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A molybdenum disulfide/nickel ferrite-modified voltammetric sensing platform for ultra-sensitive determination of clenbuterol under the presence of an external magnetic field†

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The electrochemical behavior and sensing performance of an electrode modified with NiFe₂O₄ (NFO), MoS₂, and MoS₂-NFO were thoroughly investigated using CV, EIS, DPV, and CA measurements, respectively. MoS₂-NFO/SPE provided a higher sensing performance towards the detection of clenbuterol (CLB) than other proposed electrodes. After optimization of pH and accumulation time, the current response recorded at MoS₂-NFO/SPE linearly increased with an increase of CLB concentration in the range from 1 to 50 μM, corresponding to a LOD of 0.471 μM. In the presence of an external magnetic field, there were positive impacts not only on mass transfer, ionic/charge diffusion, and absorption capacity but also on the electrocatalytic ability for redox reactions of CLB. As a result, the linear range was widened to 0.5–50 μM and the LOD value was about 0.161 μM. Furthermore, stability, repeatability, and selectivity were assessed, emphasizing their high practical applicability.

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1. Introduction

Recent years have seen renewed interest in spinel ferrite materials (MFe₂O₄) due to their unique physical and chemical properties, for example, good biocompatibility, high chemical stability, diversity of redox states, low cost, and unique magnetic properties.^{1–8} Here, NiFe₂O₄ (NFO) is a special

member of the spinel ferrite family (MFe₂O₄-M = Co²⁺, Mn²⁺, Ni²⁺, and Zn²⁺) with an inverse spinel structure, in a bulk state. Fe³⁺ ions occupy the tetrahedral sites, while the octahedral sites are shared by Fe³⁺ and Ni²⁺ ions.³ Previous studies pointed out that the surface, size, crystallinity, morphology, and composition strongly correlate with the physicochemical properties of spinel ferrite materials.^{9–13} Moreover, these properties are influenced by some advanced parameters such as dimension, dispersion, and surface area which can be changed by combining with various nanomaterials.^{13–17}

For the aim of enhancing the inherent characteristics, many spinel ferrite-based nanocomposites have been fabricated for boosting their diversity applicability from environmental, biomedical, and sensors to biotechnology applications.^{18–21} Among them, MoS₂/NFO has been considered a highly promising nanocomposite for many different applications. Benefiting from possessing a large surface area and impressive structure with three atomic layers S-Mo-S stacked by van der Waals forces, MoS₂ layers could support the effective dispersion of NFO nanoparticles (NFO NPs).^{22–24} Besides, owing to the presence of two different components within a structure, NFO NPs remarkably prevented the aggregation of MoS₂ layers, leading to better connections and interactions between MoS₂ and NFO as well as creating a larger active surface area. Accordingly, MoS₂-NFO has been used as a potential candidate for electrochemical supercapacitors, catalysis, and energy conversion applications.²⁵ For instance, M. Karpuraranjith

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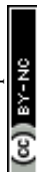
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*et al.*²⁶ reported MoS₂-NFO as an efficient dual-functional hybrid catalyst for the oxygen evolution reaction and degradation of dye pollutants. Yan Zhao *et al.*²⁷ also developed NFO-MoS₂ composites with great synergistic effects, which offered a higher-performance supercapacitor, compared with that of individual MoS₂ sheets and NFO NPs, respectively. In another research, Wenzhi Fu *et al.*²⁸ demonstrated the enhanced visible-light photocatalytic activities in the NFO-MoS₂ structure.

However, as far as we know, the greater insight into the electrochemical characteristics and sensing performance of NFO-MoS₂-modified electrodes has been not still explored while it is one of the essential goals in opening new opportunities for novel applications of not only NFO-MoS₂ but also spinel ferrite-based nanomaterials. As known, NFO-MoS₂ nanocomposites possess many advantages, which are very beneficial for electron transfer reactions, electrochemical behaviors, and electrocatalytic activities including large active surface area, high electronic conductivity, good redox chemistry, and potential electrocatalytic. Such merits promise to provide outstanding electrochemical properties and performance for NFO-MoS₂-modified electrodes. In this work, NFO, MoS₂, and MoS₂-NFO nanocomposites were prepared using simple methods including hydrothermal and probe sonication methods, aiming to modify the working electrode surface of commercial screen-printed electrodes (SPEs). The electrochemical characteristics and sensing performance towards clenbuterol (CLB) detection of the proposed electrodes were thoroughly investigated. Among modified SPEs, MoS₂-NFO (2 : 1)/SPE exhibited impressive electrochemical properties and sensing performance compared with other modified electrodes. Particularly, as demonstrated in our previous reports, the positive effect of the presence of the external magnetic fields on electrochemical behaviors and sensing performance was demonstrated.^{29–32} Herein, the influence of external magnetic field (MF) on the MoS₂-NFO (2 : 1)/SPE was also further evaluated, contributing to optimizing the new research in the future.

2. Experimental section

2.1. Chemicals

All chemicals were reagent grade and used as received: sodium hydroxide (NaOH >98%), polyvinylpyrrolidone (PVP), NiCl₂, and FeCl₃·6H₂O were obtained from Xilong Scientific Co., Ltd. (China) and Guangdong Guanghua Sci-Tech. Co., Ltd. K₃(Fe(CN)₆), K₄(Fe(CN)₆)·3H₂O, clenbuterol (CLB), and molybdenum(IV) sulfide (MoS₂) (98%, <2 μm) were purchased from Sigma-Aldrich (USA). Phosphate buffer saline (PBS, pH 7.4) was employed as a supporting electrolyte and was prepared from NaCl, KCl, Na₂HPO₄, and KH₂PO₄. Further, the pH of the buffer solution was adjusted by H₃PO₄ and NaOH solutions. The carbon screen-printed electrode (SPE) was provided by DS Dropsens, Spain. The dimensions of SPE are 3.4 × 1.0 × 0.05 cm (*L* × *W* × *T*). The structure of SPE consists on:

- + Working electrode: carbon (4 mm diameter).
- + Auxiliary electrode: carbon.
- + Reference electrode: silver or Ag/AgCl.

2.2. Methods

2.2.1 Preparation of NiFe₂O₄ nanoparticles. By using the hydrothermal method and the following annealing treatment, NiFe₂O₄ nanoparticles (NFO NPs) were prepared.^{6,7,14} Firstly, dissolved solutions of 0.3 M NiCl₂ and 0.3 M FeCl₃ were mixed under magnetic stirring for 30 min. Secondly, 200 mmol of 0.2 M NaOH was added into the solution until pH reached 9. The solution was continuously stirred for 1 h to produce a homogeneous solution. Then, this homogeneous solution was put into a hydrothermal autoclave reactor and heated at temperature *T* = 180 °C with a holding time of 20 h. After heating, the precipitation was filtered and washed several times with alcohol and dried for 6 h at *T* = 80 °C in air, and labelled as NFO samples.

2.2.2 Preparation of MoS₂ sheets. Firstly, 3 mg polyvinylpyrrolidone (PVP) and 10 mg powder of molybdenum sulfide (MoS₂) were put into 100 mL distilled water and stirred for 30 min. Secondly, the mix solution was ultrasonicated for 1 h by an UWave 2000 instrument under a power of 560 W.

2.2.3 Preparation of MoS₂-NFO nanocomposites. 1 mg NFO NPs was stirred in 10 mL distilled water for 30 min, then added the MoS₂ solution with various ratios of 1 : 1 and 1 : 2. Finally, the above-mixed solutions were ultrasonicated for 20 min.

2.2.4 Preparation of NFO/SPE, MoS₂/SPE and MoS₂-NFO/SPE. To study the electrochemical behaviors of electrodes modified with MoS₂, NFO, and MoS₂-NFO, screen-printed electrodes (SPE) were modified with proposed materials. The modified SPEs were prepared by dropping homogeneous solutions of MoS₂, NFO, and MoS₂-NFO, respectively, with a concentration of 1 mg mL⁻¹ as follows steps: step one, adding 5 mg of proposed materials into 5 mL distilled water and sonicating for 30 min to get homogeneous solutions; step two, dropping these homogeneous solutions on the working electrode surface of bare SPE and drying at 45 °C. After that, MoS₂/SPE, NFO/SPE, and MoS₂-NFO/SPE were dried in air for the following electrochemical measurements.

