe\(_2\)-E40-D10. The pore size distributions reveal that the total pore volume increases but the average pore width decreases. These results reveal that more edge-active surfaces are exposed and new active sites are formed by plasma etching and doping, in line with the SEM and TEM results.

### 2.2 Electrochemical sensing properties

The steady-state amperometric test is carried out to evaluate the feasibility of the MoSe\(_2\)-E40-D10 as an electrocatalyst in \( \text{H}_2\text{O}_2 \) sensing. As shown in Figure 3A, the response current density at \(-0.30 \text{ V} \) versus SCE increases stepwise with successive addition of \( \text{H}_2\text{O}_2 \) from 0.02 to 100 mmol/L (Figure S16) and the response time is only 2 s. Even at a small \( \text{H}_2\text{O}_2 \) concentration of 0.02 mmol/L, the signal is very obvious. The current densities at other potentials are also determined. The linear calibration curves in Figure 3B and Figure S17 indicate that a larger slope (corresponding to higher sensitivity) and \( R^2 \) (corresponding to better linear relationship) can be realized at \(-0.30 \text{ V} \) versus SCE and therefore, \(-0.30 \text{ V} \) versus SCE is used for the following...
amperometric tests to assess the sensitivity and accuracy. By calculation, the MoSe₂-E40-D14 sensor has a sensitivity of 659.80 µA/(mM cm²) in the low H₂O₂ concentration range (0.02–0.2 mmol/L) and 614.98 µA/(mM cm²) in the high concentration range (0.2–100 mmol/L) in addition to a detection limit of 12.6 nmol/L. For comparison, Figure S18 shows that the sensor prepared with the original MoSe₂ displays smaller sensitivity of 195.98 µA/(mM cm²) at the low H₂O₂ concentration and 213.70 µA/(mM cm²) at the high H₂O₂ concentration besides a higher detection limit of 55.1 nmol/L.

The CV curves acquired at different scanning rates are shown in Figure S19 and the current density increases linearly with the square root of the scanning rate, demonstrating that reduction of H₂O₂ is a diffusion-controlled process. According to the Randles-Sevcik equation, the diffusion coefficient is calculated as 2.41 × 10⁻⁶ cm²/s, which is consistent with that in the literature. In practical applications, the sensor sometimes needs to work under acidic or alkaline conditions. Therefore, amperometric detection of H₂O₂ is evaluated in 0.1 mol/L KOH and 0.05 mol/L H₂SO₄ and the results are displayed in Figure S20. Based on the calibration curves, a well-defined linear relationship can be observed from both the acidic medium (Figure 3C) and alkaline media (Figure 3D), indicating that the MoSe₂-E40-D10 sensor can be operated in a wide pH range. By comparing the slopes of the calibration curves in Figure 3B–D, the sensor has a higher sensitivity at a lower pH.

