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REVIEW ARTICLE

Recent advances in molybdenum disulfide-based electrode materials for electroanalytical applications

A. T. Ezhil Vilian[1] · Bose Dinesh[2] · Sung-Min Kang[3] · Uma Maheswari Krishnan[2] · Yun Suk Huh[3] · Young-Kyu Han[1]

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Abstract

The primary objective of this review article is to summarize the development and structural diversity of 2D/3D molybdenum disulfide (MoS_2) based modified electrodes for electrochemical sensors and biosensor applications. Hydrothermal, mechanical, and ultrasonic techniques and solution-based exfoliation have been used to synthesize graphene-like 2D MoS_2 layers. The unique physicochemical properties of MoS_2 and its nanocomposites, including high mechanical strength, high carrier transport, large surface area, excellent electrical conductivity, and rapid electron transport rate, render them useful as efficient transducers in various electrochemical applications. The present review summarizes 2D/3D MoS_2-based nanomaterials as an electrochemical platform for the detection and analysis of various biomolecules (e.g., neurotransmitters, NADH, glucose, antibiotics, DNA, proteins, and bacteria) and hazardous chemicals (e.g., heavy metal ions, organic compounds, and pesticides). The substantial improvements that have been achieved in the performance of enzyme-based amperometry, chemiluminescence, and nucleic acid sensors incorporating MoS_2-based chemically modified electrodes are also addressed. We also summarize key sensor parameters such as limits of detection (LODs), sensitivity, selectivity, response time, and durability, as well as real applications of the sensing systems in the environmental, pharmaceutical, chemical, industrial, and food analysis fields. Finally, the remaining challenges in designing MoS_2 nanostructures suitable for electroanalytical applications are outlined.

Keywords Molybdenum disulphide (MoS_2) · Electrochemical biosensors · Electrochemical detection · Neurotransmitter · Electrochemiluminescence

Introduction

Electrochemical sensors have made significant contributions to a wide range of methods which find applications in chemical, biomedical, biological, and agricultural fields to detect harmful molecules [1, 2]. Metal, glass, and carbon substrates can be modified using nanostructured materials to obtain chemically modified transducers for electrochemical and optical detection based on which portable electronic devices and electrochemical sensors have been fabricated. The electroactivity of electrode materials can be improved by enhancing their surface area, texture, functionality, and conductivity. Electrodes based on functional nanomaterials thus play a vital role in biosensor applications because of their effective surface area, diffusion length, electron transport properties, and nanoconfinement ability [3]. An inexpensive, easy-to-operate, economical, sensitive, and portable electrochemical sensors have been developed based on the recent advancement in the area of nanotechnology for the sensitive and selective detection of various analytes. The electrochemical sensors developed using chemically modified MoS_2-

✉ Uma Maheswari Krishnan
umakrishnan@sastra.edu

✉ Yun Suk Huh
yunsuk.huh@inha.ac.kr

✉ Young-Kyu Han
ykenergy@dongguk.edu

[1] Department of Energy and Materials Engineering, Dongguk University-Seoul, Seoul 04620, Republic of Korea

[2] Center for Nanotechnology & Advanced Biomaterials (CeNTAB), School of Chemical and Biotechnology, SASTRA Deemed University, Thanjavur, Tamil Nadu 613 401, India

[3] Department of Biological Engineering, Biohybrid Systems Research Center (BSRC), Inha University, Incheon 22212, Republic of Korea

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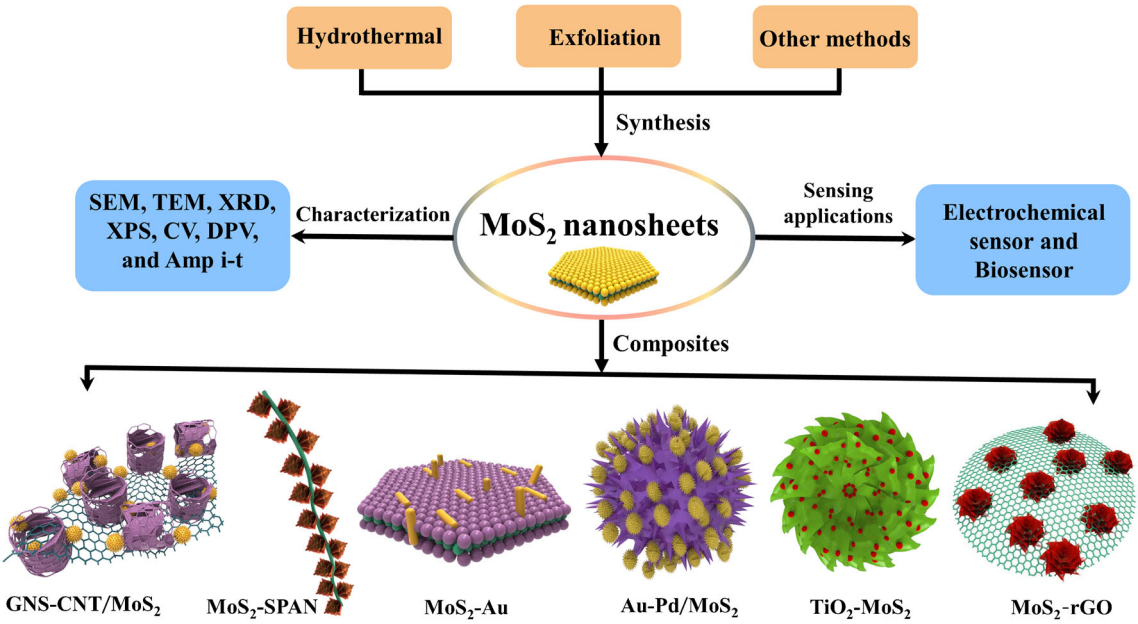
based electrodes offer the ability to detect a wide range of chemical or biological elements [4].

Research into two-dimensional (2D) nanomaterials took off after the discovery of graphene [5]. Since then, various 2D nanostructured nanomaterials including graphitic carbon nitride, hexagonal boron nitride, fluorographene, and graphene oxide, semiconductor- ($MoTe_2$, WTe_2, ZrS_2, $ZrSe_2$) and metal dichalcogenide- ($NbSe_2$, NbS_2, TaS_2, TiS_2, $NiSe_2$) layered semiconductors (GaSe, GaTe, InSe, Bi_2Se_3), metals, metal oxides, metal hydroxides, black phosphoranes, metal organic frameworks, and polymers have been developed to maximize their beneficial chemical and physical properties, such as having a large surface area, high chemical stability, high conductivity, and excellent mechanical strength, in addition to being highly functionalizable [6, 7]. Due to structures that differ from that of bulk materials, thus leading to unique crystal, electron, and optical properties, 2D nanomaterials have attracted a great deal of attention for use in various technical applications in a broad range of fields, including nanotechnology, materials science, analytical science, and biomedicine [8].

MoS_2, a member of the transition-metal dichalcogenide (TMDC) family, is a typically layered transition metal sulfide with a graphene-like 2D structure [9]. MoS_2 has a hexagonal crystal lattice, with the Mo layer sandwiched between two S layers (S-Mo-S) laminated by weak van der Waals interactions. Due to its intrinsic indirect bandgap (1.3 eV), MoS_2 is regarded as a promising next-generation 2D material [10]. The 2D nanostructure and the band gap of MoS_2 have led it to be widely used as an active material in a variety of applications, including energy storage, solar cells, catalysis, sensing, and electronic devices. Experimental and theoretical studies have proven that the catalytic activity of MoS_2 is due to its metallic edges, while the semiconducting basal plane is catalytically inactive [11]. Because there are few-layer MoS_2 nanosheets, the exposed edges can be maximized, significantly improving catalyst performance [12, 13].

The large-scale and affordable synthesis of pure MoS_2 nanosheets is a prerequisite for commercial applications. A great deal of effort has thus been spent on producing various MoS_2 nanostructures using chemical vapor deposition, direct solvothermal and hydrothermal synthesis, and mechanical exfoliation [14, 15]. It has recently been reported that MoS_2 nanosheets of different sizes can be quickly prepared from bulk MoS_2 using direct exfoliation in an organic solvent with sonication [16]. This solvent exfoliation method is effective due to its simple and convenient synthesis process [17, 18]. Also, most synthesis methods involve the decomposition of the van der Waals forces between the MoS_2 layers using ion−/molecule-intercalation, side functionalization, and sonication in an aqueous surfactant solution. The as-synthesized MoS_2 nano- and micromaterials with various shapes, including fullerene-like, spherical, flower-shaped, linear, plate-like, rod, and tubular can be fabricated [19]. Because the electronic conductivity of MoS_2 is still lower than that of graphene, few studies have evaluated MoS_2 as an electrode material in a sensor [20]. To improve the conductivity of MoS_2, many processes have been proposed that combine MoS_2 with other conductive nanomaterials and functional building blocks (such as noble metal nanoparticles, metal oxides, and organic compounds) on the surface of 2D nanomaterials to form new nanocomposites (Scheme 1). Similar to the advantages of 2D building blocks design, constructing 3D structures-based carbon materials and MoS_2-like TMDCs are of great significance. Recently, metal chalcogenides like MoS_2 were identified as efficient 2D building blocks for making the 3D textures [21]. This is due to the weak van der Waals forces adhering between the layered structures. The interlayer characteristics facilitate the accommodation of other conductive additives, resulting in abundant active sites, conductive bones for charge separation, effective transportation of electrons and deliver complimentary mechanical and electrochemical properties [22]. Superior conductivity and high surface area of interconnected 3D material networks, together with the excellent electrical contact between MoS_2 and graphene or other carbon materials would avoid the shortcomings of 2D form, which is important for the effective transportation of electrons between the electrode and a particular analyte. These studies have also demonstrated the superior performance of nanocomposites as electrode modifiers compared to TMDC-modified surfaces. The synergistic effect allows these nanocomposites to function as redox probes and enzymes and provides a new approach to the construction of biosensors [23].

In addition, MoS_2 nanocomposites with carbon-based support materials such as graphene (oxides), carbon nanotubes, carbon black, and noble metal nanocrystals (such as Au, Ag, Pt, and Pd NCs) have been reported to produce catalysts with excellent conductivity, making them more suitable for use in supercapacitors, batteries, sensors, and biosensors [24, 25]. MoS_2-based electrochemical sensors and biosensors have the potential to be powerful analytical probes in analytical and biomedical fields due to their environmentally friendly, sensitive, and selective nature [26]. The combination of functional nanomaterials with MoS_2 nanosheets has led to the fabrication of microelectrodes which can be used in the detection of heavy metals, the anions and cations of inorganic and organic compounds, poisonous gases, pesticides, antibiotics, bacteria, blood,



Scheme 1 Schematic representations for the preparation of MoS_2 based nanocomposites

metabolites glucose, double-stranded DNA, and neurotransmitters, many of which can cause health and environmental issues (Scheme 2). Several chemically modified MoS_2 electrodes have been developed with nano- or femtomolar detection limits or even lower due to the abundant active sites present on the electrode surface, making them suitable for many real-time applications [27].

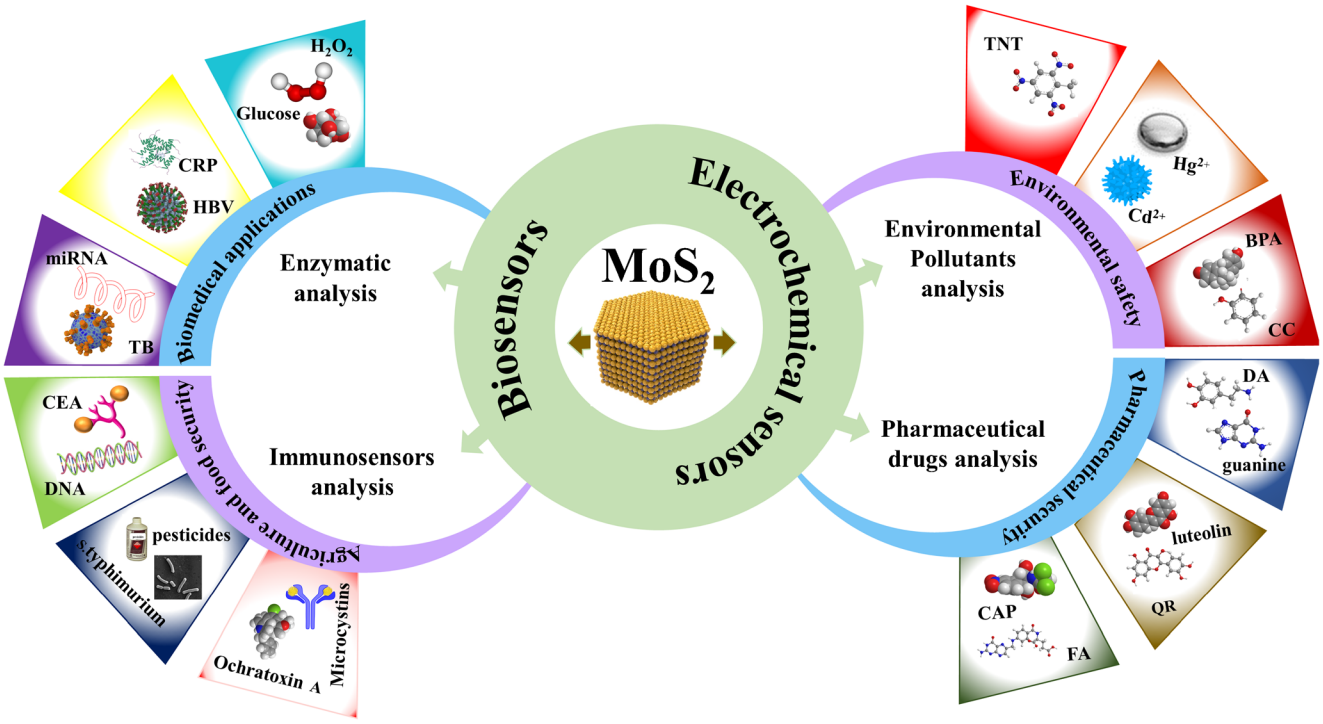
In this review, we highlight the recent advances in the environmental and human healthcare related monitoring of biomarkers using electrochemical sensors consisting of chemically modified MoS_2 electrodes. We primarily focus on the development of electrochemical sensors technology using MoS_2 nanostructures to summarize various strategies used in the detection of heavy ions, organic compounds, pesticides, antibiotics, and bacteria.

Nanostructured MoS_2 and MoS_2-based composites for multiple sensing applications

On the other hand, MoS_2 nanocomposites-based electrochemical transducers are classified in to four different types such as sensors, biosensors, immunosensors, and electrochemiluminescence sensors and their research highlights are investigated and presented in a detailed way. The unique electrical property of MoS_2 makes it a promising candidate for an electrode material, and the excellent conductivity, catalytic activity, biocompatibility, and fluorescence quenching property can be used for the production of various sensing analytical devices for real-time measurements. The classification of various MoS_2 nanosheets and MoS_2-based sensors and their electroanalytical sensing applications towards different analytes are given as flowchart (Fig. 1) and their sensing mechanisms have been explained in the respective sections. Justification pertaining to the selectivity issues, limitations based on state-of-the art methodologies, observations of electrochemical assays and earlier detection of environmental and clinical procedures have also been included.

Electrochemical sensors on MoS_2 based materials

Electrochemical sensors have been widely involved in the past few decades for clinical diagnosis, environmental monitoring, and food safety applications. Varieties of nanomaterials like metal NPs, CNTs, graphene and polymers have been widely used in this area to achieve excellent analytical parameters such as fast response, high selectivity, and low detection limit. To improve the sensing performance of electrochemical sensors, MoS_2 nanostructures are conjugated with other dimensional nanomaterials like carbon materials, noble metals, metal oxides, and polymers. MoS_2 could offer facile electron transfer behavior and provides a specific action to anchor the metal NPs, enzymes, antigens, to enhance the electronic activity. Enzyme-free electrochemical systems have been widely explored for the detection of electroactive benchmark systems like hydrogen



Scheme 2 Schematic illustration of the electrochemical sensing and biosensing applications of MoS_2-based detection devices

peroxide, glucose, and dopamine. This section has been divided into several subcategories according to the MoS_2 sensing platforms. The subsections illustrate the advancements in sensor fabrication along with the specific role of MoS_2 nanostructures in various areas of health, medicine, food, and environment (Fig. 1.)