2.3. Apparatus

2.3.1 Physical measurements: XRD, Raman, VSM, and SEM. In this study, the scanning electron microscopy (SEM) was used to observe the morphology, size, as well as distribution of the prepared samples. By using Bruker D5005 X-ray diffractometer attached Cu K_α radiation (*λ* = 0.154056 nm), the crystalline structure was analyzed to obtain the parameters and crystallographic phase of MoS₂ and NFO. Raman spectroscopy (Horiba MacroRAM™) with 785 nm laser excitation was also employed to study physicochemical characteristics. Additionally, the magnetic characteristics of the proposed materials were determined using a vibrating sample magnetometer (VSM, EV9, MicroSense) at room temperature.

2.3.2 Evaluation of electrochemical characterizations. The electrochemical characteristics of bare SPE and modified SPEs including NFO/SPE, MoS₂/SPE, and MoS₂-NFO/SPE, were performed on a Palmsens 4 electrochemical workstation (PS Trace-Netherlands), a three-electrode system, at a temperature around



298 K, by measuring cyclic voltammetry (CV), differential pulse voltammetry (DPV), and electrochemical impedance spectroscopy (EIS) measurement at various setup conditions. First of all, the synthesized samples were tested by cyclic voltammetry (CV) measurements in the potential range from -0.3 to 0.6 V at different scan rates from 20 to 70 mV s^{-1} in 0.1 M KCl solution containing 2.5 and 5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$, as a redox probe. As soon after CV measurement, in the range of frequency 0.01 to $50\,000$ Hz, all electrodes were continually executed by electrochemical impedance spectroscopy (EIS) measurement.

The second, CV and DPV were measured on the bare SPE and modified SPE in the presence of CLB without and with MF. CV measurements were performed at a scan rate of 70 mV s^{-1} in the potential range from -0.3 to 0.6 V, potential step = 0.01 V. Meanwhile, DPV measurements were also carried out as following conditions: scan rate of 6 mV s^{-1} , $E_{\text{pulse}} = 0.075$ V, $T_{\text{pulse}} = 0.25$ s, $T_{\text{equilibrium}} = 120$ – 200 s and pH difference.

3. Results and discussion

3.1. Microstructure and physical characterizations

Powder XRD diffraction of NFO, MoS_2 , and MoS_2 -NFO material was collected in the range of 2θ from 5° to 70° , as shown in Fig. 1. The patterns of MoS_2 presented peaks at 14.3° , 32.7° , 39.5° , 49.7° , and 60.07° , matching the planes of (002), (100), (103), (105), and (110) – (no. 01-075-1539 in ICDD card).³³ Fig. 1b has eight characteristic peaks of the NFO NPs with planes of (111), (220), (311), (222), (400), (422), (511), and (440), respectively – ICDD card no. 54-0964.³⁴ The size of NFO NPs was determined at about 123.72 nm by equation Scherrer's formula $d = k_s \lambda_{\text{Cu}} / \beta \cos \theta$, with k_s as Scherrer constant and β is full width at half maximum of peak $2\theta = 19.5^\circ$ (Fig. S1d†). The XRD pattern of MoS_2 -NFO nanocomposites was recognized in Fig. 1c and zoomed in Fig. 1c', one can see two well-defined broad peaks at 39.5° and 49.7° , belonging to (103) and (105) planes of MoS_2 . Meanwhile, the presence of other low peaks could be featured in XRD diffraction of NFO NPs within MoS_2 -NFO nanocomposites, indicating the co-existence of both MoS_2 sheets and NFO NPs within the MoS_2 -NFO nanocomposites. More importantly, the effective combination between NFO NPs

and MoS_2 did not cause any change in the crystal structure of components.

Fig. 2 illustrates SEM images of NFO NPs, MoS_2 sheets, and MoS_2 -NFO nanocomposites. As can be seen from Fig. 2a, the morphology of the NFO sample displayed nanoparticles with hexagonal plate-like morphology and uniform small size. By using ImageJ software, the size of NFO was accurately estimated to be 125 nm. In Fig. 2b, it is obvious that the MoS_2 sample was composed of two-dimensional ultrathin sheets, distributed randomly with around 1.15 μm dimension. For the MoS_2 -NFO nanocomposites sample, it can see the small NFO NPs were dispersedly interlaced on the MoS_2 sheets by forming heterojunctions, indicating NFO and MoS_2 were completely combined with each other with slight aggregation due to the strong magnetism of NFO NPs. By stacking NFO-NPs among 2D- MoS_2 materials through non-covalent van der Waals interactions, it displays the metallic-metallic contact without any other chemical bonds. It is suggested that the metallic nuclei in NFO with a strong affinity towards valency-deficient S atoms were preferentially anchored to the edges and defects of the MoS_2 nanosheets, where S atoms act as sites for metal nuclei seeding, leading to the uniform distribution of NFO-NPs on MoS_2 materials.^{24,35,36}

The Raman spectra of all synthesized samples (NFO, MoS_2 , and MoS_2 -NFO) were shown in Fig. S1†. It is evident to see NFO spectrum has 4 bands at 335 , 486 , 571 , and 703 cm^{-1} , as described in Fig. S1a,† matched well with earlier published reports.^{37,38} Fig. S1b† exhibited two characteristic peaks of MoS_2 at 385 and 409 cm^{-1} . These peaks were attributed due to the in-plane (E_{2g}^1) and the out-of-plane (A_{1g}) vibration modes, respectively. The difference between these two peaks of 24 cm^{-1} , suggesting that the sample MoS_2 has a few layers.^{25,39–41} For MoS_2 -NFO nanocomposites, the presence of characteristic peaks of both MoS_2 and NFO was recorded, demonstrating the co-existence of MoS_2 and NFO within the nanocomposite structure (Fig. S1c†), which is consistent with the XRD results observed.

The magnetic characteristics of synthesized samples were observed *via* the magnetic hysteresis (M - H) curves at room temperature. The hysteresis loops were described in Fig. 3, the

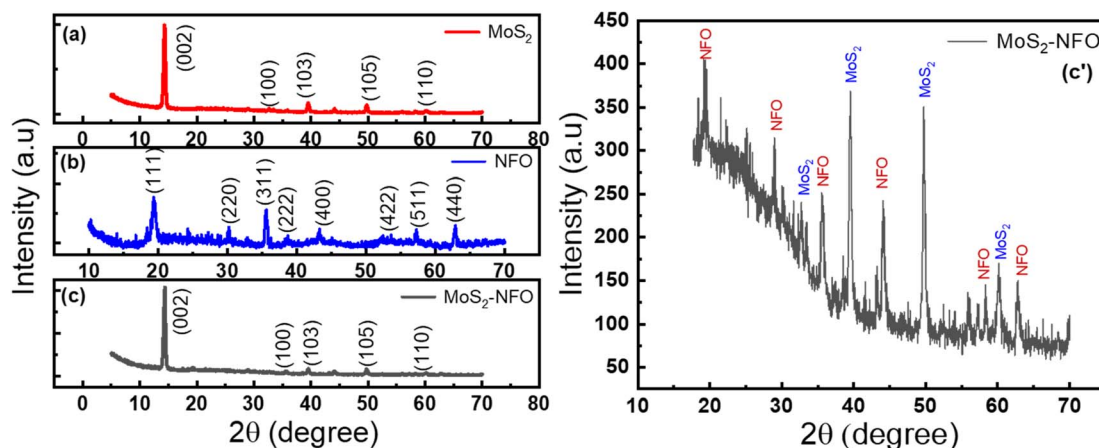


Fig. 1 (a–c) XRD spectrum of NFO, MoS_2 , MoS_2 -NFO and (c') the zoomed image of MoS_2 -NFO, respectively.

