Anchoring Metallic MoS₂ Quantum Dots over MWCNTs for Highly Sensitive Detection of Postharvest Fungicide in Traditional Chinese Medicines

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ABSTRACT: Carbendazim, a very common contamination to the traditional Chinese medicines (TCMs), has posed serious threat to the environment and human health. However, sensitive and selective detection of carbendazim (MBC) in the TCMs is a big challenge for their complex chemical constituents. In this work, a 0D/1D nanohybrid was developed by anchoring 1T-phased MoS₂ quantum dots (QDs) over multiwall carbon nanotubes (MWCNTs) via a facile assembly method. High-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, X-ray photoelectron spectroscopy, and thermogravimetric analysis (TGA) together with EIS reveal that the 1T-phased QDs can anchor over MWCNTs via van der Waals forces, and the anchoring improves the nanohybrid surface area and conductivity. Therefore, the electrochemical sensor fabricated based on the MoS₂ QDs@MWCNT nanohybrid shows excellent catalytic activity to MBC oxidation. Under optimized conditions, the sensor presents a linear voltammetry response to MBC concentration from 0.04 to 1.00 μmol·L⁻¹, a low detection limit of 2.6 × 10⁻⁸ mol·L⁻¹, as well as high selectivity, good reproducibility, and long-term stability. Moreover, the sensor has been successfully employed to determine MBC in two typical TCMs and the obtained recoveries are in good accordance with the results achieved by HPLC, showing that the constructed sensor plate holds great practical application in MBC analysis with complex matrix.

INTRODUCTION

Traditional Chinese medicines (TCMs), a treasure of human beings, have been employed to prevent and treat diseases in China for centuries. They gain ever-growing attention around the world in recent years due to their fascinating theory and long historical clinical practice. With the increasing worldwide acceptance, TCMs not only play an increasing role in global health but also contribute to other sectors including food supplements¹ and food flavoring agents,² which cause an expansion of the global TCM market. To sustain the high yield of TCM production, various pesticides such as insecticide, herbicide, and fungicide have been extensively applied during the planting process, which results in great concerns for the safety of TCMs.³⁻⁵

Carbendazim (MBC), one of the broad-spectrum benzimidazole fungicides, is especially used to control multiple kinds of fungi diseases in a variety of TCMs owing to its high efficiency and low cost.⁶ According to a previous report, more than 85% of TCMs were contaminated by carbendazim.⁷ Even worse, MBC is responsible for many diseases including germ cell apoptosis, infertility, and embryo deformity.⁸,⁹ In addition, MBC was identified by the European Commission and the US Environmental Protection Agency as a chemical substance affecting hormone secretion and potential human carcinogens,¹⁰,¹¹ and thus it has been completely banned in agricultural cultivations in these areas. But the abuse of MBC still existed in some countries. Therefore, it is important to screen the trace amount of MBC in traditional Chinese medicines with a high accuracy. However, highly sensitive and selective detection of carbendazim in TCMs is challenging for the complex matrices of TCMs.¹²

During the last decades, various analytical approaches including high-performance liquid chromatography (HPLC),¹³ liquid chromatography–mass spectrometry (LC-MS),¹⁴–¹⁶ UV–vis spectrophotometry,¹⁷ and surface-enhanced Raman scattering (SERS)¹⁸,¹⁹ have been explored for monitoring the trace amount of MBC. The above-mentioned techniques can provide relatively high sensitivity, but require time-consuming sample separation process, highly trained operators, and expensive instruments, which limit these methods for in-site rapid detection. Recently, electrochemical sensors have attracted widespread attention in the detection of...
agriculture residues with advantages such as high portability, easy operation, and high efficiency.\textsuperscript{20–25} For the electrochemical sensor, the functional nanomaterial used to modify the surface of the working electrode is the key factor to achieve a high detection performance.\textsuperscript{26–30} Among various nanomaterials, molybdenum disulfide (MoS\textsubscript{2}) has been evidenced to be effective in the development of advanced electrochemical sensors owing to its unique structure and prominent electrocatalytic activity.\textsuperscript{31,32} Compared to the nanosheet counterparts, MoS\textsubscript{2} quantum dots (QDs) possess a higher surface area with more unsaturated terminal atoms, which are helpful in electrochemical reactions.\textsuperscript{33} Therefore, MoS\textsubscript{2} QDs show a more interesting prospective as sensor materials. For example, MoS\textsubscript{2} QD-based sensors show a wide detection range (0.01–5.57 mM) and a low detection limit (1.90 \(\mu\)M) in the detection of \(\text{H}_2\text{O}_2\).\textsuperscript{34} However, MoS\textsubscript{2} QDs are randomly accumulated, resulting in a decrease of electrocatalytic activity.\textsuperscript{35} Hybridization with other conductive components such as carbon nanotubes\textsuperscript{36} and graphene\textsuperscript{37} is an effective method to improve their electrochemical catalytic performance.