Electrochemical detection of environmental pollutants on MoS_2 based modifiers

Detection of heavy metal ions Hg(II), Cd(II) and Cr(VI) are a highly toxic pollutant in aquatic and terrestrial environments. Also, it is a common wastewater contaminant produced in

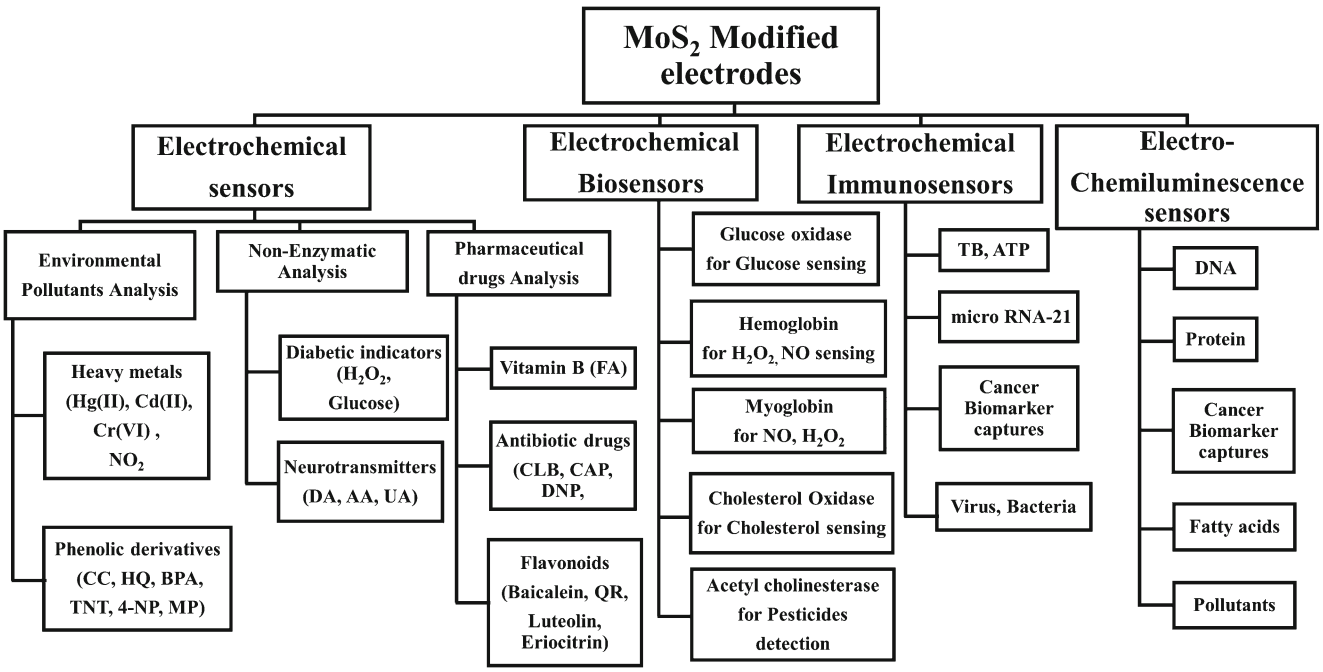


Fig. 1 Flowchart representing the applications of MoS_2-based modified electrodes towards their sensors and biosensors applications

many industrial processes such as electroplating, leather tanning, and painting; it has been banned in several countries due to its carcinogenicity.

A glassy carbon electrode (GCE) modified with a Cu_7S_4-Au-decorated MoS_2 monolayer nanocomposite that exhibited high sensitivity with a LOD value of 190 nM and improved selectivity. This might be due to the strong electrocatalytic reduction behavior arising from the abundant active edge sites of the MoS_2 and Au monolayer domains, thus improving electrocatalytic performance and demonstrating a good affinity for Hg(II), which is better than that of other nanostructures that include Cu_7S_4-Au, Cu_7S_4@S-MoS_2 and Cu_7S_4-Au@M-MoS_2 [28]. In the following study, MoS_2 nanosheets on GCEs as a sensing platform for Cd^{2+} detection in tap water from laboratory water pipes based on SWASV measurements. Their electrochemical sensor exhibited a relatively high sensitivity to Cd^{2+} detection and lower cytotoxicity for MCF-7 cells. Density functional theory (DFT) calculations and spectroscopic measurements were performed to confirm the functionalization of the electrode surface and the selective spectroscopic detection of Cd^{2+}. Their electrochemical sensor was also characterized by wide concentration ranges, low detection limits, high sensitivity, and high selectivity for Cd^{2+} [29].

An amperometric sensor for the detection of Cr(VI) was fabricated based on MoS_2 nanoflakes coated with Fe_3O_4 nanospheres on GCEs using the hydrothermal method. FTIR spectroscopy and HRTEM were used to characterize the presence of Fe–O and Mo–O vibrations and to establish whether the Fe_3O_4 nanospheres had been well dispersed on the MoS_2 nanoflakes (with a diameter of 20 to 30 nm). The Fe_3O_4/MoS_2-based sensor exhibited a significantly better amperometric response for the sensing of Cr(VI) over a wide linear range of 0.5–49 μM ($R^2 = 0.992$), 49–148 μM ($R^2 = 0.992$), and 148–328 μM ($R^2 = 0.995$), with sensitivity values of 2.294, 1.550, and 2.976 mA μM^{-1} cm^{-2}, respectively. This sensitivity and detection limit performance are comparable to other reported modified electrodes based on flower-like Fe_2O_3@MoS_2 nanocomposites [30].

Detection of Nitrite and Sulfide Nitrites are commonly found in the environment, food, and physiological systems because of their widespread use as additives and inhibitors of decay in some foods. Nitrites are potentially toxic and can form the carcinogenic nitrosamine. Also, sulphides are a serious pollutant of aquatic environments because of their toxic effects on many organisms. As a result, the detection of nitrites and sulfide is necessary to protect the environment and public health.

Wang et al. synthesized flower-like Fe_2O_3@MoS_2 composites to modify GCEs and detect nitrites in drinking and river water. The Fe_2O_3@MoS_2 exhibited a petal-like morphology with a diameter of approximately 80–100 nm. Based on CV and linear sweep voltammetry (LSV) analysis, the Fe_2O_3@MoS_2 produced excellent electrocatalytic activity in terms of the oxidation of nitrites in 0.1 M PBS (pH 4) compared to Fe_2O_3 and GCEs modified with MoS_2. The overall electrocatalytic oxidation of nitrite at Fe_2O_3@MoS_2 nanocomposite modified GC electrode was explained as follows [31]:

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \quad (1)$$

A perovskite-type $PrFeO_3$ and graphene-like MoS_2 sheets were also made using hydrothermal and sol-gel methods. The synergistic effect between $PrFeO_3$ and MoS_2 was sensitive to the electrochemical oxidation of NO_2^- because MoS_2 that has a graphene-like structure can provide adsorption sites for $PrFeO_3$ bonding. Because the large surface area of the MoS_2 and $PrFeO_3$ generated excellent electrical properties and nanoparticle confinement [32].PANI-MoS_2 nanosheets were prepared using a combination of the hydrothermal method and the in situ polymerization of an aniline monomer in the presence of MoS_2 [33]. Another related work on a composite consisting of 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) oxidized straw cellulose and MoS_2 produced with a one-step hydrothermal method. MoS_2-, TOSC-, and TOSC-MoS_2-modified electrodes were compared, the PANI-MoS_2 nanocomposite demonstrating the best electrochemical properties for the oxidation of nitrites [34]. A nanocomposite consisting of electrodeposited of Au NPs onto the surface of a multiwall carbon nanotube (MWCNT)-MoS_2 nanocomposite. In comparison with bare GCEs and GCEs modified with MoS_2 and MoS_2-MWCNTs, the MoS_2-MWCNTs-Au-modified GCE exhibited strong electrocatalytic activity in the presence of nitrites in both drinking water and pond water samples, demonstrating high sensitivity, excellent selectivity, and acceptable accuracy. This result may be due to the high specific surface area of the MWCNT and the abundant active edge sites of the MoS_2, with the Au nanoparticles allowing excellent conductivity when deposited on the surface of the GCE [35]. Likewise, Ghanei-Motlagh et al. conducted experiments on electrochemical sensors based on silver/halloysite nanotube/MoS_2 nanocomposite-modified carbon paste electrodes (CPEs) for the effective sensing of nitrites in tap water and aqueduct water [36].

A sulfide sensor based on a hybrid of metallic cobalt in MWCNT/MoS_2-modified GCE was constructed with a Nafion suspension adhesive and used to detect sulfide in pretreated fruit samples. A bulk MoS_2 solution was exfoliated into monolayer paramagnetic MoS_2 that was coated with carbon nanotubes (CNTs) using the magnetic traction force between the MoS_2 and the Co particles in the CNTs. The

Co@CNT/MoS_2-modified electrodes had excellent electrochemical activity in the presence of sulfides in buffer solutions. Amperometric sulfide sensing results show a better sensing activity comparable to that of other techniques like CV, cathodic stripping analysis, and LSV methods. They found that the electrostatic repulsion between the negatively charged Nafion and S^{2-} led to a response time for the detection of S^{2-} of <2 s, indicating rapid electron transport on the modified electrode surface [37].

Detection of Phenolic compounds Catechol (1, 2-dihydroxybenzene; CC) has a number of industrial uses and is a highly toxic environmental contaminant. Su and colleagues reported satisfactory results for the detection of CC in water samples using noble metal nanoparticles (Pt, Au, and Au@Pt) on graphene-like MoS_2 nanoplates under microwave-assisted hydrothermal and oil bath conditions. Compared with GCE modified MoS_2, Au-NP-MoS_2, and Pt-NP- MoS_2, electrode sensors based on MoS_2 modified with Au@Pt core-shell nanoparticles demonstrated a wide linear range, high sensitivity, and good stability, and the synergistic effect of the π-π interactions led to a large active surface area and a high accumulation efficiency [38]. Amperometric sensing of hydroquinone in tap water using a GCE modified with a composite consisting of graphene and MoS_2 prepared using a solvothermal method without any additives. The graphene-MoS_2/GCE, operating at a working voltage of 0.10 V (vs. Ag/AgCl), exhibited excellent catalytic activity in the presence of hydroquinone, with a linear response in the 0.5 to 300 μM concentration range and a 37 nM detection limit [39]. Whereas, detection of hydroquinone using layered MoS_2/RGO nanocomposites which were also synthesized using the solvothermal method. The modified electrode exhibited good stability, selectivity, and reproducibility for hydroquinone detection [40].

Bisphenol A (BPA) is used in many industrial products such as plastic water bottles, sports equipment, and food and beverages containers. BPA is associated with endocrine disorders, changes in the behavior and nervous system of children, a reduction in sperm quality, and an increase in cancer risk, as well as generally being harmful to wildlife. A new strategy for the selective detection of BPA using a GCE modified with a nanocomposite consisting of thin-layered MoS_2 and self-doped polyaniline (SPAN) produced using ultrasonic exfoliation (Fig. 2). The better sensing activity is due to the high anion exchange and adsorption capacity of MoS_2-SPAN [41]. MoS_2-IL-Au/Ag nanorods composites were prepared under hydrothermal and ultrasonic conditions, leading to the effective electrochemical sensing of 2,4-dichlorophenol (2,4-DCP) in both real water and lab samples. Environmental Protection Agency has pointed out 2,4-DCP is a pollutant and threshold concentration in water is 0.5 ng mL^{-1}. IL improved the dispersion of MoS_2, creating a strong electrostatic–chemical interaction between these two constituents. The MoS_2-IL-Au/Ag NRs had a large surface area, rich electroactive sites, and good conductivity [42]. Trinitrotoluene (TNT) is the most widely used explosive organic

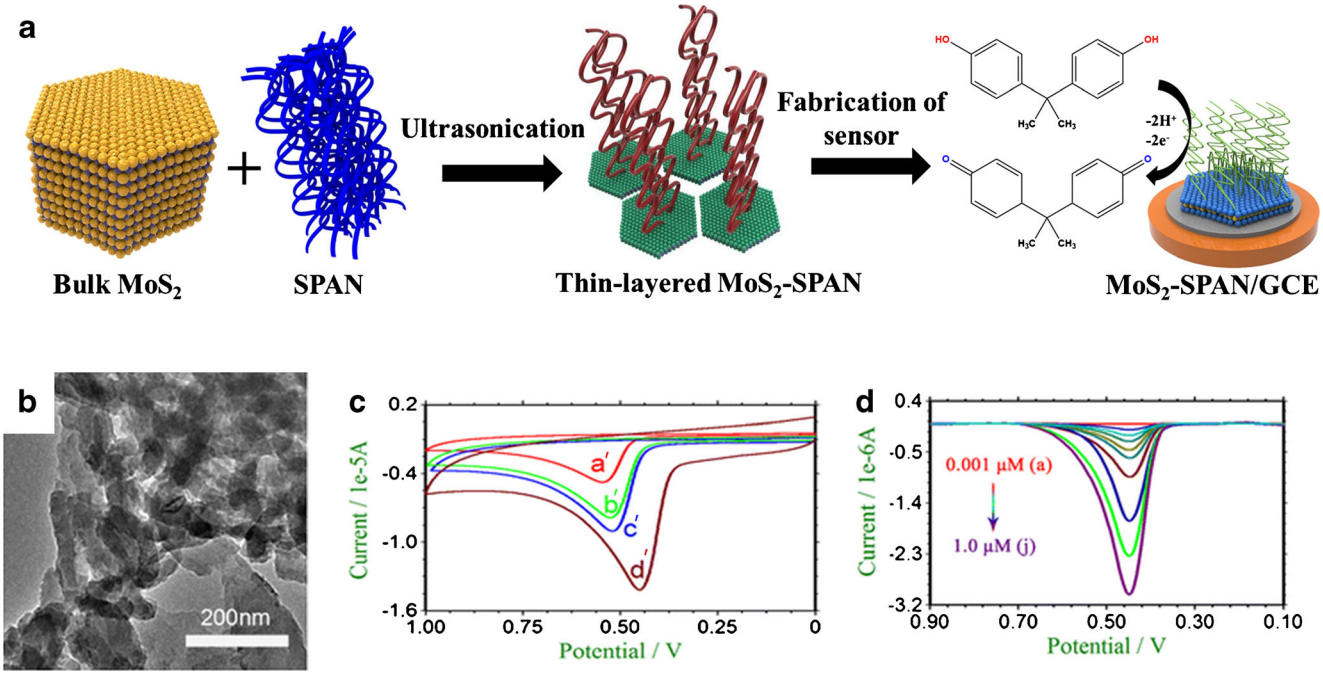


Fig. 2 **a** Schematic representations of the non-enzymatic sensor-based MoS_2-SPAN/GCE for the detection of BPA. **b** TEM images of MoS_2-SPAN, **c** DPVs of 1.0×10^{-4} M BPA at a′: GCE, b′: SPAN/GCE, c′: MoS_2/GCE and d′: MoS_2-SPAN/GCE, **d** DPV curves are corresponding to BPA with different concentrations at the MoS_2-SPAN/GCE. Reproduced from Yang et al. (2015) with permission from Springer [41]

compound in military and terrorist activities and has significant adverse effects on the environment and human health. In this work, the authors synthesized a GCE modified with a MoS_2-poly (m-aminobenzenesulfonic acid, PABSA) nanocomposite using a simple electropolymerization process to obtain excellent sensing performance for TNT. Due to the strong π-π interaction between the aromatic rings of TNT and MoS_2-PABSA, the modified electrodes based on MoS_2-PABSA exhibited excellent absorption and catalytic performance [43]. Govindasamy et al. prepared a nanocomposite composed of layered MoS_2 and graphene for the amperometric detection of methyl parathion (MP) in samples of fruits and vegetables. MP is the kind of organophosphorus pesticides owing to their bioaccumulation and toxicity disrupt the nervous system leads to several health issues. They produced a robust electrochemical MP sensor with a low detection limit, good selectivity, excellent reproducibility, and high stability [44].

In another report, ultrasonic treatment of N-N dimethylformamide and gradient centrifugation was used to prepare modified GCEs with ultrasmall MoS_2 nanostructures fabricated for the detection of m-nitrophenol in water samples. This compound has toxic effects on humans, animals, and plants, and also affects the taste and odor of drinking water at very low concentrations. SEM and TEM confirmed the morphology of the exfoliated MoS_2 samples at different centrifugal speeds. The surface of the modified MoS_2 nanosheet electrode reveals an excellent selective sensor in the presence of common interference and a rapid response due to the large proportion of edge sites [45]. Similarly, the MoS_2-based composite fabricated by Jeyapragasam et al. was used in a non-enzymatic electrochemical 4-nitrophenol (4-NP) sensor and exhibited enhanced stability and a good recovery percentage [46].