The anti-interference performance is critical to sensors in practical applications. The H₂O₂ cathodic reaction in this study is an ideal approach to develop reliable electrochemical sensors immune to interferences arising from common oxidizable endogenous/exogenous species. Common interferences in conventional detection methods such as titration, colorimetric, fluorescence, spectrophotometry, chemiluminescence, and chromatography can be avoided by designing a reasonable electrochemical sensing window. The H₂O₂ selectivity of the MoSe₂-E40-D10 sensor is investigated by amperometric tests with H₂O₂ and common interfering agents including NaCl, KCl, methanol (MeOH), ethanol (ET), glucose (GLU), sucrose (SUC), ascorbic acid (ASC), acetaminophen (APAP), uric acid (UA), and dopamine (DA).
and the results are shown in Figure 3E. Even though the concentration of the interfering agents is five times that of H$_2$O$_2$, the interfering agents have no influence on the signal of H$_2$O$_2$ corroborating the high anti-interference capability of the MoSe$_2$-E40-D10 sensor. This can be attributed to the fact that there is no overlap between the interferent sensing window and the H$_2$O$_2$ sensing window. The electrochemical sensing of H$_2$O$_2$ on MoSe$_2$-E40-D10 relies on the cathodic reductive reaction taking place at a negative potential of $-0.30$ V versus SCE, while the above interferents produce electrical signals at much more anodic potentials such as $+0.58$ V versus SCE for MeOH, $+0.48$ V versus SCE for ET, $+0.30$ V versus SCE for GLU, $+0.56$ V versus SCE for SUC, $+0.05$ V versus SCE for ASC, $+0.44$ V versus SCE for APAP, $+0.42$ V versus SCE for UA, and $+0.25$ V versus SCE for DA. NaCl and KCl cannot react electrochemically on the electrocatalyst surface to produce a current signal. Even though the concentration of the interfering agents is five times higher than H$_2$O$_2$, the extremely accurate sensing current signal of H$_2$O$_2$ proves that there is no electrochemical adsorption of such interferents on the catalyst surface, which further demonstrates the reliability of this novel sensor in the face of complex systems. The most concerning interference of oxygen reduction reaction (ORR) can also be eliminated in this study since ORR is severely suppressed on the electrocatalyst surface, as proved in Figures 3E and S21a. It is revealed that the cathodic reduction of H$_2$O$_2$ commences at $-0.30$ V versus SCE on the MoSe$_2$-E40-D10 catalyst, which is obviously more positive than the onset potential of the ORR at $-0.48$ V versus SCE, ensuring the ORR inertness of the MoSe$_2$-E40-D10 sensor. The anti-interference mechanism of the novel MoSe$_2$-E40-D10 sensor is summarized in Figure S21b for clarity. To further evaluate the long-term reliability and stability, three sensors are prepared by the same way and stored under ambient conditions for one month before assessing the performance. The signal stability and relative standard deviation (RSD) are tested every 5 days as shown in Figure 3F. The variation and RSD are $3.37\%$ and $95.32\%$ after storage for 1 month thus confirming the stability. The basal 2D structure of MoSe$_2$ didn’t be destroyed in the plasma functionalization process to ensure long-term reliability and stability. For comparison, the H$_2$O$_2$ sensing properties of recently reported nonenzymatic catalysts are summarized in Table S2 and the MoSe$_2$-E40-D10 sensor shows outstanding characteristics and extremely wide pH range. To further evaluate the structural and chemical stability of the MoSe$_2$-E40-D10 catalyst, SEM, TEM, XRD, Raman scattering, and XPS are performed after the long-term stability tests. As shown in Figure S22, the morphology, phase, surface electronic state, and chemical state show very little variation. Especially, the ESR spectra in

**FIGURE 3** (A) Amperometric response (at $-0.30$ V vs. SCE) of MoSe$_2$-E40-D10 to H$_2$O$_2$ in 0.4 mol/L phosphate buffer saline (PBS). Calibration plots of the steady-state current density versus different H$_2$O$_2$ concentrations for MoSe$_2$-E40-D10 in (B) 0.4 mol/L PBS (pH = 7.2), (C) 0.05 mol/L H$_2$SO$_4$ (pH = 1) and (D) 0.1 mol/L KOH (pH = 13), respectively. (E) Amperometric response (at $-0.30$ V vs. SCE) to 0.5 mmol/L interfering agents and 0.1 mmol/L H$_2$O$_2$, and (F) long-term stability and repeatability.
Figure S22e and high-resolution XPS spectra of N 1s in Figure S22h verify the stability of Se vacancies and heteroatomic N doping after continuous monitoring of H2O2.

The electronic structure is investigated by density functional theory (DFT) calculation and the catalytic activity of the active sites in the basal plane is determined. The calculated bandgap (1.446 eV) of the pristine MoSe2 in Figure S23a indicates that it is a typical semiconductor in agreement with previous reports.20 After introduction of Se vacancies, several new states emerge and the bandgap narrows, as shown in Figure S23b−S23d. After N doping of Se vacancies, the bandgap decreases further, as shown in Figures S23e, S25f, and S25g. This phenomenon is in accordance with our experimental results and that in the literature.31 Generally, the bandgap of MoSe2 decreases with increasing Se vacancy concentration and benefits the catalytic performance.29 Moreover, the electron local function (ELF) plots show that the charges are distributed uniformly on the basal plane and therefore, charge transfer on the basal plane is promoted.34