Based on the aforementioned considerations, a 0D/1D nanohybrid MoS\textsubscript{2} QDs@MWCNT was fabricated by integrating metallic 1T-phased MoS\textsubscript{2} QDs with carboxylated multiwall carbon nanotubes via a facile ultrasonic-assisted assembly method. The 0D/1D nanohybrid was first used to modify glassy carbon electrode (GCE) to construct an MBC sensor. The as-prepared sensor showed high performance for the detection of MBC. Furthermore, the sensor was successfully employed to quantitatively determine the MBC in two typical TCMs, and satisfactory recoveries comparable to the results of the HPLC method were achieved.

## RESULTS AND DISCUSSION

### Physical Characterization

HREM was employed to characterize the size and microstructure of obtained samples. Obviously, MoS\textsubscript{2} QDs have uniform size with an average diameter of about 2.18 ± 0.64 nm (Figure 1a,b). A highly parallel and ordered lattice fringe with a \(d\)-spacing of 0.25 nm can be indexed to the (103) faces of MoS\textsubscript{2} crystals (Figure 1a, inset).\textsuperscript{38} No common (002) lattice plane of crystalline MoS\textsubscript{2} was observed as MoS\textsubscript{2} QDs contain very few layers.\textsuperscript{39} Figure 1c presents the typical TEM images of MoS\textsubscript{2} QDs@MWCNTs, which is observed that the MoS\textsubscript{2} QDs are successfully anchored on the outer surface of MWCNTs with uniform size. The successful anchoring is due to the strong van der Waals forces occurred between MoS\textsubscript{2} QDs and the MWCNT surface.\textsuperscript{40} Figure 1d shows that MoS\textsubscript{2} QDs keep the initial crystal structure after the nanohybrid preparation process. Figure 1e shows the TG analysis of MoS\textsubscript{2} QDs and MoS\textsubscript{2} QDs@MWCNTs. The MWCNTs exhibit one mass loss stage at the initial temperature of about 617 °C, corresponding to the calcination of MWCNTs. As for the MoS\textsubscript{2} QDs@MWCNTs, the early weight loss is attributed to water evaporation followed by the calcination of MWCNTs at the onset temperature of about 500 °C. The onset temperature of MWCNT calcination in the MoS\textsubscript{2} QDs@MWCNTs sample is about 100 °C lower than that of the MWCNT sample, showing that the MWCNTs get more individualized after anchoring of MoS\textsubscript{2}.\textsuperscript{41} in good accordance with the TEM results (Figure 1e). Evidently, the well-dispersed MWCNTs and the MoS\textsubscript{2} QDs lead to enhanced surface area of MoS\textsubscript{2} QDs@MWCNTs, which will be further proved by the chronocoulometry technique in the Electrochemical Characterization section. Moreover, the total weight loss ratio of MoS\textsubscript{2} QDs@MWCNTs is about 65.23%, lower than that of the MWCNTs sample, further evidencing that MoS\textsubscript{2} QDs were successfully anchored on the MWCNT surface via the simple ultrasonication assembly method. In Figure 1f (curve a), the MWCNTs have two characteristic bands, namely, D band at 1347 cm\(^{-1}\) and G band at 1576 cm\(^{-1}\). The G band is related to the \(E_{2g}\) modes that represents the movement in opposite directions of two neighboring carbon atoms in a graphite sheet. The D band corresponds to the disorder present in the MWCNTs.\textsuperscript{43} The \(I_D/I_G\) band intensity ratio in MWCNTs is 0.496, which then decreases to 0.433 after anchoring of MoS\textsubscript{2} QDs, showing that the defect sites are reduced, which is possibly because the defect sites of MWCNTs were masked by the MoS\textsubscript{2} QDs. As for the MoS\textsubscript{2} QDs (curve b), six peaks centered at 144, 198, 280, 353, 379, and 402 cm\(^{-1}\) are detected. The peaks at 144, 198, and 336 cm\(^{-1}\) can be allocated to the \(J_1, J_2, \) and \(J_3\) modes of S=Mo=S bonds in 1T-phase MoS\textsubscript{2}, respectively, while the other three peaks at 280, 379, and 402 cm\(^{-1}\) are ascribed to the \(E_{2g}, E_{2g}', \) and \(A_{1g}\) modes from 2H-phase MoS\textsubscript{2}, respectively.\textsuperscript{44,45} The existence of 1T-phase structure endows MoS\textsubscript{2} QDs with metallic properties that can facilitate the charge transfer kinetics for its high-conductivity nature, thus leading to a dramatic enhancement in the catalytic activity.\textsuperscript{46} In addition, the thickness of MoS\textsubscript{2} QDs...
can also be estimated by the difference value between $E_{2g}$ and $A_{1g}$ modes. The difference value is 24 cm$^{-1}$ in this case, showing that MoS$_2$ QDs are four-layer thick. Commonly, very few layered structures of MoS$_2$ QDs lead to the abundance of exposed catalytic edge sites, which has been proved previously via molecular modeling and simulation.48