Non-enzymatic activity of MoS_2 electrode materials towards H_2O_2 and glucose detection

In daily life, diabetes is a high-risk chronic disease that can lead to heart disease, kidney failure, and blindness and is a global health problem that affects 150 million people worldwide. Monitoring blood glucose levels is important to the diagnosis, treatment, and control of this disease. This can be achieved through the detection of H_2O_2, which is a side product of glucose oxidation in the presence of glucose oxidase and oxygen. Enzymatic sensors have been investigated for this purpose, but they tend to be too costly and exhibit low stability. To overcome these problems, non-enzymatic sensors have been developed for the sensing of H_2O_2 and subsequent monitoring of glucose. Zhai et al. developed a highly sensitive non-enzymatic glucose sensor based solvothermal method to generate a suitably on microflower-like MoS_2 prepared using a hydrothermal technique with CTAB as a surfactant. The nanocomposite displayed good crystallinity with the nanosheets exhibiting a petal-like structure, leading to synergistic electrocatalytic detection performance and high sensitivity [47]. For more clarity, this section has been categorized by materials like metal nanoparticles, metal oxide, nanocarbons.

Electrocatalytic performance of Nobel metal nanoparticles decorated MoS_2 modifiers The large specific surface area, excellent conductivity, and excellent biocompatibility of the metallic and bimetallic nanoparticles decorated MoS_2 nanocomposite led to the excellent catalytic performance and low overpotential for H_2O_2 reduction and glucose oxidations in both neutral as well as alkaline condition.

An amperometric H_2O_2 sensor was fabricated on AgNP-functionalized, flower-like MoS_2 on a modified GCE, which was prepared using hydrothermal synthesis. The hybrid AgNP/MoS_2 nanostructure prepared for the modified GCE was much more responsive to the reduction of H_2O_2 than was the AgNP/GCE or MoS_2/GCE [48]. An H_2O_2 sensor was constructed on MoS_2 and PtNP layers, fabricated by electrochemically depositing Au NPs at the electrode surface. MoS_2 was used not only as the electrode's surface but also as a carrier matrix for effectively dispersing the PtNPs to increase the efficiency of the catalyst [49]. Similarly, Lin et al. developed a sensitive H_2O_2 sensor that employed MoS_2 nanoflowers coated with PtNPs on a GCE, synthesized using a hydrothermal method [50]. This sensor also demonstrated high sensitivity, excellent repeatability, reusability, and long-term stability.

Electrochemical reduction of H_2O_2 in a neutral solution and glucose oxidation in an alkaline solution on MoS_2 nanosheets grown on Au-Pd bimetallic nanoparticles using a facile thermal co-reduction methodology. As shown in Fig. 3 (a-e), the developed non-enzymatic electrochemical sensors had an excellent electrooxidation due to the synergistic effect of the bimetallic Au-Pd nanoparticles and the MoS_2 nanoplatelets [51]. Su and co-workers constructed a non-enzymatic glucose biosensor based on an Au@Pt core-shell NP-decorated MoS_2 nanohybrid. In an alkaline solution, the MoS_2-Au@Pt nanocomposite-modified electrode demonstrated better electrocatalytic activity towards glucose oxidation than did MoS_2-Pt- and Au@Pt-modified electrodes, proving that the MoS_2-Au@Pt nanocomposites could be used as mimetic enzymes for glucose detection in human serum samples. Their electrochemical biosensors provided a wide linear concentration-response from 10 μM to 3 mM with a LOD of 1.08 μM ($S/N = 3$) [52]. The detection of H_2O_2 released from 4 T1 breast cancer cells was achieved using a PtW/MoS_2 hybrid nanocomposite prepared using the in-situ growth of PtW nanocrystals on exfoliated MoS_2. The introduction of PtW nanocubes on the surface of the MoS_2 nanosheet increased the surface area of the electrode, enhanced the electron transfer rate, and exhibited good anti-interference in the reduction of H_2O_2 [53, 54].

Detection performance of Cu and Ni-based nanomaterials decorated MoS_2 modifiers Lin and his collaborators also

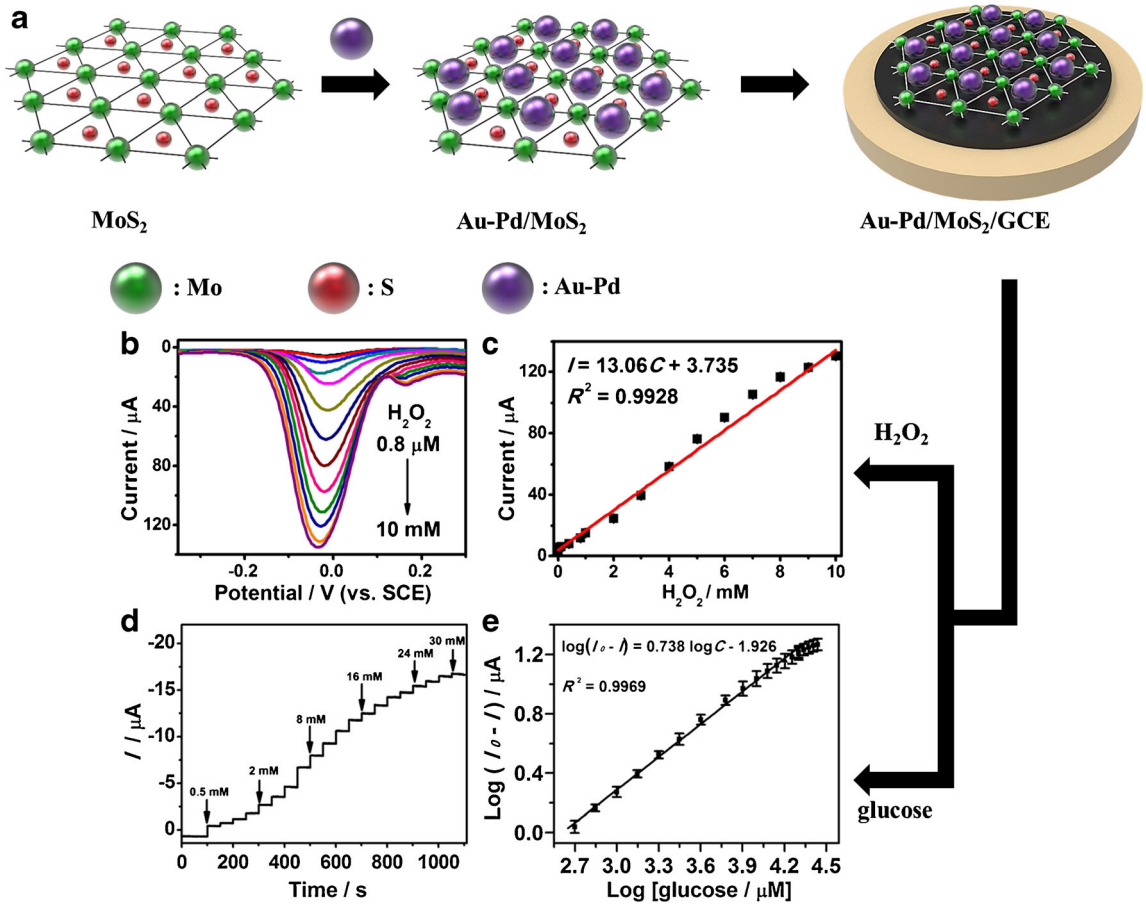


Fig. 3 **a** Schematic representations of the non-enzymatic sensor-based Au-Pd/MoS_2/GCE for the detection of H_2O_2 and glucose. **b** DPV curves are corresponding to H_2O_2 with different concentrations. **c** The plot of the DPV peak current as a function of H_2O_2 concentration. **d** Amperometric responses corresponding to glucose of different concentrations. **e** The plot of amperometric response against the logarithm of glucose concentration. Reprinted from Li and Du (2017) with permission from Elsevier [51]

fabricated a GCE based on a CuNF/MoS_2 nanocomposite with a 3D nano-flower structure for the enzyme-free detection of H_2O_2 in water and glucose in human blood serum samples. The 3D nano-flower structure created a large surface area; this combined with the synergistic and electrocatalytic effect of the CuNF and MoS_2 improved electron transfer and the subsequent detection of H_2O_2 and glucose in real samples, leading to satisfying recovery values of 97.3–106% [55]. A nanohybrid of Cu_2O NPs decorated flower-like MoS_2 was synthesized for the amperometric sensing of glucose in human serum samples. The positioning of the Cu_2O nanoparticles on the flower-like MoS_2 nanosheets was achieved through the hydrothermal reaction of $Na_2MoO_4.2H_2O$, L-cysteine, and Cu_2O. The prepared Cu_2O/MoS_2 nanohybrid promoted efficient electron transfer between the modified electrode and glucose and increased the number of reactive sites for the oxidation of glucose. Therefore, the Cu_2O/MoS_2 nanohybrid -based glucose sensor exhibited a rapid detection response (3 s) and good stability, reproducibility, and selectivity [56].

An investigation made for glucose detection in a real serum sample based on amperometry using a hybrid nanostructure consisting of a GCE modified with polyvinyl butyral and copper sulfide containing MoS_2. Compared with the MoS_2/GCE and CuS/GCE, the MoS_2-CuS-modified GCE had higher electrocatalytic activity for glucose oxidation, strong anti-interference ability, and redox (reducing) ability, the prepared non-enzymatic amperometric glucose sensor had a linear response range in a phosphate buffer (pH 7.2, 0.1 mol L^{-1}) at an applied potential of +0.18 V (vs. Ag/AgCl). The Michaelis-Menten constant and the heterogeneous electron transfer rate constant (ks) of the MoS_2-CuS/GCE was observed to be 1.34 mM and 9.6 ± 0.73 s^{-1} respectively, with satisfactory recovery values of 92.3 and 110.7% in human serum samples [57]. MoS_2 nanosheets and organic copper nanowires were used to fabricate new MoS_2-OCu nanohybrids based on a typical hydrothermal method and assessed for the non-enzymatic simultaneous detection of H_2O_2 and AA by Li et al. The large surface area of the MoS_2 nanoplatelets ensured a sufficient number of reaction sites, making the nanoplatelets an ideal active material for electrochemical substrates. The synthesized OCu nanowires also served as spacers to prevent the MoS_2 nanoplatelets from restocking, thus increasing the

active surface area of the nanoplatelets. The prepared sensor had high sensitivity, good reproducibility, and long-term stability, and demonstrated better electrochemical performance in the presence of H_2O_2 and AA [58]. MoS_2-$NiCo_2O_4$ nanostructure was fabricated for the non-enzymatic sensor for the sensitive detection of glucose in human serum samples. The MoS_2 nanosheets could be used to quickly connect the $NiCo_2O_4$ nanoplates. This novel architecture was fabricated using hydrothermal synthesis and post-calcination. Compared to the GCE, MoS_2, and $NiCo_2O_4$ nanoplates, the adhesion of MoS_2 to the $NiCo_2O_4$ nanoplate-modified GCE significantly promoted charge transfer and enhanced the electrocatalytic activity towards glucose oxidation, while the contacts between the $NiCo_2O_4$ nanoplates accelerated and increased the fast kinetics. It resisted interference from ascorbic acid, uric acid, dopamine, chloride ions, and monosaccharides and successfully detected glucose in 0.1 M NaOH [59].

Detection activity on CNT and graphene-based MoS_2 nanocomposites An example of this is a modified vitreous carbon electrode containing a nanocomposite composed of MoS_2-decorated MWCNTs to mimic peroxidase prepared using a solvothermal method to generate a suitably high electrocatalytic performance in H_2O_2 assays of enriched sterilized milk. The doped CNTs were used not only as a substrate for the immobilization of the MoS_2 but also as a conductive material to accelerate the transfer of electrons. Therefore, the MoS_2-CNT-based H_2O_2 sensor exhibited a wide linear range, a low LOD, high selectivity, and long-term stability of 1 month [60]. Non-enzymatic glucose sensors based on a nanocomposite fabricated using electrodeposition consisting of CNT/polyimide and $Ni(OH)_2/MoS_x$ have also been reported. The synergistic effect of MoS_x and $Ni(OH)_2$ created a restocking effect within the MoS_x layer, leading to excellent glucose detection properties, including a wide linear detection range (0 to 30 mM) and high sensitivity (570.71 μA mM^{-1}) [61].A non-enzymatic glucose sensor for use with human serum based on Ni-doped MoS_2/rGO has been reported, with different ratios of Mo and Ni set by calcining the corresponding precursor under N_2 flow using a precipitation synthesis method. The magnetic nanostructure and composition were confirmed with physicochemical and electrochemical analysis methods. Owing to the large surface area and the conductivity of rGO as a supporter, the Ni-MoS_2/rGO composites exhibited highly exposed catalyst sites, good conductivity, and a facile electron transport rate. In addition, the kinetic measurements of the modified electrode revealed a large D of 1.83×10^{-3} cm^2 s^{-1} and $K_{cat} = 6.26 \times 10^5$ cm^3 mol^{-1} s^{-1}, together with good selectivity, reproducibility, and stability [62].

An electrochemical sensor for the quantification of H_2O_2 levels in tap water and river water using GCEs modified with layered MoS_2-reduced graphene oxide and Prussian Blue. Under optimal conditions, this electrochemical sensor offered a LOD of 0.14 μM, a wide linear range from 0.3 μM to 1.15 mM, a sensitivity value of 2883.5 μA·μM^{-1}·cm^{-2}, and rapid response (< 10 s) at a working analytical voltage of 0.1 V [63]. In another study was involved for fabrication GCEs with 3D rGO decorated with MoS_2 quantum dots to detect H_2O_2, producing a wide linear detection range (0.01–5.57 mM), a low LOD (1.90 μM), good anti-interference performance, and long-term stability (18 days) [64]. An oxygen-implanted MoS_2-graphene nano-hybrid material was synthesized using a solvothermal process for H_2O_2 detection. The enhanced electrocatalytic activity of the modified electrode was due to the synergistic effect of the graphene and MoS_2 crystals. Under optimal conditions, the fabricated sensor exhibited a wide linear range between 0.25 and 16 mM with a low LOD of 0.12 μM and good sensitivity of 269.7 μA mM^{-1} cm^{-2}. The results demonstrated that the O-MoS_2/graphene nanocomposite offered a diffusion-controlled process for enhanced sensor performance. The obtained electrochemical sensor results were similar to those obtained using the UV-vis method, indicating that the sensor had excellent reliability [65].

Electrochemical detection of neurotransmitters using MoS_2 nanocomposites

Dopamine (DA), ascorbic acid (AA) and uric acid (UA) play a vital role in human metabolism and act as biomarkers for several diseases. DA is an essential neurotransmitter in mammalian brain tissue and is central to the functioning of the central nervous system, kidneys, hormones, and the cardiovascular system. Insufficient DA due to the loss of DA-producing cells can lead to Parkinson's disease. UA is the dominant purine metabolism based final oxidative product and is present in serum and urine. Abnormal levels of UA are associated with hyperuricemia and gout. AA is an antioxidant that is an essential nutrient in the human body, protecting the skin and preventing scurvy. Because of their importance, the quick, sensitive, and selective electrochemical sensing of these biomolecules are required for medical analysis and biological diagnosis. However, a bare electrode is irreversible, and DA, AA, and UA require high overpotentials. The oxidation potentials of DA, AA and UA overlap and significant electrode fouling occurs on the bare wire, leading to poor selectivity and reproducibility. Therefore, to design and manufacture selective electrochemical sensors, it is necessary to be able to detect one of the DA, UA, and AA in the presence of the two other species. Though a variety of modifier electrodes has been prepared for the detection of these biomolecules, selective detection if highly challenges. Hence the MoS_2 and their nanocomposites exhibit a good electrocatalytic performance at once an individual.