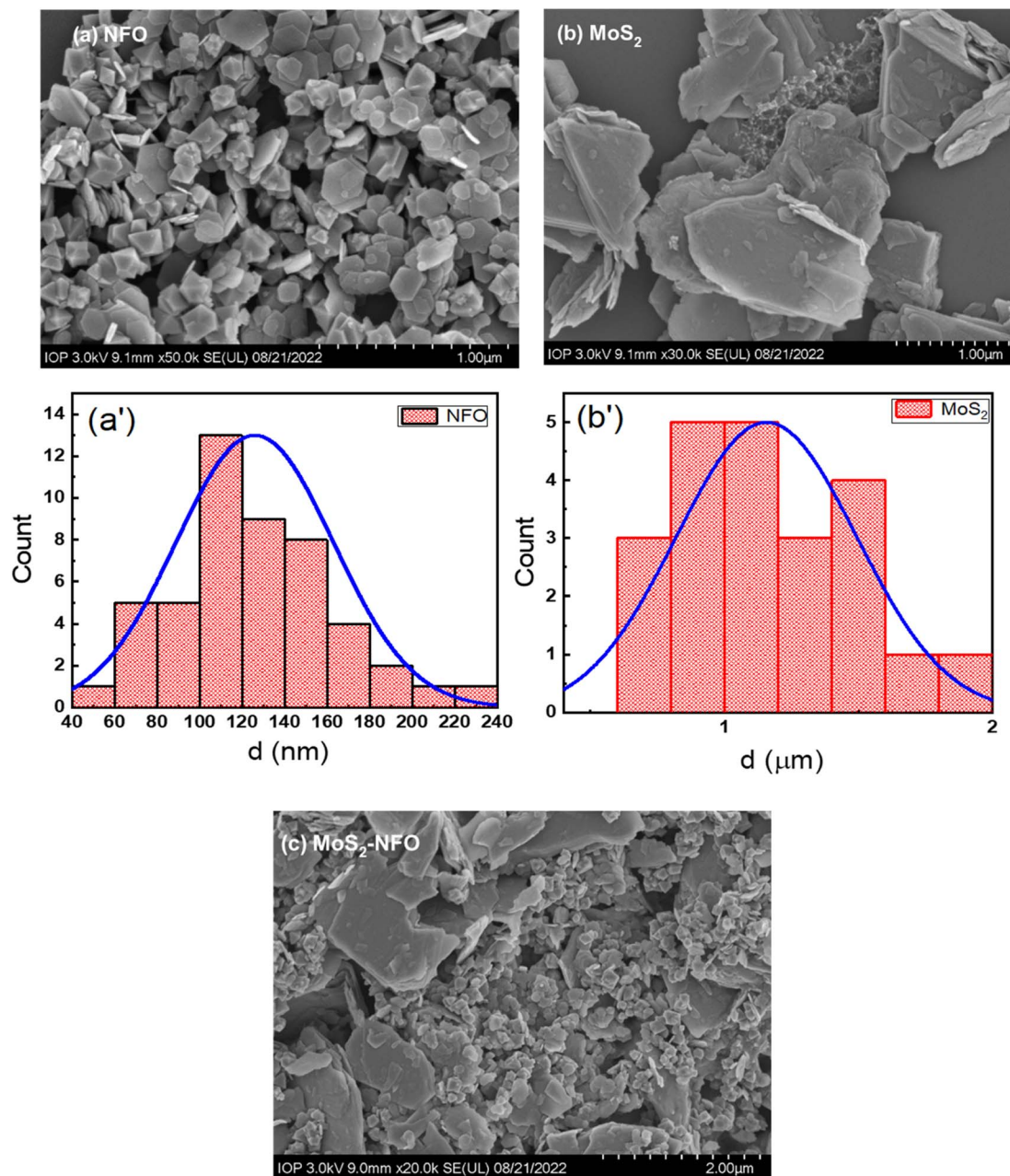


Fig. 2 (a–c) SEM images of the as-synthesized materials (NFO, MoS₂, and MoS₂-NFO); (a' and b') size distribution of NFO and MoS₂ samples.

value of saturation magnetization (M_s) was determined around 37.2 emu g^{-1} for NFO and 28.8 emu g^{-1} MoS₂-NFO samples, while the MoS₂ sample did not show a magnetic curve. The considerable decrease in M_s value when NFO NPs were combined with MoS₂, is consistent with the weak magnetic properties of MoS₂ sheets originating from the existence of zigzag edges within layered structure. Similarly, the M_r and the coercivity (H_c) values of these proposed samples were determined approximately 9.94 emu g^{-1} and 131.18 Oe for NFO, 8.6 emu g^{-1} and 140.79 Oe for MoS₂-NFO samples, respectively. Although, the increase of magnetic property at MoS₂-NFO sample was observed, it still guarantees the good magnetic response when the external magnetic field (MF) applied.

3.2. Electrochemical investigations

In the first step to investigate electrochemical characterizations of proposed electrodes, CV measurements were carried out in 0.1 M KCl solution containing $5.0 \text{ mM } [\text{Fe}(\text{CN})_6]^{3-/4-}$ at a scan rate of 50 mV s^{-1} . As can see in Fig. 4a, all recorded CV curves showed a pair of significant reversible redox peaks appeared at 0.1 V and 0.3 V , which are attributed due to the electron transfer reaction of $[\text{Fe}(\text{CN})_6]^{4-}$ reversibly into $[\text{Fe}(\text{CN})_6]^{3-}$ and at the same time $[\text{Fe}(\text{CN})_6]^{3-}$ reversibly into $[\text{Fe}(\text{CN})_6]^{2-}$. However, the remarkable difference in current response intensity at each electrode needs to be stressed. In this case, the higher current intensity was observed at the MoS₂/SPE ($176 \mu\text{A}$), MoS₂-NFO (2 : 1)/SPE ($160 \mu\text{A}$), and MoS₂-NFO (1 : 1)/SPE ($155 \mu\text{A}$) than that of



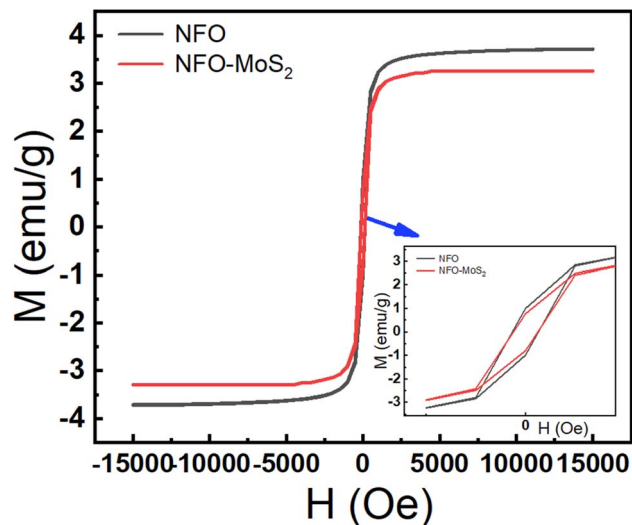


Fig. 3 Magnetization curves of NFO and MoS_2 -NFO samples.

bare SPE (116 μA) and even NFO/SPE (146 μA). To explain this, some kinetic parameters involving the electron transfer reaction of the redox probes were calculated and evaluated in detail.

Namely, the peak-to-peak separation potential ($\Delta E_p = E_{pa} - E_{pc}$) from CV curves, a critical proof, reflects the limitation in electrical conductivity and charge transfer kinetics. It was determined in the order: $\text{MoS}_2/\text{SPE} < \text{MoS}_2\text{-NFO} (2:1)/\text{SPE} < \text{MoS}_2\text{-NFO} (1:1)/\text{SPE} < \text{NFO}/\text{SPE}$, which is much lower than that of bare SPE for a single electron-transfer process. Clearly, the modification of the electrode surface brought out many positive improvements in conductivity and charge transfer, compared with bare SPE. Furthermore, when CV measurements were performed at various scan rates in the range from 20 to 70 mV s^{-1} on the proposed electrodes, the changes in response current intensity and the reversible redox peak potential were observed at all modified electrodes even in the bare SPE (Fig. S2†). In this case, the current response linearly increased in the increase of square root of the scan rate ($\nu^{1/2}$), corresponding to the regression equations:

$$I_p = 16.92\nu^{1/2} (\text{mV s}^{-1}) + 27.633 (R^2 = 0.999) \text{ for NFO/SPE}$$

$$I_p = 23.01\nu^{1/2} (\text{mV s}^{-1}) + 13.094 (R^2 = 0.999) \text{ for MoS}_2/\text{SPE}$$

$$I_p = 19.63\nu^{1/2} (\text{mV s}^{-1}) + 22.269 (R^2 = 0.999) \text{ for MoS}_2\text{-NFO} (2:1)/\text{SPE}$$