X-ray photoelectron spectroscopy (XPS) was used to investigate the composition of nanohybrid and quantify the percentage of 1T phase. According to the survey spectra (Figure 2a), the Mo element and the S element are acquired in the MoS$_2$ QDs@MWCNTs hybrid, indicating that MoS$_2$ QDs were successfully anchored on the MWCNTs. In addition, the appearance of the C element in the nanomaterial of MoS$_2$ QDs is attributed to the absorption of CO$_2$ from air. The high-resolution Mo 3d spectra of the MoS$_2$ QDs and MoS$_2$ QDs@MWCNTs hybrid are shown in Figure 2b. The peaks located at 230.2 and 233.1 eV are corresponding to Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$, indicating the Mo$^{4+}$ from 2H-phase MoS$_2$, while the peak at 235.98 eV is ascribed to Mo$^{6+}$, generated from the oxidation of Mo edges during the exfoliation process.50

Figure 2c presents the high-resolution spectra of S 2p of the two samples. The peaks at 163.38 eV (S 2p$_{3/2}$) and 164.2 eV (S 2p$_{1/2}$) represent the 2H-phase MoS$_2$, while the peaks centered at 229.3 and 232.64 eV reveal the existence of slight oxidation of Mo edges during the exfoliation process.50 The multipeak curve fitting results reveal that the percentage of 1T phase is 54%, suggesting the metallic property and high conductivity of the obtained MoS$_2$ QDs.49 The peak at 235.98 eV is ascribed to Mo$^{6+}$, generated from the oxidation of Mo edges during the exfoliation process.50 The values of charge transfer resistance ($R_{ct}$) were obtained by the typical Randle equivalent circuit considering only one time constant was detected (Figure 3b). The $R_{ct}$ value of the bare GCE is 177 Ω, which decreases to 129 and 51 Ω after being modified with MoS$_2$ QDs and MWCNTs films, respectively, revealing that both MoS$_2$ QDs and MWCNTs have better electrochemical conductivity. The high conductivity of MoS$_2$ QDs is attributed to that the 1T-phased structure of MoS$_2$ QDs has metallic property, as discussed in the Physical Characterization section. The $R_{ct}$ value decreases sharply to 14 Ω when the bare GCE was modified with the hybrid material of MoS$_2$ QDs@MWCNTs, revealing the synergy between MoS$_2$ QDs and MWCNTs. The effective surface area of each electrode was investigated with chronocoulometry (Figure 3c), and the results were calculated according to the plot of Q$\sim$t$^{1/2}$ by the following equation