Metal and metal oxides nanoparticles-MoS_2 based nanocomposites for Neurotransmitters sensing Simultaneous detection of DA and UA using a nanocomposite consisting of PtNPs and MoS_2 was prepared using microwave-influenced

hydrothermal synthesis. The prepared PtNP@MoS_2/GCE demonstrated catalytic activity suitable for the analysis of DA and UA either alone or simultaneously. The peak-to-peak spacing between AA and UA was about 160 mV due to the synergistic effect of the PtNPs and MoS_2. The PtNP@MoS_2/GCE sensors were also able to produce satisfactory results in the detection of DA and UA in human serum samples. [66] A fabrication of 0D-2D heterostructures of AuNP@MoS_2-NS on a modified GCE using the mixed spontaneous redox reaction of $HAuCl_4$ and MoS_2-NS for two minutes at room temperature without adding any other reduced reagent. The combination of the high conductance and large active area of the AuNPs@MoS_2-NSs/GCE electrode produced a synthetic effect that resulted in improvements in a number of properties, including stability, selectivity, sensitivity, and anti-interference for the simultaneous electrochemical detection of DA, AA, UA, and nitrite in human serum and urine samples [67].A non-enzymatic sensor for the detection of AA, DA, and nitrites on the binary CoS_2-MoS_2 composite and N-LC were prepared from bulk MoS_2 using hydrothermal synthesis. Compared to modified MoS_2/GCEs, CoS_2-MoS_2/GCEs and bare GCE, the GCE modified with N-LC/CoS_2-MoS_2 had better electrocatalytic activity based on the Nyquist plot of the electrochemical impedance spectrum. The proposed sensor was also highly sensitive and had excellent interference prevention and stability [68].

Polymer-MoS_2 based modified electrodes for Neurotransmitters sensing The synergistic electrocatalytic activity of the polymer-based modified electrode was due to the large surface area and negative charge, which can efficiently adsorb aromatic compounds. MoS_2 nanosheets and PEDOT assembled onto a GCE surface for the sensitive and selective detection of AA, DA, and UA in urine samples. MoS_2 nanosheets were prepared using solvent-assisted exfoliation [69]. An electrochemical sensor from a GCE modified with PABSA-rMoS_2 nanocomposites for the detection of DA in human urine. Pulse potentiostatic synthesis was adopted to fabricate the PABSA-rMoS_2 nanocomposites. The synergistic electrocatalytic activity for the oxidation of DA of the PABSA-rMoS_2 /CPE was leading to excellent selectivity, reproducibility, and stability [70]. A MoS_2/MWCNT/PPy nanocomposite was constructed by Vijayaraj and colleagues using the potentiostatic deposition in an aqueous solution at pH 7.0 for the ex vivo amperometric sensing of DA in mouse brain tissue samples from a mouse model of Parkinson's disease. A series of analytical methods were employed to examine the surface characteristics and the improved electrocatalytic effect of the MoS_2/MWCNT/PPy nanocomposite, including CV, EIS, FESEM, AFM and Raman spectroscopy. The designed sensor had a strong ability to prevent interference while providing satisfactory reproducibility and synergy [71].

Graphene-MoS_2 based nanocomposites for Neurotransmitters sensing Various graphene-based chemically modified electrodes have been designed for this purpose due to their garnered interest in engineering and technology. For example, Pramoda and coworkers prepared MoS_2-RGO composites on GCEs for the selective detection of DA and UA in the presence of AA. Few-layered MoS_2 was prepared following the simple ultrasonication-assisted hydrothermal synthesis of ammonium heptamolybdate, thiourea, and graphene. The increase in the electrocatalytic activity of the MoS_2-RGO/GCE sensor towards DA could be attributed to an increase in surface area (147 m^2/g) and the promotion of the transfer of electrons along the free edge. The oxidation current of DA was also higher than that of UA because it facilitated electron transfer through the interaction of π-π with the graphene binding surface of DA [72]. A GCE modified with a graphene-MoS_2 composite using solvothermal synthesis was used to develop an electrochemical sensor for detecting DA in bovine serum samples by Cheng et al. in 2017 [73]. The authors concluded that the negatively charged graphene-MoS_2/GCE selectively interacted with the positively charged DA (pKa = 8.89) in PBS at pH 7.5 and anionic AA (pKa = 4.1) and UA (pKa = 5.75). The electrochemical sensors demonstrated excellent selectivity and sensitivity in the detection of DA over a wide linear range and with a low detection limit. One-pot hydrothermal synthesis was involved in producing MoS_2/rGO nanocomposites for the modification of GCEs to simultaneously measure AA, DA, and UA. The porous and flower-like structural composites had a large specific surface area, and the excellent electrical conductivity improved the performance of the sensor for the simultaneous detection of AA, DA, and UA in human serum samples, with recovery rates ranging from 98.9 to 104.1% (n = 3). Also, the authors reported that the oxidation potentials of AA, DA, and UA were well separated (with oxidation peaks at −64, 168, and 320 mV, respectively, versus Ag/AgCl) and that the detection sensitivity was greatly improved (0.12, 4.11, and 1.59 μA μM^{-1} cm^{-2}, respectively) using DPV. This means that the biosensors are able to selectively detect biologically active biomolecules such as epinephrine and norepinephrine [74].

Selective electrochemical detection of cysteamine (CA) in the presence of UA in human plasma was demonstrated using MoS_2-rGO-GCE a hybrid nanocomposite. The MoS_2-NS was uniformly decorated on the rGO frame using strong adhesion. The MoS_2-rGO

nanocomposite improved conductivity and offered a large contact area between the electrode and the electrolyte [75]. Mani and colleagues reported graphene nanosheet (GNS) CNTs decorated with flower-like MoS_2 produced using hydrothermal synthesis and used for the electrochemical detection of DA at the nanomolar level in rat brain and serum samples. This nanohybrid, characterized by the electrostatic interaction between negatively charged GO-CNTs and a positively charged molybdenum precursor, had a suitable upper surface and porosity for the excellent electrochemical detection of DA. Based on Fig. 4, the developed sensor also exhibited suitable selectivity, stability, repeatability, and reproducibility [76].

Nanographitic carbon-MoS_2 based nanocomposites for Neurotransmitters sensing 3D framework MoS_2 for the simultaneous detection of DA, UA, and AA, ultra-thin MoS_2 nanosheets were prepared using ammonium molybdate, thiourea, and a layered g-C_3N_4 template with pyrolysis. The MoS_2 nanosheets exhibited a significantly improved porous structure, large pore volumes, and electrocatalytic activity for the oxidation of AA, DA, and UA. The peak-to-peak separation of AA-DA, DA-UA, and AA-UA were 208.3 mV, 128.0 mV, and 336.3 mV, respectively, which corresponds with other MoS_2-based electrodes. In particular, the edge sites of MoS_2 are important regions of catalytic activity because the MoS_2 plane is chemically inert. It should be noted that these edge sites produce a positive charge within the MoS_2 and facilitate the absorption of small negatively charged molecules thought to contribute to the electrocatalysis of UA, AA, and DA [77].

For the detection of DA, Dolinska et al. also employed a GCE modified with porous carbon-MoS_2 nanohybrids based on negatively or positively charged carbon nanoparticles and MoS_2 nanopetals. Interestingly, a wide range of concentrations (0–1 μM) and a LOD of 0.02 μM was obtained using DPV in the presence of AA and UA. It was observed that the porous carbon-MoS_2 nanocomposite had electrocatalytic properties for selected biomolecules and excellent electrochemical properties due to the electrostatic repulsion between the negatively charged MoS_2/CNP surface and the negatively charged surfaces of ascorbate and urate [78].

Electrochemical detection of pharmaceutical drug using MoS_2 nanocomposites

Detection of Vitamin B Folic acid (FA) is a water-soluble B vitamin that is needed to maintain healthy cells and synthesize, methylate, and repair DNA. FA is especially important in biochemistry because of its antioxidant and cancer prevention activity. Chekin et al. developed a new matrix of MoS_2-rGO hybrids using simple sonication to detect FA in human serum samples. The MoS_2-rGO-modified

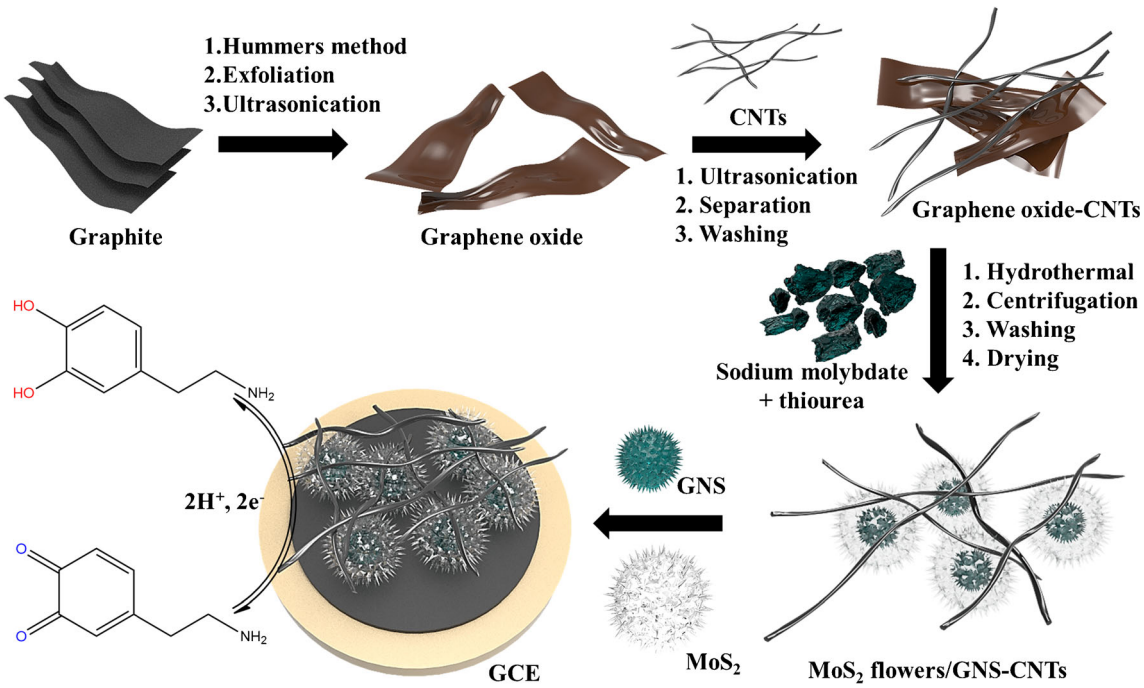
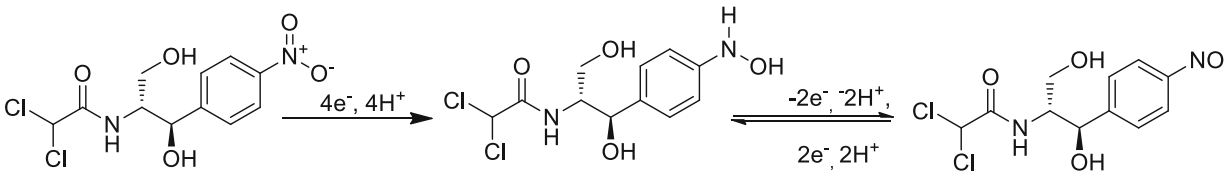


Fig. 4 Schematic diagram for the fabrication of a GNS-CNT/MoS_2 hybrid nanostructure and the electrochemical sensing of dopamine in biological and pharmaceutical samples [76]

electrode exhibited high electrical conductivity with excellent catalytic oxidation of FA by combining the finely wrinkled rGO structure with the MoS_2 flake structure. The FA oxidation potential was ~0.7 V for the MoS_2-rGO/GCE in the presence of common interferences [79]. Another research group has also developed a screen-printed carbon electrode (SPCE) consisting of graphene, MoS_2, and AuNPs for the detection of FA in human urine samples. The morphology, composition, conductivity, and electrochemical properties of the GNS-MoS_2-AuNP ternary nanocomposite was described in detail. Interestingly, they found that, due to the synergistic effect between the GNS, MoS_2, and AuNPs, the modified sensor had excellent electrocatalytic activity and excellent repeatability, stability, and sensor selectivity towards the oxidation of FA compared to an unmodified SPCE, MoS_2/SPCE, and GNS-MoS_2/SPCE under the same experimental conditions [80].

Detection of Antibiotic drugs Clenbuterol ($C_{12}H_{18}Cl_2N_2O$; CLB) is a β-agonist taken orally for the treatment of pulmonary diseases and asthma in humans and animals. However, the treatment of animals may lead to the accumulation in their muscle and liver tissue, leading to pharmacological consequences for humans. A sensitive method for the detection of CLB is required, but little research to date has been conducted on the direct electrochemical detection. Therefore, it is essential to develop a modified electrode with excellent electrochemical properties to monitor CLB. For example, Yang and co-workers investigated the non-enzymatic detection of CLB in pork samples using a GCE modified with a MoS_2-Au-PEI-hemin layered nanocomposite. The MoS_2-Au-PEI nanocomposite was prepared using the in-situ decoration of Au nanoparticles with an average diameter of about 50 nm, a PEI layer on 2-D MoS_2 nanosheets. Then hemin was then coupled with the MoS_2-Au-PEI-modified GCE using EDC/NHS-activated hemin to generate amide bonds, leading to good reproducibility and stability for the detection of CLB [81]. An electrochemical aptasensor for tetracycline detection based on a MoS_2-TiO_2@Au ternary composite. Cylinder-shaped TiO_2 nanorods attached to MoS_2 nanospheres were synthesized using hydrothermal synthesis, and these were then aminated. The prepared aptasensor exhibited good selectivity, a wide concentration range (1.5×10^{-10} to 6.0×10^{-6} M), and a low detection limit (5×10^{-11} M) [82].

Chloramphenicol (CAP) is an antibiotic that is strongly bactericidal and therapeutically efficient. However, it can have severe toxic side effects for the hematopoietic lineage, leading to disorders such as aplastic anemia. The long-term use of CAP can also cause an imbalance in the microflora of the body. As such, Yang and his colleagues presented a new electrochemical detection platform for CAP in eye drops using MoS_2 sandwiched between SPAN fabricated with the ultrasonic exfoliation method. This SPAN-MoS_2 nanocomposite was prepared by negatively charged SPAN intercalated into a few MoS_2 nanosheets that had been exfoliated from bulk MoS_2. They reported the electrostatic interaction between the positively charged CAP, the large conjugate structure, and the negatively charged SPAN-MoS_2 surface, leading to CAP adsorption and subsequent electrocatalytic detection (Tables 1, 2 and 3). Their proposed detection platform had repeatability, long-term stability, high sensitivity, and low detection limits and can be used in biosensors and medical applications [83]. Similarly, Chen and his colleagues produced thin-layered MoS_2/PANI nanocomposites using the ultrasonic exfoliation of bulk MoS_2 and the in-situ polymerization of aniline for the voltammetric detection of CAP. Their MoS_2/PANI-modified CPE had excellent electrical conductivity and a large electroactive surface area, which may be due to the synergistic effect between the aromatic aniline and the MoS_2 basal plane. The improved MoS_2/PANI/CPE also had high sensitivity, a wide detection range, a low detection limit, and excellent CAP detection reproducibility and stability [84]. Electrochemical detection of CAP using hydrothermal synthesis, in which negatively charged f-MWCNTs actively combined with MoS_2 sheets to form an interconnected nanostructured network of 3D MoS_2/f-MWCNTs. The MoS_2/f-MWCNT sensor exhibited good reproducibility, stability, and selectivity when the concentration of the interfering substance was high. Satisfactory recovery results were achieved in the electrochemical detection of CAP in milk and honey samples by the MoS_2/f-MWCNT/GCE. The essential parameters of the sensor, such as its LOD and linear range, were significantly lower than those of electrodes modified with MoS_2/self-adapted polyaniline [85]. The electrochemical reaction of CAP at MoS_2/*f*–MWCNTs/GCE was explained as follows:



(2)

Table 1 Electrochemical sensors based on molybdenum sulfide and its nanocomposites for the detection of analytes