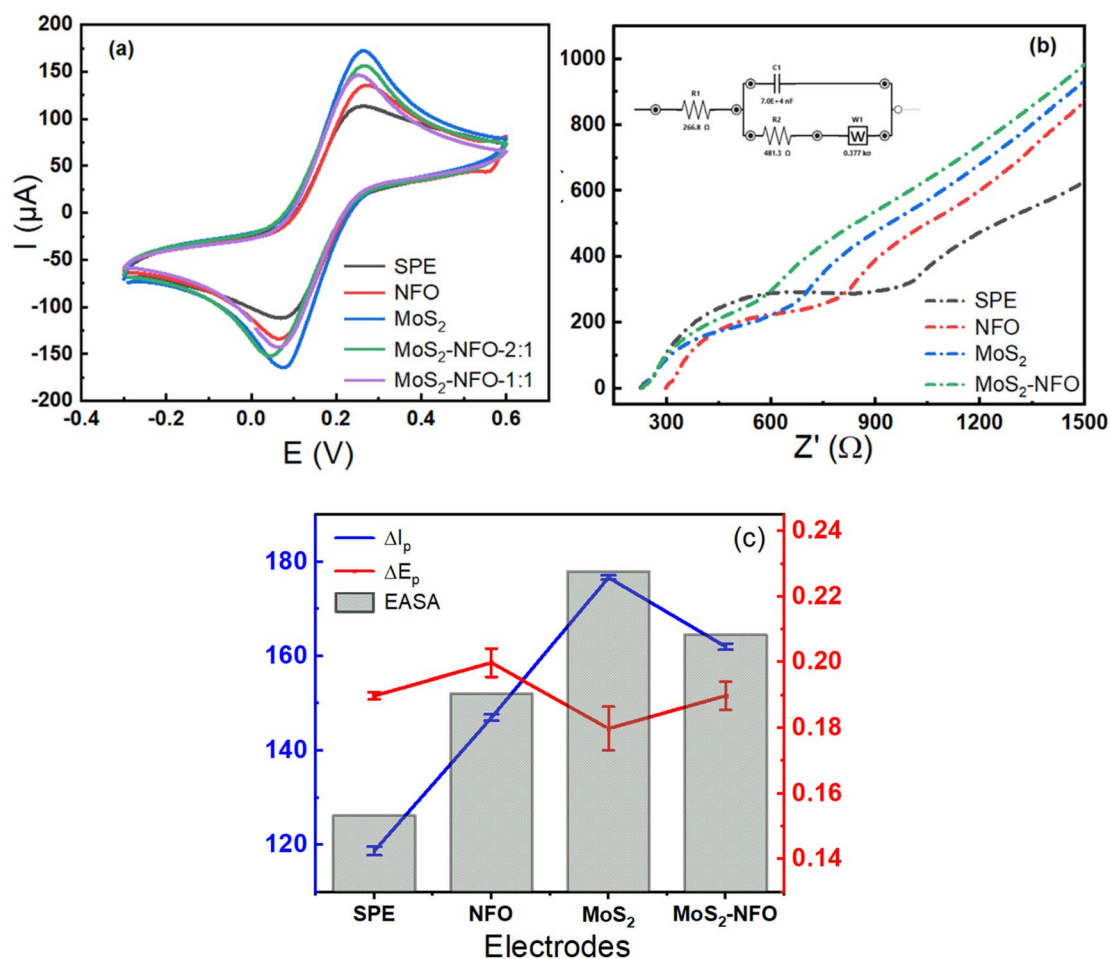


Fig. 4 (a and b) CV profiles and EIS plots of bare SPE and SPEs modified with NFO, MoS_2 , $\text{MoS}_2\text{-NFO} (2:1)$, and $\text{MoS}_2\text{-NFO} (1:1)$; (c) the obtained values of I and AESA recorded on various electrodes in 0.1 M KCl solution containing 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$.

$$I_p = 20.44\nu^{1/2} \text{ (mV s}^{-1}\text{)} + 17.227 \text{ (} R^2 = 0.999 \text{) for MoS}_2\text{-NFO (1 : 1)/SPE}$$

From that, the electrochemical active surface area (EASA or A) was calculated using the Randles–Sevcik equation (25 °C) as described by equation:^{7,23,42,43}

$$I_p = (2.69 \times 10^5)n^{3/2}D^{1/2}A\nu^{1/2}C$$

where n stands for the number of the electron in a redox reaction, D represents the diffusion coefficient of $7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, A refers to the electrochemical active electrode surface area (cm^2), C indicates the bulk concentration of $[\text{Fe}(\text{CN})_6]^{3-/4-}$. According to that, the value of EASA was calculated at about 0.153 cm^2 for bare SPE, 0.191 cm^2 for NFO/SPE, 0.229 cm^2 for MoS_2/NFO , 0.202 cm^2 for $\text{MoS}_2\text{-NFO (1 : 1)/SPE}$, and 0.209 cm^2 for $\text{MoS}_2\text{-NFO (2 : 1)/SPE}$, respectively. As can see, the highest value of EASA and the lowest value of separation potential (ΔE_p) were achieved at MoS_2/SPE , it is in accordance with the highest value of current intensity at this electrode. This result might be since the fact that MoS_2 sheets have a much larger surface area and higher electrical conductivity than NFO NPs, which facilitates an effective raise of the electron transfer and interaction in the middle of the probe molecules with the electrode surface. Further to mention, the good combination at a weight ratio of 1 : 2 between NFO and MoS_2 also brought excellent enhancements for EASA and ΔE_p values. As indicated in SEM images, NFO NPs were uniformly distributed onto MoS_2 sheets, leading to effectively inhibiting the self-aggregation of NFO NPs and MoS_2 sheets. This is beneficial for the exposure of active sites and therefore improving the conductivity and electron transfer. Additionally, the close contact between NFO NPs and MoS_2 sheets suggested a strong interaction was generated at their interface. However, it needs to be noted that, at the higher weight ratio of NFO within $\text{MoS}_2\text{-NFO (1 : 1)}$ nanocomposites, the values of peak current recorded seem to have a decreasing trend, compared with that of the $\text{MoS}_2\text{-NFO (2 : 1)}$ sample. This could be followed by the excess increase of NFO NPs led to agglomeration and break of the structure of MoS_2 sheets into smaller pieces. Consistency of these proposes with the values of EASA and separation potential (ΔE_p) was found.

To further verify the great improvement of electrical conductivity and charge transfer kinetics arising from the modification of the electrode surface with proposed synthetic samples, electrochemical impedance spectroscopy (EIS) is considered the effective direct method to evaluate charge transfer ability onto the electrode surface.⁴⁴ Fig. 4b shows Nyquist diagrams of various electrodes in a mixture solution of 0.1 M KCl solution containing 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$, which confirms the difference in the electron transfer process occurring at each different electrode. In which, the electron transfer resistance (R_{ct}) value is one of the most parameters controlling the kinetics of the electron transfer reactions of the redox probes at the electrode/electrolyte interface. This value is directly determined *via* the semicircle diameter in the high-frequency range. As seen, the R_{ct} value could be estimated as approximately 487.3, 242.8, 180.9, 214.5, and 200.6 Ω for bare

SPE, NFO/SPE, MoS_2/SPE , $\text{MoS}_2\text{-NFO (1 : 1)/SPE}$, and $\text{MoS}_2\text{-NFO (2 : 1)/SPE}$, respectively. It is interesting to see that the obtained results fitted well with the CV response and separation potential (ΔE_p) of all electrodes recorded. Worthy of note, the R_{ct} value was employed to estimate the standard heterogeneous rate constant (k_{et}) for all electrodes:^{23,29,45}

$$k_{et} = RT/(n^2F^2R_{ct}AC_o)$$

here R , T , and F are used with their usual meaning, A donates electrochemical active area (cm^2), C_o refers to the bulk concentration of $[\text{Fe}(\text{CN})_6]^{3-/4-}$, R_{ct} implies the electron transfer resistance (Ω). The k_{et} value was found for the bare SPE, NFO/SPE, MoS_2/NFO , $\text{MoS}_2\text{-NFO (1 : 1)/SPE}$, and $\text{MoS}_2\text{-NFO (2 : 1)/SPE}$ to be around 7.1×10^{-4} , 1.15×10^{-3} , 1.27×10^{-3} , 1.23×10^{-3} , and 1.27×10^{-3} , respectively. The above results manifest that benefiting from possessing high EASA, low separation potential (ΔE_p) value, and small electron transfer resistance (R_{ct}) value helped MoS_2/SPE to achieve the highest k_{et} value. More interestingly, the similar value was also observed at the $\text{MoS}_2\text{-NFO (2 : 1)/SPE}$, demonstrating that the effective combination between MoS_2 sheets and NFO NPs at the optimized ratio contributed to creating an excellent approach towards faster and easier electrons transfer reactions onto the electron surface as well as the electrode/electrolyte interface. Therefore, $\text{MoS}_2\text{-NFO (2 : 1)/SPE}$ was chosen as the optimum modified electrode for the next experiments.