$$Q(t) = \frac{2nFAdQ_{dl}^{1/2}t^{1/2}}{\pi^{1/2}} + Q_{dl} + Q_{ads}$$

where $A$ is the electrode effective area, $n$ presents the transferred electron number, $F$ is the faraday constant, $c$ expresses the concentration of the [Fe(CN)$_6$]$^{3-}/[^{4-}$, $D$ is the diffusion coefficient of the [Fe(CN)$_6$]$^{3-}/[^{4-}$ solution (7.6 × 10$^{-6}$ cm$^2$/s), and $Q_{dl}$ and $Q_{ads}$ present the double-layer charge and faradic charge, respectively. According to the linear regression equation of Q$\sim$t$^{1/2}$ (Figure 3d), the effective areas of MoS$_2$ QDs@MWCNTs/GCE, MoS$_2$ QDs/GCE, MWCNTs/GCE, and bare GCE are calculated to be 0.13837, 0.07766, 0.06394, and 0.04028 cm$^2$, respectively.

Figure 3. Nyquist diagrams (a) and Bode plots (b) of various electrodes in 5.0 mmol·L$^{-1}$ [Fe(CN)$_6$]$_3$/[Fe(CN)$_6$]$_4$ (1:1) containing 0.1 mol·L$^{-1}$ KCl; Q$\sim$t (c) and Q$\sim$t$^{1/2}$ (d) plots of bare GCE (curve a), MWCNTs/GCE (curve b), MoS$_2$ QDs/GCE (curve c), and MoS$_2$ QDs@MWCNTs/GCE (curve d).
The enhancement of the effective surface area of MoS2 QDs@MWCNTs/GCE can be attributed to that MWCNTs and MoS2 QDs can improve the mutual dispersion properties, as evidenced by the TEM results.

**Electrochemical Behavior of MBC.** The electrochemical behavior of MBC at various electrodes was evaluated via CV and SWV in phosphate buffer solution (pH = 7.0; 0.1 M), as shown in Figure 4. Basically, only one well-resolved electrochemical oxidation peak is observed for various modified electrodes, showing that the oxidation process is a quasi-reversible process (Figure 4a). However, the electrochemical activity toward MBC oxidation varied with the modified materials (Figure 4b). The metallic MoS2 QD-modified GCE shows poor electrochemical activity compared to bare GCE, which is attributed to the heavy aggregation of QDs. However, the MoS2 QDs@MWCNTs/GCE shows notable electrocatalytic oxidation activity to MBC. Characterization results indicate that the enhanced oxidation activity to MBC is due, on the one hand, to the enhanced dispersion degree of both MoS2 QDs and MWCNTs generating more active surface sites and, on the other hand, to the enhanced charge transfer kinetics derived from the high-conductivity nature of metallic MoS2 QDs and MWCNTs. Also note that the background currents vary for different electrodes. Among them, the background current of MoS2 QDs@MWCNTs/GCE is the largest and that of the bare electrode is the least. In general, the background current is in correlation with the value of capacity, while the value of capacity is directly proportional to surface area because the dielectric constant is almost constant in the same aqueous system. Therefore, the background current for MoS2 QDs@MWCNTs/GCE among the modified electrodes is possibly attributed to the largest surface area, consistent with the surface area results.

**Effect of the Mass Ratio between MoS2 QDs and MWCNTs and the Amount of Hybrid Material.** According to previous reports, the response of oxidation current peak can be significantly influenced by the modification amount of MoS2 QDs and MWCNTs. To explore the most suitable concentration ratio between MoS2 and MWCNTs, the ratio between MoS2 QDs and MWCNTs (optimized concentration for MWCNTs is 1 mg·L−1) was explored. As shown in Figure 5a, the peak current response attains the maximum when the concentration of MoS2 QDs is 2 mg·L−1. This means that the low concentration of MoS2 QDs was not enough to combine with MWCNTs, which cannot create enough reaction activity sites. However, the excessive MoS2 QDs may result in an overload phenomenon, leading to decreased electrode surface. Therefore, a 2:1 mass ratio between MoS2 QDs and MWCNTs was selected as the optimal loading volume in the subsequent experiment.

The influence of the amount of hybrid material on the electrode response to 1.0 μmol·L−1 MBC was shown in Figure 5b. The peak current gradually increases with the loading amount (3–5 μL), and the maximum peak current response appears at 5 μL of hybrid material, whereas the peak current decreases sharply when the loading volume of nanohybrid increases from 5 to 7 μL. This result may be attributed to the fact that the electrode surface did not get full coverage with less loading amount of nanohybrid, but too much loading volume extends the electron-transfer distance, resulting in a decrease of peak current response. Therefore, 5 μL of hybrid material was selected as the optimal loading volume in the subsequent experiment.