Electrode	Analyte	Method	Supporting electrolyte	Real sample	Sensitivity (μA μM^{-1} cm^{-2}	Linear range (μM)	LOD (μM)	Ref.
MoS_2-a/GCE	Cd^{2+}	SWASV	ABS (pH 7.0)	River and tap water	–	0.002–20	2×10^{-4}	[29]
Fe_3O_4/MoS_2 /GCE	(nitrate) NO_2	Amp i-t	PBS (pH 5.0)	–	0.043	1–2630	0.5	[30]
Fe_2O_3@MoS_2/GCE	NO_2	Amp i-t	PBS (pH 4.0)	Drinking water	1.247, 4.386, 10.15	2.0–6730	1.0	[31]
$PrFeO_3$-MoS_2/CS/GCE	NO_2	CV	ABS (pH 4.5)	River and tap water	0.327	0.005–3.0	1.67	[32]
PANI-MoS_2/GCE	NO_2	Amp i-t	PBS (pH 5.0)	Drinking and river water	0.68, 6.50, 28.68	4.0–94, 94–1034, 1034–4834	1.0	[33]
TOSC-MoS_2/GCE	NO_2	Amp i-t	PBS (pH 5.0)	Drinking and river water	3.42, 17.76	6.0–3140, 3140–4200	2.0	[34]
MoS_2-MWCNTs-Au	NO_2	Amp i-t	PBS (pH 7.0)	Pond water	1.734, 6.735	12–2110, 2100–6500	4.0	[35]
Ag/HNTs/MoS_2-CPE	NO_2	Amp i-t	PBS (pH 4.0)	Tap water	0.0899	2–425	0.7	[36]
Co@CNT/MoS_2/Nf/	S^{2-}	Amp i-t	PBS (pH 7.5)	Apple & Orange	0.23×10^{-3}	5.0–60	7.6×10^{-3}	[37]
Au@Pt-MoS_2/GCE	CC (catechol)	DPV	PBS (pH 7.0)	River and tap water	–	2.0–1000	0.44	[38]
Graphene/MoS_2 GCE	HQ (hydroquinone)	DPV	PBS (pH 7.5)	Tap water	–	0.5–300	0.037	[39]
MoS_2/RGO/GCE	HQ	DPV	PBS (pH 7.4)	Tap water	–	0.001–0.009	3×10^{-4}	[40]
MoS_2-SPAN/GCE	BPA (bisphenol A)	DPV	PBS (pH 7.0)	Plastic samples	–	0.001–1.0	6.0×10^{-4}	[41]
MoS_2/IL/Au NR/GCE	2,4-DCP (dichlorophenol)	DPV	PBS (pH 7.0)	River water	0.12	0.01–50	0.0026	[42]
MoS_2/graphene/GCE	MP	Amp i-t	PBS (pH 7.0)	Apple, kiwi, tomato, cabbage	0.457	0.01–1905	3.23	[44]
MoS_2/GCE	m-NP	CV	PBS pH 7.0)	Tap water	–	10–1500	7.0	[45]
MoS_2/GCE	4-NP (nitrophenol)	DPV	PBS (pH 6.0)	Water	0.491	4–0.02	0.01	[46]

A GCE modified with the composite consists of Pt nanoparticles (NPs), Pd nanoflakes, and MoS_2 to obtain a modified electrode for H_2O_2 detection. It was used to sense H_2O_2 at an applied potential of −0.35 V vs. Ag|AgCl with a 3.4 μM lower limit of detection. The sensitivity is 7.64 μA μM^{-1} cm^{-2} and the dynamic range extends from 10 to 80 μM [54]

Table 2 Electrochemical detection of H_2O_2 and glucose using molybdenum sulfide and its nanocomposites

Electrode	Sensing Analyte	Method	Electrolyte	Real sample	Sensitivity (μA/μM/cm^2)	Linear range (μM)	LOD (μM)	Ref.
MoS_2-PtNP/GCE	H_2O_2	Amp i-t	0.1 M PBS (pH 7.4)	–	–	20–4720	0.345	[50]
Au-Pd/MoS_2/GCE	H_2O_2 glucose,	DPV Amp i-t	0.01 M PBS 0.1 M NaOH	–	0.19	0.8–10,000 500–20,000	0.16, 400	[51]
Pt-Pd/MoS_2/GCE	H_2O_2	Amp i-t	0.1 M PB (pH 7.0)	–	7.64	10 to 80	3.4	[54]
3D-CuNFs-MoS_2/GCE	H_2O_2 Glucose	Amp i-t	0.1 M PBS (pH 7.0) 0.1 M NaOH	Tap water and Human serum	–	0.04–1.88 1.88–35.6 1.0–20 20–70	0.021 0.32	[55]
Cu_2O/MoS_2/GCE	glucose	Amp i-t	0.1 M NaOH	Human serum	3.11	0.01–4000	1.0	[56]
MoS_2-$NiCo_2O_4$/GCE	glucose	Amp i-t	0.1 M NaOH	Human serum	1.75	1–1600, 1600–11,100	0.152	[59]
Ni-MoS_2–3/rGO/NF/GCE	glucose	Amp i-t	0.1 M NaOH	Human serum	0.25	0.005–8.2	2.7	[62]
Hb-AuNPs@MoS_2	H_2O_2, NO	CV	0.1 M PBS (pH 7.0)	–	–	10–300 10–1100	4.0 5.0	[92]
GO@MoS_2/Mb	H_2O_2	Amp i-t	0.1 M PBS (pH 7.4)	–	–	–	0.02	[96]
CAT/MoS_2-Au/chitosan	H_2O_2	Amp i-t	0.1 M PBS (pH 7.4)	SP2/0 cells	0.187×10^{-3}	0.5–200	0.1	[99]
GO_x/2DMoS_2/rGO/GCE	glucose	Amp i-t	0.1 M PBS	–	0.106×10^{-3}	2000–20,000	920	[101]
MoS_2/AuNPs/GOx	glucose	Amp i-t	0.1 M PBS (pH 7.4)	–	13.80	250–13,200	0.042	[102]

Table 3 Summary of electrochemical sensors based on MoS_2 and its nanocomposites for the detection of biomolecules

Electrode	Sensing Analyte	Method	Electrolyte	Real sample	Sensitivity (μA/μM/cm^2)	Linear range (μM)	LOD (μM)	Ref.
PtNPs@MoS_2/GCE	DA (dopamine) UA (uric acid)	DPV	0.1 PBS (pH 7.0)	Human serum	–	0.5–150 5–1000	0.17 0.98	[66]
AuNPs@MoS_2-NSs/GCE	DA AA (ascorbic acid) UA NO_2	DPV	B-RBS (pH 4.0)	Human serum	–	20.0–300 5.00–200 20.0–400 5.00–260	3.0 1.0 5.0 0.5	[67]
N-LC/CoS_2-MoS_2	AA DA NO_2	Amp i-t	0.1 M PBS (pH 7.4)	Human urine	–	9.9–4800 0.99–262 0.5–5160	3.00 0.25 0.20	[68]
PABSA-rMoS_2/CPE	DA	DPV	0.1 M PBS (pH 7)	Human urine	–	1.0–50	0.22	[70]
GCE-MoS_2/MWCNT/PPy	DA	Amp i-t	0.1 M PBS (pH 7)	Mouse brain tissue	1.130	0.025–1.0	0.01	[71]
Graphene-MoS_2/GCE	DA	DPV	0.1 M PBS (pH 7.5)	Bovine serum	–	0.05–10	0.007	[73]
MoS_2/rGO/GCE	AA DA UA	DPV	0.1 M PBS (pH 7.0)	Human serum	0.12 4.11 1.59	12–5402 5.0–545 25–2745	0.72 0.05 0.46	[74]
MoS_2-rGO/GCE	CA	Amp i-t	0.1 M PBS (pH 7.4)	Human serum	1.40	0.01–20	0.007	[75]
GNS-CNTs/MoS_2/GCE	DA	DPV	0.1 M PBS (pH 7.0)	Human serum	10.81	0.1–100	0.05	[76]
MoS_2/GCE	AA DA UA	DPV	0.1 M PBS (pH 7.0)	–	–	5.0–1200 1.0–900 1.0–60.0	0.82 0.15 0.06	[77]
MoS_2-GCE/rGO	FA	CV	0.1 M PBS (pH 7.4	Human serum	1400	0.01–100	0.01	[79]
GNS-MoS_2-AuNPs	FA (folic acid)	Amp i-t	0.1 M PBS (pH 7)	Human urine	8.8×10^{-4}	0.05–1150	0.038	[80]
SPAN-MoS_2/CPE	CAP (chloramphenicol)	DPV	0.1 M PBS (pH 7)	Eye drops		10–1000 0.1–1 × 10	6.5×10^{-2}	[83]
MoS_2/PANI/CPE	CAP	DPV	0.3 M PBS (pH 7.0)	–	–	0.1–100	6.9×10^{-2}	[84]
MoS_2/f-MWCNTs	CAP	Amp i-t	PBS (pH 7)	Milk and Honey	0.355×10^{-8}	0.08–1392	0.015	[85]
MoS_2-DNP/ GCE	VA	DPV	0.1 M PBS (pH 7)	serum samples	0.74	0.9–5.5	0.27	[86]
MoS_2/GCE	Baicalin	DPV	0.01 M PBS (pH 7.0)	Oral liquid	–	0.125–12.5	0.05	[87]
CuS-MoS_2/CFME	Mb (myoglobin)	CV	0.01 M PBS (pH 7.2)	Human serum	–	0.005–20.0	1.20	[96]
CSPE-MoS_2-GQDs-TvL	Caffeic acid Chlorogenic Epicatechin	Amp i-t	0.1 M ABS (pH 5.0)	Red wine	0.018 0.001 0.016	0.38–10.0 0.38–8.26 2.86–100	0.32 0.19 2.04	[101]
Nf/Chox/MoS_2-AuNPs	Cholesterol	Amp i-t	0.05 M PBS (pH 7.0)	Egg yolk and Pork liver	4.46	0.5–48.0	0.26	[102]
AuNPs/N-GO/GCE	Thrombin	DPV	0.1 M PBS (pH 7.0)	Human serum	–	1×10^{-10} -1×10^{-4}	2.7×10^{-11}	[109]
AuNPs/MoS_2/GCE	microRNA	DPV	0.1 M PBS (pH 7.0)	Human serum	–	1×10^{-10}-1×10^{-4}	8.6×10^{-11}	[114]
2D-MoS_2/ Au electrode	Ochratoxin A	Amp i-t	PBF (pH 7.4)	red win	–	0.0005–10 ng mL^{-1}	0.23 pg mL^{-1}	[135].
MoS_2-AuPt/GCE	CLB (clenbuterol)	DPV	PBS, pH = 7.4	pork samples	–	0.01–100 ng.mL^{-1}	6.9 pg.mL^{-1}	[138]

An electrochemical sensor fabricated by the successive coating of MoS_2 nanosheets and diamond nanoparticles (DNP), respectively, on GCE surface was used to determine the anticonvulsant drug valproic acid. The EIS studies suggest that the presence of DNP markedly decreases the charge transfer resistance and enhance the synergistic performance compared to MoS_2 and the modified electrode exhibited high sensitivity, low LOD and an excellent 8% reproducibility (RSD) in addition to the retention of 99% of its initial response after 45 days of storage [86].

Detection of Flavonoids Flavonoids are present in many plants and foods and have been used for treating coughs, removing phlegm, reducing inflammation, and preventing cancer. It has been shown to have health benefits for humans due to its anti-inflammatory, anti-

HIV, anti-cancer, free radical scavenging, and antioxidant activity. However, an overdose of flavonoids can have serious side effects. Therefore, the accurate measurement of baicalein is important in clinical practice.

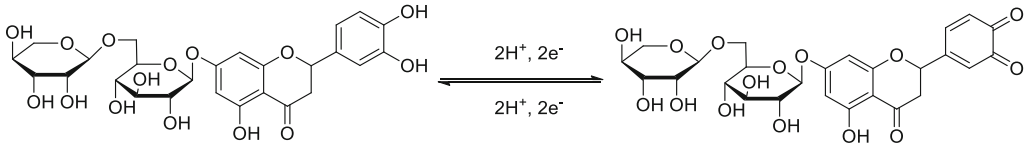
A report on GCE modified with MoS_2 nanosheets that exhibited electrochemical behavior useful for the detection of baicalin in Chinese medicine. The modified MoS_2 on the surface of the GCE was able to adsorb more baicalin, with the baicalin forming a conjugated system through non-covalent π-π stacking interactions. The proposed sensor had a wide linear range, low detection limit, and acceptable reproducibility and stability [87]. A nanocomposite was prepared by an ionic liquid, ordered mesoporous carbon (OMC) and Pd/MoS_2 (Pd/MoS_2-IL-OMC) for the detection of quercetin (QR) in juice samples. The IL-functionalized OMC exhibited a large surface area, good conductivity, and strong binding, and the PdNPs and MoS_2 provided excellent electrocatalysis. The proposed sensor had a wide linear range (0.020–10.0 μM) and a low LOD (8.0 nM) with good stability [88]. Similarly, Zhang et al. developed a chemically modified MIP/MIL-101 (Cr)/MoS_2/GCE for the sensitive analysis of QR in honey. The MIP sensor demonstrated excellent reproducibility, stability, and selectivity, with a wide concentration range (0.1–700 μM), a low detection limit (0.02 μM), and good sensitivity (0.285 μA μM^{-1}) [89].

A non-enzymatic luteolin sensor was constructed based on an electrode consisting of molecularly imprinted polycarbazole on MoS_2/graphene-CNTs. The reported MoS_2/GN-CNT nanocomposite was prepared using hydrothermal synthesis. Its linear range of concentration and LOD were 0.040–2.0 μM and 9.0 nM ($S/N = 3$), respectively, with a sensitivity value of 381.3 μA μM^{-1} cm^{-2}. The sensor was applied to the detection of luteolin in vegetables and tea samples and obtained recovery values similar to those obtained through high-performance liquid chromatography [90]. Recently, Zhang and co-workers devised an electrochemical sensor based on poly (diallyldimethylammonium chloride)-functionalized graphene (CoS_2-MoS_2-PDDA-GR) decorated with CoS_2 nanoparticles and MoS_2 nanosheets to detect eriocitrin in lemons with reasonable results. DPV results of eriocitrin detection based on CoS_2-MoS_2-PDDA-GR/GCE shows a wider linear range and a lower detection limit, good sensitivity, and stability. A reasonable mechanism for the electrochemical oxidation of eriocitrin at CoS_2-MoS_2-PDDA-GR-/GCE was illustrated as follows [91].

Detection of DNA purine bases Guanine and adenine are essential components of DNA and RNA and have many other biological uses. Changes in the concentration of these compounds in an organism can be used to monitor immune system deficiencies and various diseases. A designed was made by using electropolymerization of PXa-MoS_2 film to detect guanine and adenine. Positively charged guanine and adenine adsorb onto the negatively charged surface of the PXa-MoS_2 nanocomposite. Compared to electrodes modified with PXa or MoS_2 only, the PXa-MoS_2 hybrid interface produced a significant synergistic effect on guanine and adenine [92]. Similarly, an adenine and guanine sensor was constructed from a MoS_2-SPAN/CPE. The thin-layered MoS_2 nanosheets were exfoliated ultrasonically, and a copolymer of aniline and m-aminobenzenesulfonic acid was attached to the nanosheets. The MoS_2-SPAN/CPE had a large surface area and an excellent electrocatalytic capability based on its negative charge and special conjugated structure [93].

Electrochemical biosensors on MoS_2 based materials

Electrochemical biosensors are distinguished from electrochemical sensors because they are systems composed of a biorecognition element such as enzymes, antibodies, drug receptors, or DNA, among others, immobilized in an electroactive material. Moreover, various biohybrids of MoS_2 with enzymes, aptamers, and antibodies hold promising sensing applications, which are called electrochemical biosensors and Electrochemical Immunosensors. Electrochemical biosensors based on enzymes/proteins such as laccase, myoglobin (Mb), hemoglobin (Hb), cholesterol oxidase (ChOx), glucose oxidase (GOx), catalase (CAT), acetylcholinesterase (AChE) are essential in clinical diagnostics and environmental pollution monitoring due to their selective sensing of a particular analyte. These biosensors have been used for detecting caffeic acid, chlorogenic acid, (−) epicatechin, H_2O_2, cholesterol, NO, and glucose. Enzyme immobilization is carried out via non-covalent, covalent, or physical entrapment on the electrode surface. The main limitation of enzyme-based biosensors is that a number of factors can degrade enzyme activity, such as temperature and pH. Numerous attempts have been made to solve this issue using a variety of promising nanomaterials, such as metal NPs, metal nanowires, metal oxide nanoparticles, and carbon nanotubes, due to their conductivity, large surface area, and excellent biocompatibility. In particular, MoS_2 is a useful material for enzyme immobilization in biosensing applications, with a number of reports on MoS_2-based biosensors having been published in recent years.



(3)

Immobilization of metalloproteins onto MoS_2 based materials and its sensing activity

Hemoglobin for H_2O_2 sensing Development of a highly selective electrochemical sensor for H_2O_2 and NO was done in neutral conditions on Hb-immobilized, AuNP-decorated MoS_2 nanosheets modified GCEs. The AuNPs were grown on the surface of the MoS_2 nanosheets using a microwave-assisted one-pot method. They observed that the AuNP@MoS_2 nanocomposite exhibited a biocompatible environment and enhanced the electron transfer between Hb immobilized electrode and the sensing analytes [94]. Flower-like MoS_2 decorated on rGO nanocomposite was prepared using hydrothermal synthesis as demonstrated in Fig. 5a-f. The MoS_2-rGO provided a suitable microenvironment for Hb to retain its biological activity and stability. The amperometric i-t sensor demonstrated a wide linear range (0.1 to 250 μM), high sensitivity (346.6 μA mM^{-1} cm^{-2}), and an ultra-low LOD (25 nM) [95].