3.3. Electrochemical behaviors of CLB on modified electrodes

The electrochemical activities of MoS_2/SPE , NFO/SPE, and $\text{MoS}_2\text{-NFO (2 : 1)/SPE}$ were assessed through the redox reaction of CLB, proving the positive influence of surface modification with MoS_2 , NFO, and $\text{MoS}_2\text{-NFO (2 : 1)}$ on the sensing performance. CV measurements were traced in the presence and absence of CLB molecules at all electrodes. As mentioned in the literature, the irreversible oxidation of CLB molecules during the first anodic sweep usually occurs at around 0.8–1.0 V. At the next CV measurements, in addition to this irreversible oxidation peak, a pair of reversible redox peaks in the potential range from 0.15 to 0.3 V was recorded, reflecting the redox reaction of clenbuterol dimer molecules by an azo bond. Namely, in this case, the redox reaction of the irreversible oxidation of CLB at high potential still could be observed when the potential window of CV measurement was widened until +1.0 V (Fig. S3a†). However, this peak current intensity in the second lap decreased remarkably. In contrast, the presence of a pair of redox peaks with higher intensity at around +0.23/+0.05 V was recorded at even the first cycle as described in Fig. S3a.† To explain this phenomenon, the pre-formation of CLB dimers from hydrazobenzene derivative, which is created by the protonation of CLB molecules in solution when using the analytical standard of clenbuterol hydrochloride, is an important reason. Hence, to maintain good stability and repeatability for measurements as well as ease in observing, the redox peaks at +0.23/+0.05 V were chosen to investigate in more detail the electrochemical performance. Thus, CV measurements were



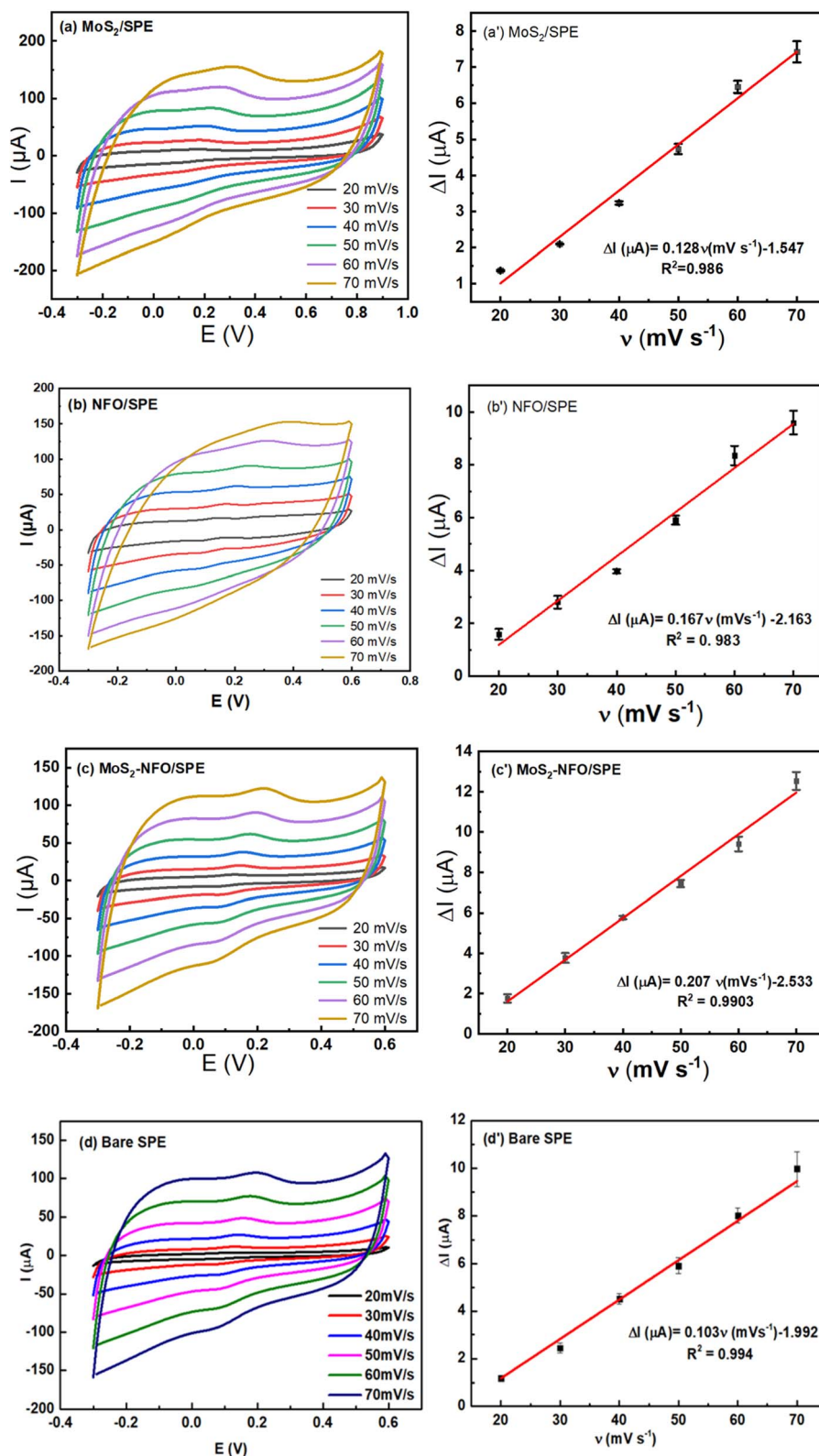


Fig. 5 CVs responses of 50 μM CLB at bare SPE (d), and the modified electrodes with MoS_2 (a), NFO (b), and $\text{MoS}_2\text{-NFO}$ (2 : 1) (c) in 0.1 M PBS buffer at different scan rates; corresponding to the plot of peak current (I) versus scan rate (ν) (a'–d').

carried out in the potential range from -0.3 to $+0.6$ V. Fig. S3b† illustrates the CV curves of bare SPE, MoS₂/SPE, NFO/SPE, and MoS₂-NFO (2 : 1)/SPE in pH 7.4 PBS buffer containing 50 μ M CLB, respectively. The obtained results manifest that there was an increase of anodic response current and cathodic peak current at electrodes modified, particularly for MoS₂-NFO (2 : 1)/SPE, which is attributed due to strong synergistic effect and excellent electrocatalytic activity within nanocomposite structure of MoS₂-NFO (2 : 1). In the circumstance, CLB dimer molecules arising from formation of azo bond between hydrazobenzene derivatives attended redox reactions, corresponding to anodic/cathodic peak potential was observed at about $+0.23/+0.05$ V (Fig. S3a†). Also, a characteristics oxidation potential of CLB was recorded at $+0.23$ V while no obvious reduction peak is observed, indicating that the oxidation of CLB is irreversible. More particularly, the oxidation peak at $+0.23$ V was higher and clearly than that of the oxidation peak at $+0.81$ V. Hence, the redox peaks at $+0.23/+0.05$ V were chosen to investigate in more detail the electrochemical performance. In addition to the difference in current intensity, the shift of the potential position of anodic peaks at various electrodes also needs to be stressed. If at bare SPE, it was observed at 0.39 V, meanwhile, at MoS₂/SPE, NFO/SPE, and MoS₂-NFO (2 : 1)/SPE, the oxidation reaction occurred at lower potential values of 0.34 , 0.38 , and 0.37 V (Fig. S3b†). This further reflects clearly the significant improvement in electrochemical catalytic activity and electron transfer reaction kinetics at modified electrodes.

To investigate the reaction kinetics of CLB on the modified electrodes, CV measurements in pH 7.4 PBS buffer containing 50 μ M CLB were carried out in the scan rate range from 20 to 70 mV s^{-1} . The above results manifest that the anodic/cathodic peak current of all electrodes increased gradually with the increase in scan rate. The relationship between I_{pa} and ν was illustrated in Fig. 5a'-c', according to that it showed a high degree of linearity with linear regression equations of:

$$I_p (\mu\text{A}) = 0.103\nu (\text{mV s}^{-1}) - 1.992 (R^2 = 0.994) \text{ for bare SPE}$$

$$I_p (\mu\text{A}) = 0.128\nu (\text{mV s}^{-1}) - 1.547 (R^2 = 0.986) \text{ for MoS}_2/\text{SPE}$$

$$I_p (\mu\text{A}) = 0.167\nu (\text{mV s}^{-1}) - 2.163 (R^2 = 0.983) \text{ for NFO/SPE}$$

$$I_p (\mu\text{A}) = 0.207\nu (\text{mV s}^{-1}) - 2.533 (R^2 = 0.990) \text{ for MoS}_2\text{-NFO (2 : 1)/SPE}$$