**Effect of pH.** CV was used to investigate the influence of pH on the electrochemical oxidation of carbendazim (1 μM) at the MoS2 QDs@MWCNTs-COOH/GCE. As shown in Figure 6a, the peak current increases gradually as the pH increases from 5.0 to 7.0 and then decreases rapidly from 7.0 to 9.0. Therefore, pH 7.0 was selected for the subsequent experiments. The variation tendency may be caused by the instability of MBC in acidic and alkaline media. As reported by Chen et al., the MBC can be converted into a soluble salt in the acidic medium and undergoes decomposition in the alkaline medium, which are in contrast to the electrochemical reaction. In addition, the oxidation peak potential shifts to negative values with the increase of pH, suggesting that protons are involved in the carbendazim oxidation process. The linear correlation between oxidation potential (Epa) and pH follows the regression equation of \( E_{pa} = -0.0549pH + 1.147 \) (\( R^2 = 0.9930 \)), as shown in Figure 6b. Obviously, the slope value (−0.0549) is close to the theoretical value (0.0592), showing
that equal number of electrons and protons are involved in the MBC oxidation reaction.

**Effect of Scan Rate.** The effect of scan rate (50–450 mV·s⁻¹) on the detection of MBC (1.0 μmol·L⁻¹) at the MoS₂ QDs@MWCNTs/GCE was investigated by CV in phosphate buffer solution (pH 7.0; 0.1 M). The peak currents increase with scan rates and can be expressed as the following linear regression equation: \( I_{pa} (\mu A) = -0.4938 \times n^{1/2} (\text{mV/s})^{1/2} + 2.5479 \) \((R^2 = 0.9968)\), revealing a typical diffusion-controlled electrochemical reversible process. The relationship between the peak potentials and the square root of the scan rate is shown in Figure 7d, following the equation

\[
E_p = E^0 + \frac{RT}{\alpha n F} \ln \frac{RT^n}{\alpha n F} + \frac{RT}{\alpha n F} \ln v
\]

where \( T \) represents the temperature (298 K), \( F \) is the Faraday constant (96,480 C·mol⁻¹), \( R \) is the universal gas constant (8.314 J·mol⁻¹·K⁻¹), and \( \alpha \) and \( n \) are, respectively, the electron-transfer coefficient and electron-transfer number; \( n = 4 \) when \( \alpha = 0.51 \). Therefore, there are four electrons and four protons involved in the electrochemical reaction of MBC. In our previous work, the density functional theory (DFT) calculation has revealed that the most probable sites for the oxidation of carbendazim are the nitrogen atom in the amide and the nitrogen atom in the pyridine ring because the two sites have almost equal distribution of Mulliken charges and equal heat formation for dehydrogenation. Besides, the nitrogen atom in the amide can oxidize to N+O⁻ proceeding with two electrons and two protons. Therefore, the possible oxidation mechanism for the MBC is described as Figure 8.

**Calibration Curve (SWV).** Square-wave voltammetry (SWV) was used for the determination of MBC at the MoS₂ QDs@MWCNTs/GCE under optimum conditions. As shown in Figure 9a, the peak current increases linearly with the increase of MBC concentration in the range of 0.04–1.00 μmol·L⁻¹. The linear regression equation is expressed as \( I_{pa} = -12.0171 ± 0.3775 \times + 0.284 ± 0.0328 \times (R^2 = 0.9951)\). The limit of detection (LOD) is calculated to be 0.026 μM according to the equation \( \text{LOD} = \frac{3\sigma}{S} \), where \( S \) is the slope of the linear regression equation and \( \sigma \) is the standard deviation of \( n \) (\( n = 3 \)). Compared to other previously reported works as shown in Table 1, the sensor developed in this work has a good sensing performance either. Evidently, as discussed in the characterization part, the good sensing performances are attributed to the fact that the anchoring of MoS₂ QDs

![Figure 7](image-url)

**Figure 7.** (a) Cyclic voltammograms of MoS₂ QDs@MWCNTs/GCE in 0.1 M phosphate buffer solution (pH 7.0; 0.1 M) containing 1.0 μmol·L⁻¹ MBC at scan rates of 50, 75, 100, 150, 200, 250, 300, 350, 400, and 450 mV·s⁻¹. (b) Relationship between the peak current and the square root of the scan rate. (c) Relationship between the peak current and scan rate. (d) Relationship between redox peak potential \( (E_p) \) and the natural logarithm of the scan rate \( (\ln v) \).