Myoglobin for H_2O_2 sensing For the detection of H_2O_2, an electrochemical biosensor was constructed by modifying a gold electrode with Mb on MoS_2 NPs encapsulated with GO. The MoS_2 NPs were modified with GO, the surface area of the gold electrode was increased via a chemical linker, and a biomolecular probe of metalloprotein was immobilized on the GO-MoS_2 complex with electrostatic bonding. The electrochemical signal of the biosensor had a redox peak current value of −1.86 μA and 1.95 μA at their oxidation and reduction potentials respectively which is much higher than Mb, Mb/GO, or Mb/MoS_2 NPs. This biosensor also demonstrated high reproducibility and maintained a stable redox peak current after 9 days at ambient conditions. A reasonable reaction mechanism of electrochemical reduction of H_2O_2 was proposed as below [96]:

$$\text{Mb Heme}\left(Fe^{III}\right) + e^{-} \leftrightarrow \text{Mb Heme}\left(Fe^{II}\right) \quad (4)$$

$$2\,\text{Mb Heme}\left(Fe^{II}\right) + 2H^{+} + H_2O_2 \rightarrow 2\,\text{Mb Heme}\left(Fe^{III}\right) + 2H_2O \quad (5)$$

Fabrication of a hybrid electrode composed of amine-modified MoS_2 NPs, GO, and Mb for the detection of NO. Carboxylated moieties of GO exhibited electrostatic interactions with the amine-modified surface of the MoS_2, providing a large surface area and good conductivity. The amperometric sensor based on the amine-modified MoS_2/GO/Mb hybrid electrode produced a sharp redox peak and a low detection limit of 3.6 nM [97]. An enzyme-free electrochemical immunoassay method was employed using a CuS-MoS_2 nanohybrid as a nano-enzyme mimic to detect Mb in human serum samples from patients with cardiovascular disease. CuS-functionalized MoS_2 nanocrystals were synthesized using a wet chemistry method. They were used as an electronic mediator, acting not only as a nano-enzyme mimic but also as a Cu^{2+}/Cu^{3+} redox couple in place of a native enzyme (GOx). Under optimum conditions, the electrochemical immunosensor exhibited a broad linear range with high specificity, good accuracy, reproducibility, and an acceptable LOD of 1.2 pg mL^{-1}. The sensor data was compared with that obtained from an ELISA kit (Abcam, SimpleStep ab171580) [98].

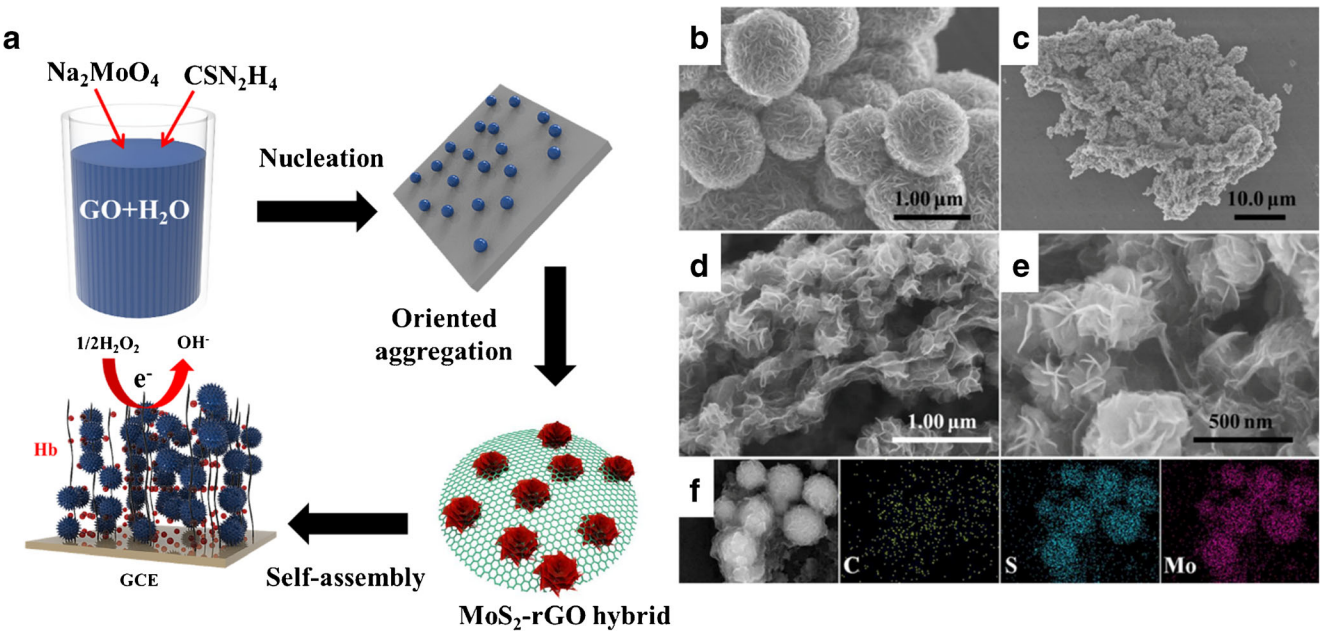


Fig. 5 **a** Schematic illustration of a biosensor based on a Nafion/Hb/MoS_2-rGO hybrid for the detection of H_2O_2. **b** Morphology of pure MoS_2 and (**c**-**e**) MoS_2 grown on rGO captured by SEM images. **f** EDS mapping of MoS_2-rGO. Reproduced from Liu et al. (2015) with permission from ECS [95]

Horseradish peroxidase and catalase for H_2O_2 sensing A novel amperometric biosensor for the electrochemical detection of H_2O_2 released from SP2/0 cells was constructed by immobilizing CAT on a MoS_2 nanosheet-AuNR hybrid film on a GCE. The results of FT-IR, UV-Vis and Raman spectroscopy indicated that the immobilized CAT molecules retained their natural structure and biological activity. The active surface area of the catalyzed MoS_2-Au hybrid was found to accelerate the DET between CAT and the electrode materials [99]. Kim and his colleagues also developed an electrochemical biosensor for H_2O_2 using an Au-MoS_2/IgG-HRP nanocomposite. A bulk layer of MoS_2 was synthesized in situ on a polymer printed circuit board at 300 °C. The negative charge of the layered MoS_2 was used to form Au-MoS_2/HRP hybrids by immobilizing IgG bound to HRP by electrostatic attraction. The CV was used to electrochemically reduce H_2O_2, leading to a wide linear range when hydroquinone HQ was used as a mediator [100].

Glucose oxidase for Glucose sensing 3D aerogels composed of 2D MoS_2 and graphene for the sensitive detection of H_2O_2 and glucose. This biosensor offered a high surface area for the effective immobilization of GOx and a continuous skeleton of highly conductive graphene sheets. As a result, it demonstrated high sensitivity, a low LOD, and fast response time (~7 s) based on flow-injection amperometric measurements [101]. An electrochemical biosensor for glucose in the presence of ferrocene as a mediator by GOx conjugated with AuNPs on a MoS_2 hybrid modified electrode. This sensor had a wide linear response range, high sensitivity, high selectivity, a low LOD, and high stability, arising from electrochemical properties such as a high Faraday current-to-capacity ratio, high current density, high electron mobility, and faster mass transfer. The overall mechanism of glucose oxidation at MoS_2/Au NPs/GOx hybrid structure on the gold electrode was shown as follows [102]:

$$\text{Glucose} + \text{GOx (FAD)} \rightarrow \text{Gluconolactone} + \text{GOx (FADH}_2\text{)} \quad (6)$$

$$\text{GOx (FADH}_2\text{)} + \text{O}_2 \rightarrow \text{GOx (FAD)} + \text{H}_2\text{O}_2 \quad (7)$$

Laccase for Phenolic compounds detection Vasilescu et al. immobilized *Trametes versicolor* laccase (TvL) on nanoflaked MoS_2 and graphene quantum dot (GQD) modified CSPEs for the sensitive detection of the phenolic compounds caffeic acid, chlorogenic acid, and (−)epicatechin in red wine. These phenolic acids are naturally found in fruit, vegetables, wine, olive oil, and coffee. They have antioxidant activities and health benefits associated with the prevention of coronary heart disease and cancer. The GQDs were produced using one-step hydrothermal synthesis with microwaves. The biosensor showed a wide linear range, a low LOD, and improved sensitivity, stability, and reproducibility. The biosensor results for the detection of caffeic acid were in agreement with those obtained using the Folin-Ciocalteu method [103].

Cholesterol oxidase for Cholesterol sensing A cholesterol biosensor was assembled using a ChOx-encapsulated MoS_2-AuNP composite to analyze cholesterol levels in egg yolk and pig liver. MoS_2-AuNPs were synthesized using the hydrothermal and electrodeposition methods. The sulfur atoms in the MoS_2 layer directly connected with the AuNPs, providing a large specific surface area and absorbing cholesterol oxidase molecules for cholesterol sensing. The synergistic catalytic effect of MoS_2 and AuNP led to satisfactory sensitivity, reproducibility, and stability, with the apparent Michaelis-Menten constant and sensitivity estimated to be 0.325 mM and 4460 μAmM^{-1} cm^{-2}, respectively. The proposed mechanism of Cho_x catalyzes the oxidation of cholesterol to H_2O_2 and cholest-4-en-3-one are given as below [104]:

$$\text{Cholesterol} + \text{O}_2 \rightarrow \text{Cholest-4-en-3-one} + \text{H}_2\text{O}_2 \quad (8)$$

Huang et al. assembled a cholesterol biosensor based on GO and Au-Ag NPs on an SPE. Their cholesterol biosensor demonstrated a wide linear range (0.01 to 5000 μg/mL), a low LOD (0.001 μg/mL; S/N = 3), good recovery, high selectivity, acceptable reproducibility, and stability [105].

Acetylcholinesterase for Organophosphorus pesticides detection A report on AChE immobilized onto Ag NPs decorated MoS_2 nanosheet for the detection of the organophosphorus pesticides monocrotophos and chlorpyrifos. AChE/CNT-NH_2/AgNP-N-F-MoS_2 bioelectrodes thus exhibited a wide linear detection range with long-term storage stability [106]. In related work by Song, an AChE-Chit/PdNi NWs/m-MoS_2/GCE nanocomposite was employed in the electrochemical detection of omethoate in commercial vegetables. The biosensor demonstrated high sensitivity, a wide linear range (10^{-13} M to 10^{-7} M), a low LOD (0.05 pM), and good specificity [107].

Electrochemical Immunosensors using MoS_2 nanocomposites

Electrochemical immunosensor is a kind of biosensor combination of electrochemical procedures with the immunological approach. MoS_2 nanocomposites have been used for the direct electrochemical detection of antibody-antigen recognition which is usually not possible at simply modified electrodes.

Electrochemical immunosensors are considered promising for protein biomarker detection. Immunosensors host a stable complex reaction between an antibody (Ab) and an antigen (Ag) and can be utilized in environmental monitoring and the biological detection of carcinoembryonic antigen (CEA), thrombin (TB), vitamin B_2 (riboflavin), α-fetoprotein (AFP),

prostate-specific antigen (PSA), and platelet-derived growth factor (PDGF).

Immunosensors on MoS_2 for thrombin and adenosine triphosphate A sandwich-type electrochemical aptasensor for the detection of TB in human serum was fabricated by using PdNPs decorating the flower-like structure of PDDA-G-MoS_2. The PDDA-G-MoS_2 nanocarrier was prepared directly using hydrothermal synthesis and used as a glucose oxidase immobilization platform. A hemin/G-quadruplex was then used as an HRP-simulated DNAzyme-modified GCE to amplify the electrochemical signals. The fabricated electrochemical aptaensor exhibited a relatively low LOD (0.062 pM), a broad linear range (0.0001–40 nM), and satisfactory selectivity and reproducibility, indicating that it can be useful for the analysis of target proteins in biological and clinical applications [108]. An ultrasensitive electrochemical aptasensor for the detection of TB in healthy human serum samples was made on the coupling of N-GO and MoS_2 with HCR and the amplification of the enzymatic signal. A large N-GO specific area that can be used to charge AuNP/MoS_2, immobilize tApt1. The AuNP/MoS_2 hybrid was an effective carrier for more constraining sites, leading to an improved signal response [109]. Electrochemical impedance spectroscopy (EIS) biosensor with MoS_2 nanosheets functionalized with an aptamer for the non-faradaic detection of TB without labels in human serum samples. A platinum electrode modified with a composite containing MoS_2 bound with a functionalized thiol-ssDNA aptamer was used as a biosensor for the selective and specific capture of TB in PBS and human serum with good sensitivity, a wide dynamic linear range (53 pM-854 pM), and a low LOD (53 pM) [110].

Adenosine triphosphate (ATP) plays vital roles in biosynthesis, cellular metabolism, and DNA transcription, but abnormal levels of ATP in a living organism can lead to pathogenesis. Su and his colleagues thus developed a dual-target electrochemical sensor derived from the modification of a GCE with MoS_2 decorated with AuNPs to enable high sensitivity, high selectivity, and the simultaneous detection of TB and ATP. Two probes labeled with the aptamers of Fc and MB (a hairpin and double-stranded structure, respectively) were simultaneously immobilized on the AuNPs-MoS_2 nanocomposite via Au-S bonding. The MoS_2-based aptamer sensor was able to simultaneously detect ATP and TB with a linear range of 1 nM-10 mM for ATP and 0.01 nM-10 μM for TB, a detection limit of 0.74 nM for ATP and 0.0012 nM for TB, and operational stability [111].

Immunosensors on MoS_2 for detection of microRNA-21 and DNA An electrochemical biosensor for the analysis of microRNA-21 (miRNA-21) and riboflavin using a GCE modified by AuNP-decorated MoS_2 was fabricated. The electrochemical activity of thiolated DNA1 functionalized on the AuNPs attached to MoS_2 was studied using standard redox probes of $[Fe(CN)_6]^{3-/4-}$ and $[Ru(NH_3)_6]^{3+}$. As demonstrated in Fig. 6a-c, the MoS_2-based biosensor was proven to be highly suitable for clinical diagnosis and biochemical studies of DNA/miRNA [112]. Zhu and his colleagues also reported an electrode consisting of MoS_2 functionalized with thionine and AuNPs (MoS_2-Thi-AuNPs) prepared using microwave-treated hydrothermal synthesis for the detection of miRNA-21 in biological samples with satisfactory results. The high sensitivity of their electrode arose due to the large surface area of the MoS_2-Thi-AuNP nanocomposite, which allowed the

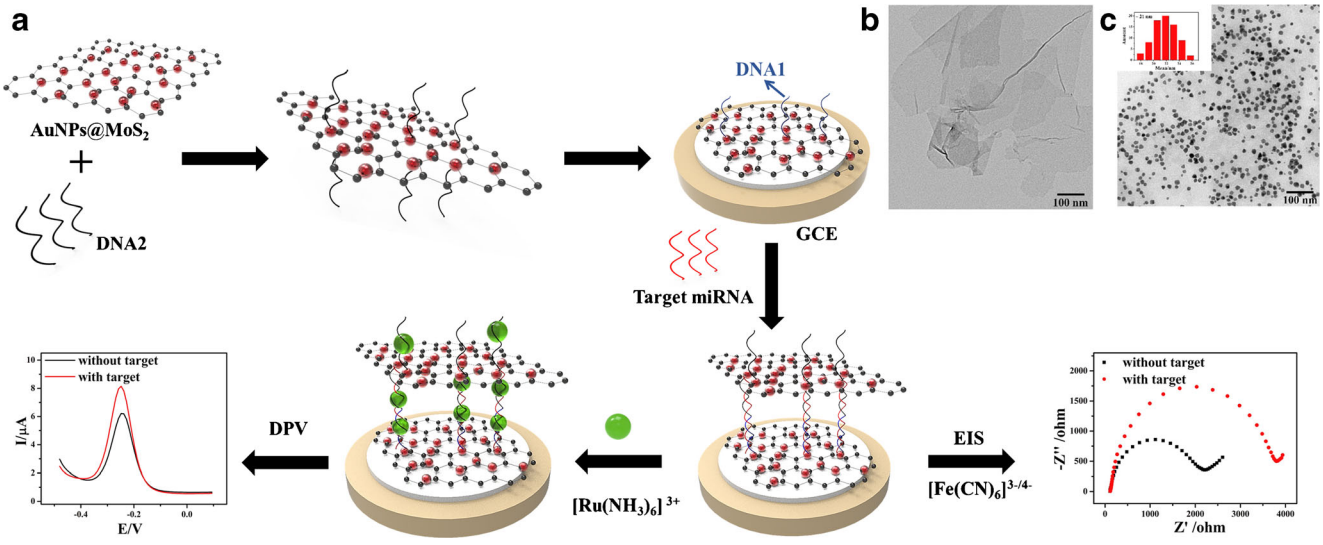


Fig. 6 **a** Schematic illustration of the fabrication of AuNP-decorated MoS_2 nanosheets for label-free and dual-mode electrochemical assays for microRNA-21 detection. TEM images of **b** MoS_2 and **c** the AuNPs@MoS_2 nanocomposite. Inset: The statistical diameter of AuNPs decorated on the MoS_2 nanosheet surface. Reproduced from Su et al. (2017) with permission from Elsevier Publishing Group [112]

loading of a large amount of probe DNA for the capture of the miRNA-21 target and thionine. The AuNPs not only facilitated the immobilization of the probe DNA via Au bonds but also increased the conductivity of the electrode, increasing the performance of the biosensor [113].