From that, it can be inferred that the adsorption-controlled characteristics occurred in surface-confined reactions for their electrode process. It is interesting that from the slope value of I_p vs. scan rate, the adsorption capacity (Γ) of CLB on the various electrodes was estimated at 6.9×10^{-10} , 4.53×10^{-10} , 7.96×10^{-10} , and 4.39×10^{-10} for NFO/SPE, MoS₂/SPE, MoS₂-NFO (2 : 1)/SPE, and bare SPE, respectively by using equation: $I_p = n^2 F^2 A \Gamma \nu / 4RT$. Besides, the effect of scan rate on the slight shift of peak potential was studied in detail. In this case, the linear relationship between E_p and the natural logarithm of scan rate $\ln(\nu)$ was described in Fig. S4,† corresponding to the regression equations as:

$$E_p (\text{V}) = 0.114 \ln(\nu) (\text{mV s}^{-1}) - 0.282 (R^2 = 0.992) \text{ for bare SPE}$$

$$E_p (\text{V}) = 0.119 \ln(\nu) (\text{mV s}^{-1}) - 0.203 (R^2 = 0.989) \text{ for MoS}_2/\text{SPE}$$

$$E_p (\text{V}) = 0.169 \ln(\nu) (\text{mV s}^{-1}) - 0.398 (R^2 = 0.991) \text{ for NFO/SPE}$$

$$E_p (\text{V}) = 0.078 \ln(\nu) (\text{mV s}^{-1}) - 0.123 (R^2 = 0.989) \text{ for MoS}_2\text{-NFO (2 : 1)/SPE}$$

According to the Laviron theory, the relationship between E_p and scan rate in an adsorption-controlled irreversible process can be also expressed as:⁴⁶⁻⁴⁸

$$E_p = E_0 + (RT/\alpha nF) \ln(RT k_0 / \alpha nF) - (RT/\alpha nF) \ln(\nu)$$

From that, the slope value of the above lines is equal to $RT/\alpha nF$, thus, the value of αn can be also determined directly. As the number of electrons transferred is equal to 1, the electron transfer coefficient value (α) of bare SPE, NFO/SPE, MoS₂/SPE, and MoS₂-NFO (2 : 1)/SPE was calculated to be 0.225, 0.151, 0.207, and 0.328. More importantly, the value of the electron transfer rate constant (k_s) of the redox reaction of CLB at these modified electrodes was also calculated based on the equation:

$$\ln(k_s) = \alpha \ln(1 - \alpha) + (1 - \alpha) \ln \alpha - \ln(RT/nF\nu) - \alpha(1 - \alpha)(nF\Delta E_p/RT)$$

As shown by the results, the highest value of k_s was recorded at MoS₂-NFO (2 : 1)/SPE of approximately 0.504 s^{-1} , while this value only reached about 0.283, 0.331, and 0.265 s^{-1} at NFO/SPE, MoS₂/SPE, and bare SPE, respectively. By the calculated results, although in the previous section, MoS₂/SPE showed many more excellent electrochemical characteristics of electrical conductivity and the values of EASA and k_{et} , herein, the electrochemical behaviors of CLB on the MoS₂-NFO (2 : 1)/SPE exhibited more impressive improvements. Not only possessed a higher electrochemical response of CLB but the kinetic parameters related to the redox reaction of CLB showed significant enhancements. As pointed out in our previous report, CLB is a complex and bulky organic molecule, resulting in a poor flat structure when adsorbed on the electrode surface. Along with that, the CLB molecules can be protonated and self-bonded with each other, leading to the creation of a huge steric hindrance, which causes remarkable dead spaces and limitation in the adsorption ability, interaction, electron transport, and charge diffusion of CLB onto the electrode surface. More importantly, the research proved that to get higher detection efficiency for CLB, the development of unique electrodes having better charge/electron transfer and electrocatalytic activity for the redox reactions of CLB should be given priority. Maybe, in this case, MoS₂-NFO (2 : 1) nanocomposite structure through the suitable and effective combination supported considerably the strong interaction and charge/electron transfer between the active material and targeted CLB molecules. Furthermore, the co-existence of MoS₂ and NFO provided many active sites for



better electrocatalytic activity in the redox reaction of CLB, compared with other modified electrodes.

As we know, one of the most unique properties of NFO nanomaterial is the response to magnetic fields and good electrocatalytic ability similar to other magnetic nanomaterials. In our previous research, the positive influence of external stationary MF on electrochemical behaviors of Fe_3O_4 -carbon spheres based-electrode as well as its sensing performance towards detecting chloramphenicol was thoroughly reported.^{8,29,30,32,49–51} Some impact mechanisms were proposed, explaining for the enhancement in mass transfer, ionic/charge diffusion in the electrolyte solution, as well as higher absorption capacity and better electrocatalytic ability at modified electrodes. According to this inevitable trend, the utilization of MF with the aim of promoting the inherent electrochemical characteristics of MoS_2 -NFO (2:1)/SPE such as electrical conductivity, adsorption capability, and electrocatalytic activity was carried out. Also, it is expected to enhance the electrolyte's physicochemical properties, in pursuit of better response-ability and higher sensing efficiency at the modified electrode.

Indeed, under the presence of external MF, the peak current response in the CV curves of MoS_2 -NFO (2:1)/SPE increased by about 5.4% compared with the initial value when without MF. Besides, the decrease in the ΔE_p value was recorded, indicating the significant enhancement of electrical conductivity and

transfer kinetics in the reversible electron transfer reaction of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probes (Fig. S5†). More interestingly, for further investigation of the MF impacts on the sensing performance of CLB, a series of kinetic parameters involving the redox reaction of CLB onto the electrode surface was calculated. Namely, from CVs curves obtained at various scan rates in 0.1 M PBS containing 50 μM CLB under the presence of MF, it still displays a linear relationship between I_p and scan rate (ν) in the range of 20–70 mV s^{-1} and it can be expressed as $I_p (\mu\text{A}) = 0.413\nu (\text{mV s}^{-1}) - 5.188$ ($R^2 = 0.995$) as Fig. S6.† Furthermore, the linear equation of E_p and logarithm of scan rate was also estimated as $E_p (\text{V}) = 0.148 \ln(\nu) (\text{mV s}^{-1}) - 0.278$ ($R^2 = 0.978$). According to that, k_s and adsorption capacity (Γ) values of CLB achieved about 0.521 s^{-1} and 1.57×10^{-9} , demonstrating the remarkable enhancement of electron transfer rate constant (k_s) and adsorption capacity (Γ), compared with that of without MF under the same experimental condition.

To get more insight into the influence of MF on electrocatalytic activity within MoS_2 -NFO (2:1)/SPE, CA measurements were taken with and without external MF. As shown in Fig. 6a and d, the linear increase of current response for diffusion-limited electrocatalytic techniques vs. $t^{-1/2}$ were found at various concentrations in both two cases. Based on Cottrell's equation:^{29,52,53}

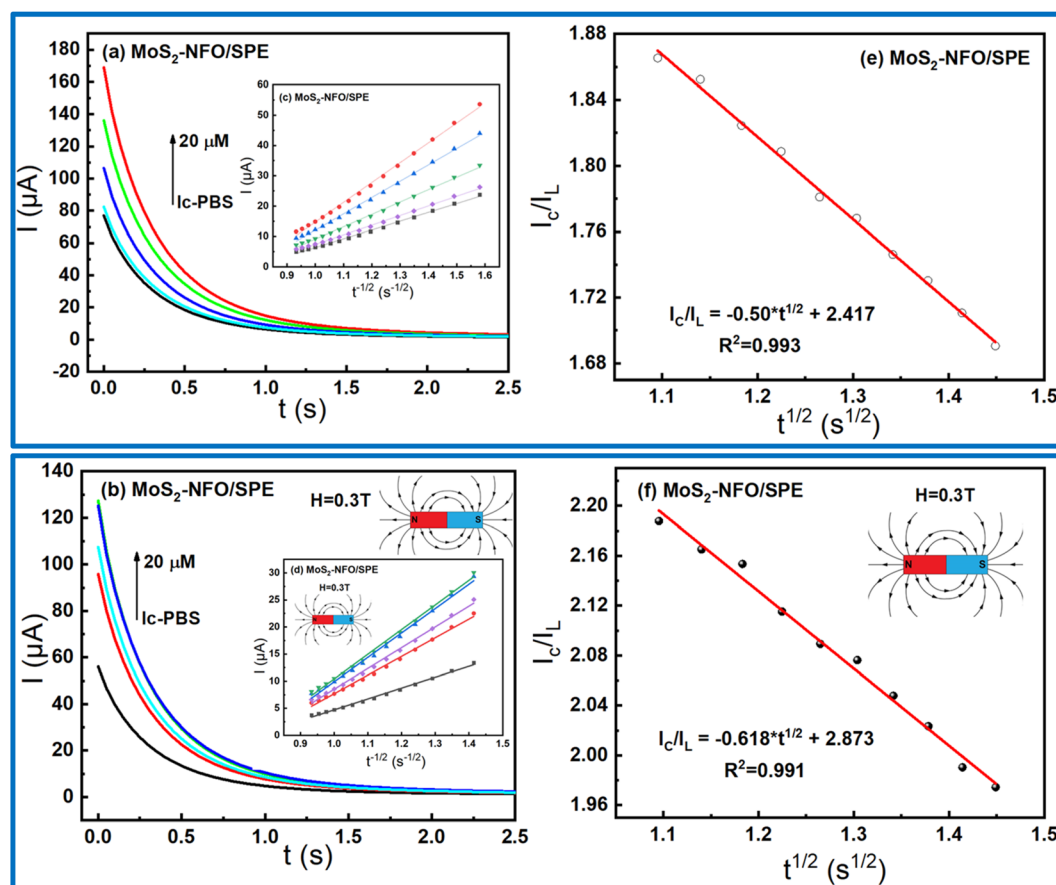


Fig. 6 (a and b) Chronoamperograms obtained at MoS_2 -NFO in 0.1 M PBS containing various concentrations of CLB with and without external MF; (c and d) plots of I vs. $t^{-1/2}$; (e and f) plots of I_c/I_L vs. $t^{1/2}$ at 15 μM CLB in 0.1 M PBS buffer.