As shown in Figure 4A,B, a negative adsorption energy indicates the H2O2 molecule could be absorbed on the surface of pristine MoSe2 or MoSe2 with DDN,2. The doping of an N atom could greatly enhance the adsorption strength of H2O2. Then, we explore the catalysis activation of the surface of pristine MoSe2 and MoSe with DDN,2. According to the aforementioned decomposition mechanism, the free energy diagram along with the H2O2 reduction process is plotted in Figure 4C. Obviously, except for the first step of H2O2 adsorption, the other reaction steps are exothermic and spontaneous. Hence, the adsorption of H2O2 is identified as the rate-determining step. The calculated limiting potentials are −0.22 and −0.04 V for the surface of pristine MoSe2 and MoSe with DDN,2, respectively, which indicate that both doping and vacancy could improve the catalysis activation from H2O2 to H2O.

2.3  Applicability to real samples and device assembly

Real samples of human serum, municipal wastewater, and commercial milk are employed to assess the commercial feasibility of the MoSe2-E40-D10 sensor for H2O2 detection. Figure 5A−C shows the amperometric responses to H2O2 in the samples premixed with human serum, wastewater, and milk and the high sensitivity is retained. Table S3 shows recovery in the range of 100.9%−102.0% for human serum, 99.0%−101.5% for wastewater, and 98.0%−101.4% for milk, which rival the accuracy of UV-Vis spectroscopy. Furthermore, the RSD values are all below 2.46% confirming the large commercial potential.

To conduct more convenient detection of H2O2, a screen-printed electrode (SPE) comprising the MoSe2-E40-D10 catalyst is fabricated as a portable and disposable sensor as shown in Figure S24. In the detection process, the portable SPE sensor requires a significantly smaller amount of solution of only 50 μL than conventional UV-Vis spectroscopy which requires a liquid sample of 3 mL, as demonstrated in Figure S25. The finite element method (FEM) simulation results in Figure S26 show that the diffusion layer thickness of H2O2 (~500 μm) with a bulk concentration of 20 mmol/L is much less than the 50 μL−liquid film thickness (~1600 μm) on the SPE sensor, theoretically indicating that 50 μL analyte is sufficient for H2O2 detection of at least 20 mmol/L for the portable SPE sensor. The amperometric response curves and corresponding calibration plots are exhibited in Figure 5D,E, respectively. According to the calibration plots, the sensitivity is calculated to be 16.22 μA/(mm·cm2) at low H2O2 concentrations (0.02−0.2 mmol/L) and 15.68 μA/(mm·cm2) at high H2O2 concentrations (0.2−20 mmol/L). The detection limit is 462.4 nmol/L. The portable SPE sensor also has excellent anti-interference capability, long-term stability, repeatability, and commercial potential, as shown in Figures S27, S28 and Table S4. In fact, continuous monitoring of H2O2 can be accomplished by immersing the SPE sensor into the sample solution.
sensor in the fluid as shown in Figure 5F and the continuous amperometric results are presented in Figure S29.

3 | CONCLUSION

2D MoSe₂ is processed by plasma etching and doping and used as a highly efficient catalyst for high-performance electrochemical sensing of H₂O₂. This plasma-modified defective structure shows excellent electrocatalytic activity in H₂O₂ detection. The Se vacancies and N dopants produce new active sites, expose more edge active surfaces, decrease the bandgap, and strengthen binding with ·OH. The MoSe₂-catalyzed sensor delivers competitive performance with a low detection limit of 12.6 nmol/L, rapid response time of 2 s, wide concentration range of 20 μmol/L – 100 mmol/L, wide pH range of 1–13, long-term stability, and high selectivity. The commercial potential is demonstrated with real samples such as human serum, municipal wastewater, and milk. DFT calculation confirms increased electron transfer and enhanced adsorption of ·OH on the MoSe₂ surface in the presence of Se vacancies and N dopants. The portable SPE sensor based on the novel MoSe₂ catalyst shows the capability of convenient detection and continuous monitoring of H₂O₂. The research not only reveals the design principle of a practical and high-performance H₂O₂ sensor, but also provides insights into plasma surface modification of catalytic materials.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the supplementary material of this article.

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