Shuai and his collaborator prepared an ultrasensitive electrochemical biosensor for the detection of miRNA-21 based on GCE electrodes modified with AuNPs and hollow MoS_2 microspheres. Biotinylated ssDNA capture probes were immobilized on AuNPs/MoS_2 microcubes using the signal amplification of dual-specificity nucleases and ECC redox cycles. This immunosensor exhibited a sensitive response to miRNA-21 with respect to its linear range and LOD, had high sensitivity and selectivity, and illustrated that miRNA-21 could be detected in human serum samples using DPV [114]. Chen et al. proposed a sandwich-type biosensor for miRNA-21 detection in human serum samples using carbon sphere-MoS_2 fabricated with hydrothermal synthesis. The target miRNA-21 and avidin-horseradish peroxidase (avidin-HRP) enzymes attached to the electrode, which acted as a signal indicator and led to the catalytic reaction of H_2O_2 with the HQ redox system. The biosensor demonstrated a wide linear range of 1×10^{-16} to 1×10^{-10} M and a LOD of 0.016 fM [115].

Wang's research group described the preparation of a label-free ultrasensitive electrochemical DNA sensor based on a thin-layered MoS_2-modified CPE for the DPV detection of DNA. A simple ultrasonic exfoliation process produced thin MoS_2 nanosheets from bulk MoS_2. Compared with bulk MoS_2, positively charged guanine and adenine were more readily adsorbed on the nano-MoS_2 surface due to van der Waals forces and the sensor had higher electrochemical detection of target DNA with good selectivity via the electrostatic adsorption of the active sites [116]. Wang's research team prepared an electrochemical sensor based on 32-mer homologous adenine DNA (A32) at MoS_2-graphene nanocomposite-modified Au electrode for the detection of riboflavin (RF). The MoS_2-graphene nanocomposite was synthesized using a modified L-cysteine-assisted hydrothermal method. The proposed sensor was analyzed using SEM, XPS, CV, and EIS and it was found to have a wide linear range, high sensitivity, and good stability [117]. Sumathi's research group demonstrated the detection of RF in urine and multivitamin samples using an SPCE modified by a strong π-π stacking DNA hybrid with PEDOT on carbon-supported MoS_2 and the iron oxide film. The proposed biosensor provided a broader linear range and strong electrocatalytic behavior [118]. Xiong's research team demonstrated dual-signal electrochemical ratiometry, and an exonuclease III (Exo III) assisted target recycling strategy using a mimetic biomembrane-AuNP-graphene hybrid matrix for the detection of target DNA (T-DNA). The presence of T-DNA changes the structure of the stem-loop (hairpin) DNA capture probe (HP) on the sensor's surface, generating a nicking site for Exo III and causing the linear chain cleavage of HP. Gold bonding provokes changes in the peak currents of MB and Fc on the gold electrode surface. The electrochemical biosensor exhibited satisfactory stability, specificity, and reproducibility [119]. Shim and colleagues prepared modified GCE with silver nanoparticles using nanopores and the methyl-binding protein (MBP) MBD1x in MoS_2 membranes for the detection of cytosine nucleotides in DNA [120].

Immunosensors on MoS_2 detection of Cancer biomarker The detection of circulating tumor cells (CTCs) has clinical significance in breast cancer therapy. Tian and colleagues used a magnetic field-assisted cytosensor on Fe_3O_4 and rGO/MoS_2-modified GCE for the detection of MCF-7 CTCs in human blood serum samples. The nanosheet RGO/MoS_2 nanocomposite had a larger active surface area, and the more integrity of the individual constituents of MoS_2 and rGO provides a larger number of electroactive sites per unit area. The rGO/MoS_2 composite subsequently demonstrated good catalytic performance towards the synergistic catalysis of H_2O_2 with Fe_3O_4NPs. The sensor also had good selectivity with a LOD of 6 cells mL^{-1} [121].

A label-free electrochemical immunosensor consisting of shape-controlled AuNPs decorated on thionine-MoS_2 (AuNP-Thi-MoS_2) for the highly sensitive detection of CEA in human serum samples. The AuNPs were loaded on Thi-MoS_2 using a microwave-assisted hydrothermal method. The prepared AuNP-Thi-MoS_2 nanocomposite not only retained the electrochemical activity of thionine but also increased the CEA load. The electrochemical immunosensor demonstrated high sensitivity, excellent selectivity, and long-term stability [122]. Another report an immunosensor based on Ag/MoS_2@Fe_3O_4 for the detection of CEA in human serum samples was done by Wang et al. The sensor exhibited a suitable detection range (0.0001 ng/mL to 20 ng/mL) and LOD (0.03 pg/mL) [123]. Wang and colleagues also reported accurate label-free electrochemical CEA detection in human serum samples and the direct fabrication of an electrochemical immunosensor based on flower-like AgNPs and a MoS_2/rGO nanocomposite. The synergistic effect of the AgNPs and the MoS_2/rGO nanocomposite led to acceptable reproducibility, excellent selectivity, and satisfactory stability. The electrochemical response of their proposed immunosensor exhibited high sensitivity and a low LOD using an amperometric i-t curve [124]. A highly dispersed, shape-controlled Prussian blue nanocubes (PBNCs) on a MoS_2 nanosheet surface was fabricated for the detection of non-enzymatic H_2O_2 and label-free CEA in serum samples, with satisfactory results. The MoS_2-PBNC nanocomposite was successfully synthesized with a simple method using K_3[Fe $(CN)_6$] and $FeCl_3$. Characterized by TEM, XRD, FTIR, and XPS, the proposed nanocomposite detected non-enzymatic H_2O_2 and label-free CEA with high selectivity and high stability [125].

SPE electrodes modified by amine-derivatized MoS_2 nanosheets for the label-free electrochemical detection of PSA in spiked serum samples of healthy subjects, exhibiting high sensitivity and a LOD of 10^{-3} ng/mL over a very wide quantitation range (10^{-3} to 200 ng/mL). The sensor analysis results revealed that the -NH_2-modified MoS_2 nanosheets bio-interfaced with the anti-PSA antibodies EDC-NHS as a crosslinker [126]. Duan et al. reported a nanocomposite of graphitic carbon nitride (g-C_3N_4) nanosheets and MoS_2 QDs with chitosan-stabilized AuNPs for the selective detection of PSA in blood serum samples. Their MoS_2QD@g-C_3N_4@CS-AuNP aptasensor exhibited a fast response and a highly sensitive LOD (0.020 pM) for PSA concentrations ranging from 2.85×10^{-5} to 0.0285 nM, in addition to excellent selectivity, regeneration, stability, and reproducibility [127]. Qiao et al. created aptamer-MoS_2 nanoconjugates for the detection of cardiac troponin I (cTnI), which is a specific biomarker for the early diagnosis of acute myocardial infarction. The MoS_2-nanosheet-based aptasensor had a linear range of 10 pM to 1.0 μM, with a lower detection limit of 0.95 pM [128].

A unique dual sandwich electrochemical aptasensor for the sensitive detection of platelet-derived growth factor-BP (PDGF-BB) in serum samples was developed from thiol-terminated PDGF-BB aptamer-1 (Apt1)/AuNP/MoS_2/CA and AuNPs with thiol-terminated PDGF-BB aptamer-2 (Apt2) and 6-ferrocenyl hexanethiol (Fc). The developed electrochemical sensor exhibited specificity for PDGF-BB [129].

Immunosensors on MoS_2 for detection of virus and Bacteria Hepatitis B virus (HBV) is one of the causative agents in chronic clinical treatments. Li and colleagues reported an immunosensor based on a MoS_2@Cu_2O-Pt nanohybrid as an enzyme mimic for the detection of hepatitis B surface antigen (HBsAg). The amperometric HBsAg sensor results indicated excellent sensitivity and selectivity [130]. Similarly, Gao's research team synthesized MoS_2-functionalized MWCNT-loaded Au@Pd NPs, which were used to modify a GCE. Their sensitive sandwich electrochemical immunosensor was used in the quantitative electrochemical detection of HBsAg in serum samples. A simple one-step solvothermal process was used to synthesize the MoS_2@MWCNTs. The proposed immunosensor had a good linear range, LOD, specificity, repeatability, and stability [131]. Chekin and his collaborators investigated the performance of modified electrodes assembled with rGO and MoS_2 for the selective detection of human papillomavirus (HPV) in biological samples. The DPV sensor had a detection range of 3.5 pM to 35.3 pM with a LOD of 0.1 ng mL^{-1} (1.75 pM) [132].

Microcystins are a known group of toxins produced by cyanobacteria that have a harmful effect on mammals. Zhang and colleagues recently developed a sensitive electrochemical immunosensor for the detection of microcystin LR in water using a MoS_2/AuNR nano complex and HRP antibody-modified Au electrodes. AuNRs improved the electronic conductivity of MoS_2 and inhibited the restocking of MoS_2. The proposed immunosensor had the advantages of high sensitivity and good reusability [133]. *Salmonella typhimurium*, a Gram-negative pathogen, is one of the most common bacteria responsible for food-borne illnesses. Recently, Singh and colleagues designed a microfluidic immunosensor based on CTAB-functionalized MoS_2 nanosheets deposited onto an ITO microfluidic immunochip electrode for the label-free, rapid, and reliable detection of *S. typhimurium*. The CTAB-functionalized MoS_2 was synthesized using chemical exfoliation. The results from EIS indicated that CTAB-MoS_2-NS had an excellent wide detection range, a low detection limit, and increased sensitivity [134].

A highly sensitive electrochemical aptamer for Ochratoxin A (OTA) detection based on the selective binding of 2D MoS_2 with the aptamer. Single-stranded OTA aptamer hybridizes with an auxiliary DNA strand immobilized on Au electrode, generating a rigid dsDNA. In the presence of target OTA, the OTA-aptamer binds with OTA competitively, causing the unwinding of dsDNA. Then the 2D MoS_2 can adsorb on an electrode surface through the single-stranded aDNA left on the electrode. The 2D MoS_2 possesses peroxidase-like activity can catalyze the hydroquinone/benzoquinone redox system to exhibit amplified electrochemical signal. Amperometric sensing was operated at −0.2 V vs. SCE for OTA determination in the concentration range from 0.5 pg mL^{-1} to 1.0 ng mL^{-1}, with a low LOD of 0.23 pg mL^{-1}. Also, determination of OTA was checked in spiked red wine for real applicability measurements [135].

Immunosensors on MoS_2 for detection of protein C-reactive protein (CRP) is a liver-synthesized protein for which any abnormal change in CRP levels in serum may indicate the presence of inflammation and disease. In particular, CRP is the most powerful predictor of cardiovascular disease, so its detection is essential in clinical diagnosis. Zheang et al. developed a rapid, ultrasensitive, and practical label-free electrochemical immunosensor that employed GCE-modified MoS_2-PANI-GNPs for the detection of CRP in human serum with satisfactory results. Compared with a bare electrode, MoS_2-PANI-GNP exhibits 10 times better catalytic peak current value. In addition, MoS_2-PANI-GNP had a large number of adsorption sites and a large surface area, which greatly increased the loading of antibodies, thus significantly improving bio-induction performance [136].

Alpha-fetoprotein (AFP), an important clinical tumor marker for hepatocellular carcinoma (HCC), is a plasma protein produced by the yolk sac and secreted from the liver of a developing fetus. Therefore, a rapid, sensitive, and reliable analytical method for AFP detection is of great importance for the early clinical diagnosis and long-term treatment of HCC. He et al. used a modified GCE, and a primary antibody

(Ab1) immobilized on gold nanoparticles to decorate a sandwich-type biosensor-based empty MoS_2 microbox for the electrochemical detection of AFP in human serum samples. This detection system was synthesized in three steps: (1) the primary antibody (Ab1) was immobilized on the AuNP surface, (2) a secondary antibody (Ab_2) was bound to DNA primers, and (3) long DNA concatemers from HCR were used as a carrier for two horseradish peroxidases via the biotin-avidin reaction. DPV was used to achieve a wide linear range and a low LOD, and the sensor had excellent selectivity, being able to distinguish the difference between various proteins and AFP [137].

Immunosensors on MoS_2 for drug sensing An electrochemical immunosensor was developed for clenbuterol determination based on MoS_2-AuPt nanocomposite and the biotin-streptavidin system. First, the L-cysteine-functionalized MoS_2 nanosheets were modified on a GCE then AuPt-NPs were coated for electron transfer and signal amplification. To further improve the sensitivity and selectivity, a biotin-streptavidin system was employed on the sensor surface. The biotin-streptavidin system was an efficient way to enrich active sites. Finally, the proposed sensor catalyzed the reduction of H_2O_2 and exhibited an excellent electrochemical activity in terms of high selectivity, a wide linear concentration range, a low LOD, and acceptable reproducibility and stability and can be used for CLB detection in real pork samples [138].

Electrochemiluminescence sensors for MoS_2 nanocomposites

Electrochemiluminescence (ECL) is chemiluminescence induced and controlled by an electrochemical technique that provokes the electron transfer reaction of a luminescent species on an electrode so that it reaches an excited state and emits light. It is widely used to detect a variety of chemical and biological analytes because of its high versatility, low LODs, wide linear detection range, low background noise, simple optical instrumentation setup, easy handling, and excellent repeatability. Over the last few years, chalcogenide nanomaterials such as semiconductor quantum dots (QDs), carbon-based materials, metal nanoclusters (NCs), and upconverted nanoparticles (UCNPs) have been used as luminescentmaterials. However, the most commonly used ECL materials, such as CdTe, CdS, and CdSe have several disadvantages, such as high toxicity, and non-recyclable solutions. In order to overcome these problems, layered MoS_2-based AuNPs, CdS, and ZnS-CdS nanocomposites provide excellent biocompatibility and have been successfully used as a substrate for the detection of H_2O_2, glucose, immunoglobulin E (IgE), concanavalin A (Con A), carcinoembryonic antigen (CEA), parathyroid hormone (PTH), prostate-specific antigen (PSA), 2-methyl-4-chlorophenoxyacetic acid (MCPA), tetrabromobisphenol A (TBBPA), non-esterified fatty acids (NEFA), beta-hydroxybutyrate (βHBA), Pb(II), kanamycin, and platelet-derived growth factor-BB in real samples.

Electrochemiluminescence performance on MoS_2 for DNA sensing Recently, fullerene MoS_2 nanostructures have demonstrated excellent catalytic and tribological properties and have been successfully prepared and used in ECL applications. Therefore, MoS_2-based composites containing low toxicity or non-toxic ECL species and offering outstanding stability and better recyclability have been recommended as the basis for a new analytical sensing platform for ECL applications. For example, a modified GCE was prepared using PEI-CdS/ZnS QDs, which acted as solid support for capturing DNA (S1), with MoS_2-Au acting as a supporter of reporter DNA (S3). This sensor was employed to measure target DNA concentrations in the range of 0.05–1000 fM with a detection limit of 0.023 fM. It was also found that the prepared MoS_2-Au was capable of excellent H_2O_2 catalytic performance in the reduction reaction [139].