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2}$$

the D ($\text{cm}^2 \text{s}^{-1}$), which stands for the CLB diffusion coefficient, was determined around 7.89×10^{-9} without using MF and 2.84×10^{-8} with using MF, respectively. Besides, Galus method was employed to study the catalytic rate constant (k_{cat}) to redox reaction between CLB molecules and active materials on the electrode surface *via* tuning the working electrode potential at 0.25 V:

$$I_C/I_L = \pi^{1/2}(k_{\text{cat}}Ct)^{1/2};$$

where I_C reflects the catalytic current of the redox reaction of CLB, I_L implies the limited current in 0.1 M PBS.

From the direct slope values obtained in Fig. 6e and f at 20 μM CLB, the k_{cat} were estimated around 0.0237 and 0.0329 without and with the support of MF. Consequently, it shows that the presence of MF offered many positive increases in the electrocatalytic activity of the electrode modified with MoS_2 -NFO (2 : 1) as expected.

The electrochemical response was remarkably affected by the pH value of the PBS buffer and accumulation time during measurement. Thus, there is necessary to optimize the experimental conditions to obtain the highest electrochemical response. In this work, DPV measurements were analyzed at

various pH values, using 1 M NaOH and H_3PO_4 solution for controlling the pH value in the range from 3 to 11. As displayed in Fig. 7b, it shows that the peak current gradually increased with increasing pH from 3 to 5 and reached a maximum value at pH 7.4, then decreased with over-increasing pH. With the maximum current, pH 7.4 was chosen as the optimal pH value for all the subsequent electrochemical measurements. In addition, the linear shift of peak potential with the increase of pH was found as expressed by the following equation: E_p (V) = $-0.034\text{pH} + 0.419$ ($R^2 = 0.992$) in Fig. 7c. Fixing on the pH 7.4, the accumulation time was measured from 20 to 200 s to find the accumulation optimization. Fig. 7d exhibits the response current achieved a maximum value at 60 s and lower at other times, which could be attributed due to the saturated adsorption state of CLB onto the electrode surface.⁵⁴ Finally, the pH of 7.4 and accumulation time of 60 s was employed as the best condition parameters for further electrochemical measurement in this work.

In order to investigate the sensitivity of electrochemical response with different concentrations of CLB at MoS_2 -NFO/SPE, especially in the experiment without and with MF, DPV were conducted in 0.1 M PBS buffer at the optimized experimental conditions. The DPV curves with different concentrations of CLB were displayed in Fig. 8a and b, respectively. All figures display that the peak current decreased to lower values with the

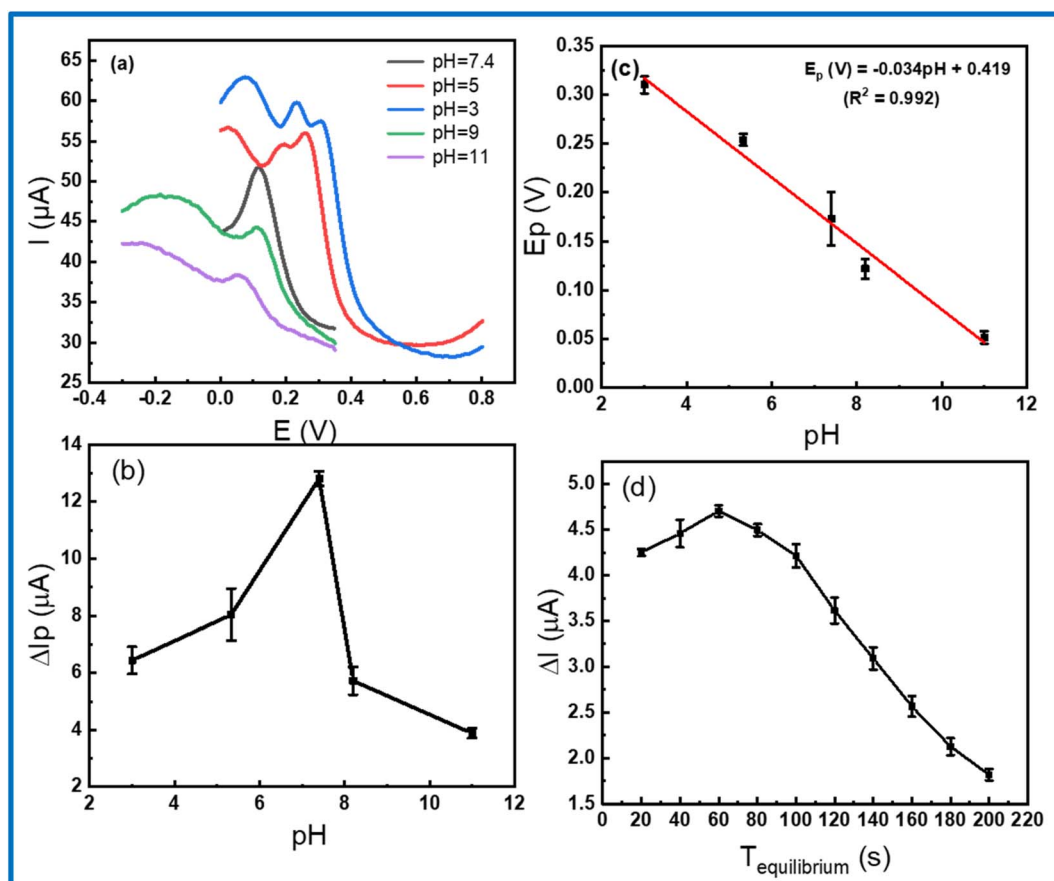


Fig. 7 (a) DPV curves on MoS_2 -NFO (2 : 1)/SPE in 0.1 M PBS containing 50 μM CLB at various pH values; (b and c) the plots of peak current vs. pH; (d) current response vs. $T_{\text{equilibrium}}$ value from DPV measurements in 0.1 M PBS containing 20 μM CLB.