A photoelectrochemical biosensor for DNA sensing based on a CdS/MoS_2 heterojunction and luminal as chemiluminescent. The capture DNA (C-DNA) was immobilized on the CdS/MoS_2 attached ITO surface by an amide reaction followed by hemin interaction to oxidize the luminol and produce chemiluminescence. The proposed photoelectrode was able to detect target DNA concentrations in the range of 1 fM to 100 pM and had a LOD of 0.39 fM [140]. Label-free electrochemical cycling tumour DNA-sensing platform based on nano-MoS_2/graphene composites have also been reported. This material was fabricated by simply combining nano-MoS_2 and graphene using hydrothermal and ultrasonic methods. The nucleobase-graphene intermolecular π-π stacking interaction also contributed to the immobilization of ssDNA on the 2D MoS_2/graphene composite-modified GCE. This sensor had a detection limit of 1×10^{-17} M and a linear detection range of 1.0×10^{-16} M to 1.0×10^{-13} M using DPV [141]. In other research, a thin layer of MoS_2 was prepared from bulk MoS_2 by ultrasonic exfoliation, and free-supporting ZnO nanosheets were then electrodeposited onto the MoS_2 scaffold for DNA sensing. The ZnO/MoS_2 nanosheets were used as an excellent biosensing platform with methylene blue as an indicator. The functionalized ZnO/MoS_2 biosensor had high sensitivity, a detection range of 1.0×10^{-15} M to 1.0×10^{-6} M, and a detection limit of 6.6×10^{-16} M [142]. A highly sensitive DNA sensor was developed by Sun et al. They synthesized 3D flower-like MoS_2/GO/o-MWNTs nanohybrids and used them to immobilize quaternary Cu-Zn-In-S nanocrystals. Here, semicarbazide (Sem) was used as a coupling agent to attach the NCs to MoS_2/GO/o-MWNT, but also as a novel co-reaction promoter to increase ECL intensity. The authors reported that the sensor displayed a linear range of 10 nM to 10 pM and a LOD of 10 aM for tDNA detection, along with low

toxicity, excellent stability, and remarkable specificity [143]. Parathyroid hormone (PTH) is a polypeptide with 84 amino acids that closely regulates calcium and phosphate metabolism in bone, kidneys, intestines, and extracellular fluids. Because of its importance to body functions, a simple, highly sensitive, low-cost, and selective detection method for PTH is required. For this purpose, Kim et al. reported a biosensor based on a MoS_2-MG composite prepared using hydrothermal synthesis, assisted by L-cysteine, to modify an Au electrode. The multifunctional groups within L-cysteine (such as -SH, -NH_2 and COO^-) contributed to the alteration/functionalization of biomolecules, hormones, proteins and nucleic acids on the surface of the MG. The interaction between PTH and MG was analyzed using electrochemical sensing techniques. A sandwich enzyme-linked immunosorbent assay (ELISA) was used as a modified MG electrode with PTH, and alkaline phosphatase (ALP)-MG sensor performance was investigated using CV to evaluate its linearity, repeatability, and reproducibility. The ALP-PTH-MG sensor exhibited a linear response to PTH in artificial serum in the range of 1–50 pg mL^{-1} [144].

Electrochemiluminescence on MoS_2 for Sensing of Protein An innovative MoS_2-based electrochemical platform was used for the highly sensitive quantification of iron-binding protein and bovine serum albumin (BSA). An Au SPCE was modified with MoS_2 nanoflakes and then bioconjugated with anti-BSA antibodies. The binding of the antibodies to the surface of the MoS_2 was achieved only with hydrophobic interactions. Using a bioelectrode, CV analysis was performed in the presence of Fe^{3+}/Fe^{2+} redox probes, generating a linear response to peak currents at different BSA concentrations over a wide range of concentrations from 0.01 to 10 ng/mL and a very low LOD (0.006 ng/mL) [145]. An ECL aptasensor was prepared by using CdS-MoS_2 with a DNAzyme as a quencher for the sensing of IgE in blood samples. The flower-like CdS-MoS_2 composite was prepared using hydrothermal synthesis. A GCE was modified with complementary ssDNA (NH2-ssDNA) attached CdS-MoS_2 complex and IgE aptamer (T-Apt). Following this, the conjugate of DNAzyme-AuNP and T-Apt was hybridized with NH_2-ss DNA to form dsDNA. The fabricated aptasensor exhibited high sensitivity, a wide linear concentration range (0.001–10.0 nM), and a low LOD (0.34 pM; $S/N = 3$) [146]. Electrochemiluminescence biosensor based on Ag-polyamidoamine dendrimer-luminol-GOx nanocubes (AgNCs-PAMAM-luminol- GOx) to detect Con A in human serum samples as shown in Fig. 7. The faradaic current was proportional to Con A concentration within the range of 5.0×10^{-6}-2.0×10^{-2} μg/mL with a detection limit of 1.7×10^{-6} μg/mL. The AgNCs and MoS_2 also had the ability to generate reactive oxygen species from H_2O_2, further improving the intensity of ECL [147]. Wu et al. designed a PEC biosensor for glucose based on a MoS_2-GOD-modified ITO substrate. MoS_2 nanosheets are obtained using a simple thermolytic method and a C_3N_4 sacrificial template. The 3D porous framework of the ultra-thin MoS_2 nanosheets offered a large surface area and a uniform pore size distribution, which was conducive to the adsorption of GOx and thus facilitated

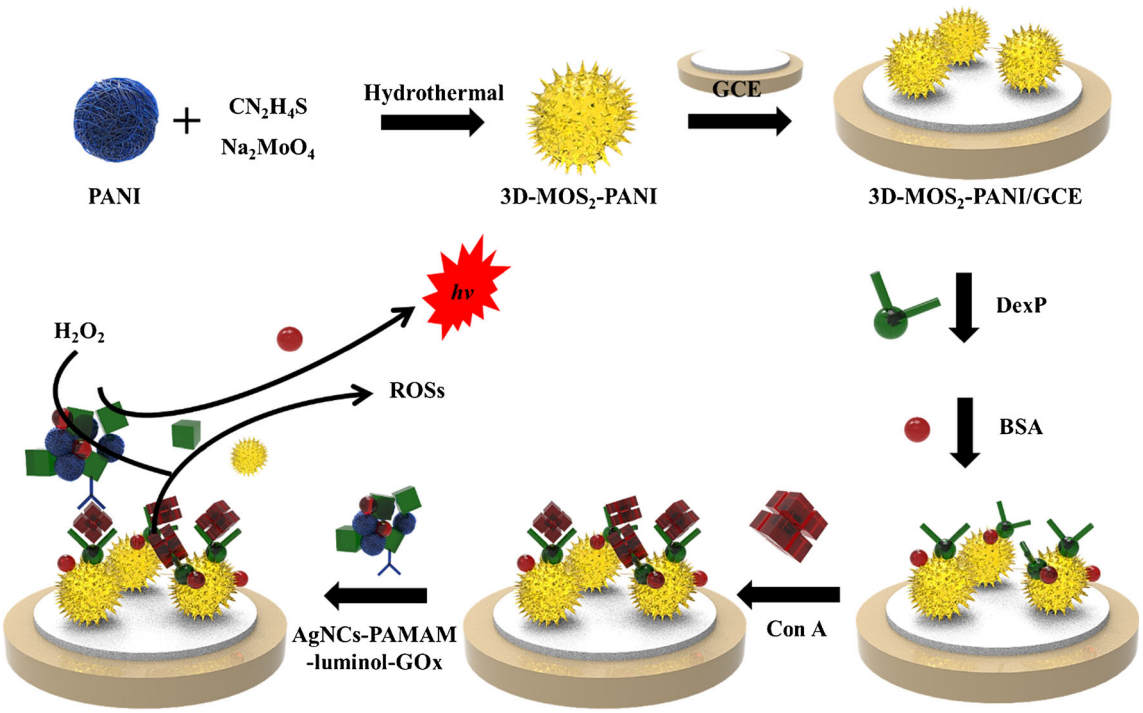


Fig. 7 Schematic diagram of the preparation of a 3D-MoS_2-PANI-based ECL biosensor [147]

selectivity for glucose absorption by immobilizing GOx on its surface. As an innovative photocatalytic material sensitive to visible light, ultrafine MoS_2 nanosheets have a detection limit of ~0.61 nM [148]. Liu et al. developed a composite material consisting of MoS_2 nanosheets and TiO_2 nanorods on which GOx was immobilized to act as a biosensor for glucose. During the hydrothermal reaction, the TiO_2 nanostructures acted as the growth templates to prevent the MoS_2 nanosheets from restacking. The PEC glucose biosensor exhibited a linear range of 0.1–10.5 mM, a sensitivity of 0.81 μA mM-1, and a LOD of 0.015 mM within the visible spectrum [149].

Electrochemiluminescence on MoS_2 for Cancer Biomarker detection The early detection of cancer plays a key role in clinical research, biomedical diagnosis, and clinical treatment. CEA (molecular weight: 200 kDa) and PSA are glycoprotein cancer biomarkers produced by human tumour cells and are used in the clinical identification and treatment of many cancers, such as colon, lung, ovarian and breast cancer. Therefore, it is essential to develop effective ECL biosensors for the early detection of CEA. For instance, Wang et al. developed an ECL aptasensor based on ZnS-CdS nanoflower-decorated MoS_2 for the detection of CEA in human serum samples. It had a linear range of 0.05 to 20 ng mL^{-1} and a LOD of 0.031 ng mL^{-1} with specificity against interfering proteins [150]. An electrochemiluminescence (ECL) immunosensor was fabricated by sandwich process. The MoS_2-PEI-Au nanocomposites and Au@BSAcore/shell was constructed for the ultrasensitive detection of AFP in serum samples. The developed sensor provides a very low detection limit of 1.0×10^{-5} ng/mL in the linear concentration range berween 0.0001 ng/mL and 200.0 ng/mL of AFP [151].

Kukkar et al. successfully established an efficient synthesis method for MoS_2 nanosheets and demonstrated their application in the label-free detection of the PSA cancer marker. For this purpose, few-layered Na^+ intercalated MoS_2 based FET biosensor was fabricated. This method created a powerful site-directed immunodetection device by the sulfhydryl (-SH) group in biologically exposed antibodies that contacted the surface S atoms of the MoS_2. This device had a significant LOD of 10^{-5} ng/mL [152]. Another related work developed a sensitive and selective electrochemical immunosensor for the detection of prostate-specific antigen (PSA) concentrations in spiked serum samples using physical adsorption on biological electrodes. The MoS_2-QD was synthesized from pre-exfoliated MoS_2 nanosheets. As a zero-dimensional material, MoS_2-QDs were decorated on an SPCE, which offered useful electronic properties due to quantum confinement and edge effects. The optimal CV response to PSA ranged from 0.1 pg·mL^{-1} to 10 ng·mL^{-1} (scan rate: 0.05 mVs^{-1}). When EIS was used, a wide dynamic concentration range (0.01 pg·mL^{-1} to 200 ng·mL^{-1}) and a LOD of 0.01 pg·mL^{-1} was reported [153].

Electrochemiluminescence study on MoS_2 for Sensing of fatty acids The levels of non-esterified fatty acids (NEFAs) can be used to assess the risk of clinical malignancy in cattle, including impaired fertility, reduced milk production, loss of immunity, uterine infections, mammary infections, and loss of appetite. Tuteja and colleagues reported a MoS_2-based portable immunosensor with anti-NEFA antibodies for the detection of NEFAs. The MoS_2 nanostructure significantly improved the electron transfer signal generated during the AB and antigen binding events in the electrochemical reactions [154]. The NEFA sensor provided a dynamic range of 0.1 to 5 mM ($R^2 = 0.995$). The same research group also successfully developed an electrochemical biosensor for βHBA in spiked serum, milk, blood and real serum samples with a relatively low LOD and a dynamic linear response range of 0.7 mM to 10 mM by utilizing a 2D MoS_2-antigen nanocomposite. The MoS_2 nanosheet was exfoliated in the liquid phase by ultrasonication and subsequently deposited on an SPE modified with an Au colloid. The 2D MoS_2 not only amplified the electron transfer but also served as an ideal electrode material for protein immobilization with high retention activity in the electrochemical reaction when used as a biosensor [155]. Hassanzadeh et al. reported an ultrasensitive chemiluminescent biosensor for the detection of cholesterol in human serum samples and obtained a LOD of 35 nmol L^{-1} ($S/N = 3$) and a linear range of 0.08–300 μmol L^{-1} with good specificity, stability, and reproducibility [156]. TiO_2-MoS_2-AuNP flower-like nanocomposite was synthesized and used it as a scaffold on an ITO electrode to develop a PEC aptasensor, which exhibited good selectivity, a wide linear range of 0.2–450 nM, and a LOD of 0.05 nM for the detection of kanamycin in milk samples under visible light [157].

Electrochemiluminescence on MoS_2 for Sensing of Pollutants A molecularly imprinted ECL sensor was developed for the detection of MCPA based on a MoS_2-GQD hybrid nanocomposite. MCPA is an herbicide which has been used to control broad-leaved weeds in cereal and grass seed crops. The detection limit of this sensor system was 5.5 pmol L^{-1} (S/N = 3) with the linear range of 10 pmol L^{-1} to 0.1 μmol L^{-1}, which indicates its potential for the detection of trace amounts of pesticides and veterinary drugs in food [158]. A photoelectrochemical immunosensing system was prepared for the detection of TBBPA, which has been found in sediments, sewage, wildlife, and human serum, using an AuNC/MoS_2 nanocomposite. A photocurrent response in the MoS_2 nanosheets can be achieved with the integration of Au nanocrystals due to energy transfer based on surface plasmon resonance effects. The TTR/AuCN/MoS_2/GCE photoelectrochemical sensor showed high sensitivity and the ability to sense TBBPA in water samples with excellent recovery rates [159]. Du et al. reported another example of a novel ECL biosensor based on CdSe@CdS QD-

functionalized MoS_2 for the sensitive detection of Pb (II) in the Jingmi River [160]. The sensor results showed a LOD of 0.98 fM and a wide linear range for Pb (II) detection (1.0×10^{-15} to 1.0×10^{-11} M).

Conclusion and future outlook

This review summarizes the development of MoS_2-based chemically modified electrodes, a field of research that holds enormous potential and attracts significant interest in electroanalytical chemistry. Layered MoS_2 has been triggering materials science researchers to designing and producing a novel exciting 2D or 3D hybrid components with combination of MoS_2 and other 1D/2D blocks. Several progresses have been made for the fabrication of 3D MoS_2, it still lacks from some limitations as complicated preparation steps and inherent activity. Hence, stable preparation high quality MoS_2 in large area for technological applications remains to be explored. Highly sensitive and selective MoS_2 nanohybrids that incorporate functional materials such as metal NPs, metal oxides NPs, polymeric NPs, carbon nanomaterials have been discussed, and their excellent electrocatalytic properties have been emphasized. The MoS_2 nanohybrids can also be produced using hydrothermal synthesis, ultrasonic exfoliation, electrochemical deposition, and physical methods. Each of these methods in principle has a common goal of achieving nanosized materials, interesting morphology, excellent conductivity, and stable functional materials. However, challenges in control of size, crystallinity, and defects (edges) in 2D MoS_2 needs to be addressed clearly to understand their role in enhancing the kinetics, charge transport, sensitivity and selectivity of electrochemical sensors.

This review particularly emphasizes recent advances in the synthesis of thin 2D nanosheets without stacking or aggregation and their applications in biosensors, photoelectrochemical sensors, chemiluminescence sensors, and immunosensors. MoS_2-based electrode materials have demonstrated high electrocatalytic activity and selectivity due to outstanding electronic, structural and physicochemical properties. These materials also provide a suitable biocompatible environment for enzyme immobilization, markedly improving the sensitivity of these sensing devices toward the analytes of multiple interests. The research in MoS_2 based electrochemical sensing system for environmental pollutants, neurological markers, and pharmaceutical drugs for cancer, diabetes and Alzheimer disease can garner interest in different technologies since they can be optimized to detect these analytes. However, some challenging aspects must be addressed for the practical viability including large scale production, safety, miniaturization and affordability of these sensors. Several MoS_2 based materials used in the development of sensors and biosensors are still cumbersome to fabricate, and the modified electrodes do not meet all the essential requirements for analytical procedures, validity and field measurements, and threshold concentration ranges of environmental and clinical applications. Fabrication of prototypes for commercial exploration of electrochemical sensors and biosensors for the pharmaceutical fields belong to an unexplored area. The applicability of these developed sensing systems depends on the reduction of the financial crisis and the usage of materials. In addition, wearable MoS_2 sensing products like electronic skin patches a promising for several clinical, securities and environmental protect sensing devices which needs to be structured. It is expected that by fabricating sensitive, flexible and wearable micro- or nano-electrode arrays in large scale, 2D MoS_2-based electrochemical sensing devices will become commercially available in the future. Significant effort is still needed to implement these ultrasensitive sensors in real-world applications and point of care clinical analysis.

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