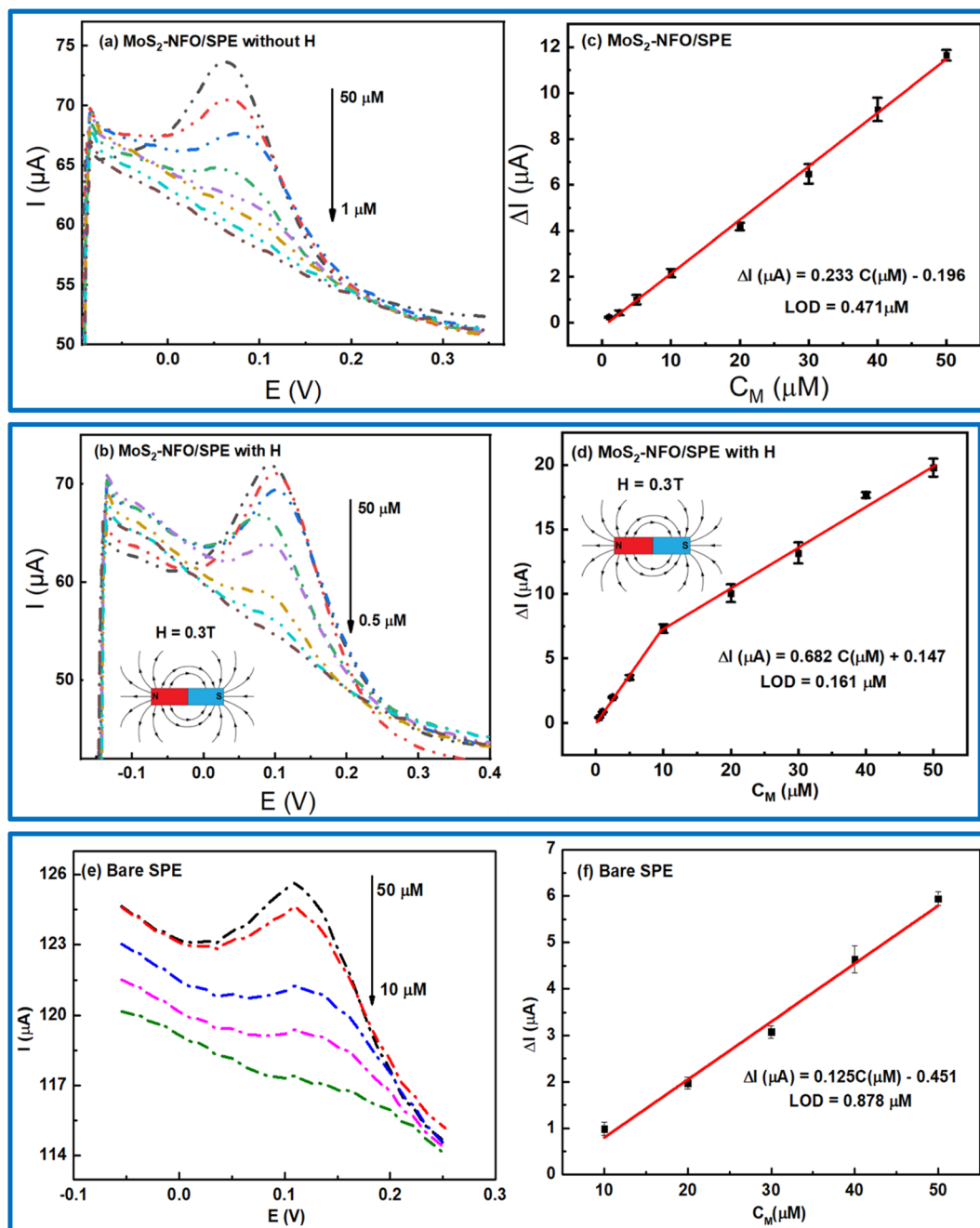


Fig. 8 (a, b and e) DPV curves recorded at the MoS₂-NFO (2 : 1)-modified SPE in 0.1 M PBS (pH = 7.4) containing various concentrations of CLB without and with MF and bare SPE, respectively; (c, d and f) the plots of peak current as a function of C_{CAP} in the different concentration ranges.

reduction of CLB concentration. However, in comparison to the response current without and with MF, the electrochemical response with the presence of MF was considerably higher, corresponding to the wider linear range of CLB concentration from 0.5 to 50 μM, compared with that without the presence of MF from 1 to 50 μM, particularly, for bare SPE with the limited linear range from 10 to 50 μM. As a result, the linear relationship between the current response and the concentration of CLB was recorded in both three cases: $\Delta I_p (\mu A) = 0.233 C_{CLB} (\mu M) - 0.196$ without MF; $\Delta I_p (\mu A) = 0.682 C_{CLB} (\mu M) + 0.147$ with MF; and $\Delta I_p (\mu A) = 0.125 C_{CLB} (\mu M) - 0.451$ for bare SPE. The limit of detection

(LOD) for bare SPE, and MoS₂-NFO (2 : 1)/SPE without and with MF was computed from the calibration curve of 0.878, 0.471, and 0.161 μM, respectively (Fig. 8c, d and f).

Table 1 Determination of CLB in milk sample (n = 3)

Samples	Spiked (μM)	Found (μM)	Recovery (%)	RSD (%)
Milk	40	38.48	96.20	1.14
	30	28.89	96.32	1.07
	20	18.19	90.97	2.01

Table 2 Comparison of some analytical parameters in electrochemical sensors toward CLB detection

Modified electrode	Measurements	Linear range (μM)	LOD (μM)	Repeatability	Ref.
NiFe ₂ O ₄ -MoS ₂ /SPE	DPV	1–50	0.471	97.7/10	This work
	DPV	0.5–50	0.161	97.7/10	This work
KVB-Nf (IP)/FCE	DPV	0.95–14.31	0.75	99.48/10	55
BCNO/GCE	DPV	0.03–16	0.017	—	56
MoS ₂ -Au-PEI-hemin/GCE	DPV	10–2000	1.92	—	57
Cl/MIP/Au	DPV	2–100	0.031	—	58

Investigating the stability, repeatability, and selectivity of the modified electrode, DPV measurements were carried out at MoS₂-NFO (2 : 1)/SPE. Firstly, for evaluating the long-term stability, MoS₂-NFO (2 : 1)/SPE was remained for 2 weeks at room temperature and atmosphere conditions, and then, it observed any change in the current response at the DPV curve for this electrode. As expected, only 3.4% of the initial value of the current response was reduced, exhibiting the good stability of the proposed electrode. Secondary, DPV measurements were repeated ten times in 0.1 M PBS (pH = 7.4) containing 20 μM CLB at 50 mV s^{-1} to assess the repeatability. The obtained result indicates that the MoS₂-NFO (2 : 1)/SPE had outstanding repeatability with RSD value of 2.3%. Finally, some ions and organic molecules at 20-fold higher concentrations compared with 50 μM CLB such as Fe³⁺, Ni²⁺, Co²⁺, Cl[−], NO₃[−], SO₄^{2−}, Mg²⁺, Mn²⁺, ascorbic acid, glucose, urea, and nitrophenol were used as interfering substances to check the selectivity of the MoS₂-NFO (2 : 1)/SPE towards the redox reactions of CLB. As pointed out, no significant influence on the current response of CLB was observed even under high concentration of interfering substances, corresponding to deviations below 4.2%. Notably, adding high concentrations of ascorbic acid owning an intense oxidation signal at about 0.17 V seems to lead to overlapping with the characteristic oxidation peak of CLB. In this case, a deconvolution tool to separate both individual signals was used. As a result, after deconvoluting this peak, the oxidation peak of CLB still displayed a high stability in response intensity as other studied interfering substances. The results recorded from stability, repeatability, and selectivity tests exhibited that MoS₂-NFO (2 : 1)/SPE might be considered the best choice for the analytical application. More interestingly, in a comparison of sensing performance with other modified electrodes in the literature, it still exhibits a great enhancement in electrochemical performance toward CLB detection (Table 2). Besides, the presence of external MF is considered a promising development approach to increase performance instead of focusing on developing new synthesis methods and composites as in other reports.

To evaluate the practical application of MoS₂-NFO/SPE as working electrode for detecting CLB, DPV measurements were taken in various spiked milk samples by the standard addition method. Milk concentration were added into 10-folds CLB sample. As exhibited in Table 1, it was clear that the recovery result of spiked samples was in the range from 90 to 96.32%. Meanwhile, RSD values of three times paralleled detection were obtained from 1.07 to 2.01%. These obtained results

demonstrated that the proposed electrode based on MoS₂-NFO was suitable accuracy and can be applied to determine the presence and concentration off CLB analysis in real matrices.

4. Conclusions

In this study, NFO, MoS₂ and MoS₂-NFO nanomaterials were synthesized by using the hydrothermal and probe sonication methods. The crystallization, structure, particle size, morphology, and magnetic properties were observed and analysed by XRD, Raman, SEM, and VSM, respectively. The electrodes modified with MoS₂, NFO, and MoS₂-NFO were used, aiming to study electrochemical characteristics and sensing performance for the CLB sensitive detection under the absence/present applied magnetic fields *via* CV, EIS, DPV, and CA measurements. The obtained result pointed out that MoS₂-NFO (2 : 1)/SPE was the best and most promising electrode for CLB detection. Also, the presence of MF enhanced the electrochemical features of MoS₂-NFO (2 : 1)/SPE and a series of kinetic parameters in the redox reaction of CLB. By optimizing the experimental conditions in terms of the pH and accumulation time, the highest electrochemical response was recorded, corresponding to the pH at 7.4 and 60 s for the accumulation time. In addition, the work also reported the added advantages such as stability, repeatability, and selectivity of the proposed electrodes. The limit of detection for MoS₂-NFO (2 : 1)/SPE in the absence/present MF were 0.471 and 0.161 μM , respectively, which promises MoS₂-NFO (2 : 1)/SPE will be ideally suited to develop new sensor electrodes for further effective and fast detection towards different analytical molecules.

Conflicts of interest

There are no conflicts to declare.

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