![Figure 8](image-url)

**Figure 8.** Scheme of the suggested electro-oxidation mechanism of MBC at the MoS₂ QDs@MWCNTs/GCE.
Table 2. Recovery Results for the Determination of MBC in Real Samples via the Proposed Electrochemical Sensor and the Conventional HPLC (n = 3)

| Samples            | SWV        | HPLC       |
|--------------------|------------|------------|
|                    | found (μmol·L⁻¹) | recovery (%) | RSD (%) | found (μmol·L⁻¹) | recovery (%) | RSD (%) |
| platycodon grandi| 0.3        | 0.30 ± 0.005 | 99.91   | 2.40           | 0.29 ± 0.003 | 95.57   | 1.18   |
|                    | 0.7        | 0.68 ± 0.011 | 97.31   | 2.24           | 0.67 ± 0.014 | 95.04   | 2.15   |
|                    | 1.0        | 1.05 ± 0.010 | 105.57  | 1.33           | 0.87 ± 0.003 | 87.15   | 0.39   |
|                    | 0.3        | 0.30 ± 0.005 | 100.53  | 2.34           | 0.29 ± 0.001 | 97.38   | 0.48   |
|                    | 0.7        | 0.71 ± 0.009 | 102.13  | 1.62           | 0.68 ± 0.004 | 96.81   | 0.53   |
|                    | 1.0        | 0.99 ± 0.008 | 98.79   | 1.18           | 0.92 ± 0.034 | 91.86   | 3.68   |
| pears              | 0.3        | 0.30 ± 0.005 | 100.53  | 2.34           | 0.29 ± 0.001 | 97.38   | 0.48   |
|                    | 0.7        | 0.71 ± 0.009 | 102.13  | 1.62           | 0.68 ± 0.004 | 96.81   | 0.53   |
|                    | 1.0        | 0.99 ± 0.008 | 98.79   | 1.18           | 0.92 ± 0.034 | 91.86   | 3.68   |

Figure 10. SWV response of 0.2 μmol·L⁻¹ MBC in the absence and presence of 100-fold ascorbic acid, MgCl₂, CaCl₂, KCl, Pb(NO₃)₂, and carotene (n = 3) at the MoS₂ QDs@MWCNTs/GCE under phosphate buffer solution (pH 7.0; 0.1 M).

increases the van der Waals interaction between the side wall of MWCNTs, and meanwhile, the MWCNTs provide support to the MoS₂ QDs, which prevent the aggregation of MoS₂ QDs, leading to the high exposed surface area of nanohybrid MoS₂ QDs@MWCNTs. In addition, the conductivity of MoS₂ QDs@MWCNTs gets enhanced via the hybrid process, as shown by EIS results, which contributes to the charge transfer kinetics and ultimately results in a high catalytic performance.⁴⁰

Practical Application. To investigate the performance of the electrochemical method in practical application, the proposed sensor and HPLC were used to detect MBC in real samples, respectively. Actual samples include two typical traditional Chinese medicines, namely, platycodon grandi and pears. As shown in Table 2, 95.03–105.57% recoveries were obtained in two traditional Chinese medicine samples, in good agreement with the results obtained via HPLC, proving that the proposed sensor shows high potential for practical application in MBC screening.

Reproducibility, Selectivity, and Long-Term Stability. The reproducibility of the proposed electrochemical sensor was evaluated by SWV using seven different modified electrodes at an MBC concentration of 0.2 μmol·L⁻¹. The relative standard deviation (RSD) for three experiments was calculated to be 3.9%, revealing that the proposed electrode has high reproducibility in the detection of MBC. Interference experiments were performed via SWV under the optimized conditions to evaluate the selectivity of the prepared MoS₂ QDs@MWCNTs/GCE for MBC detection. MgCl₂, CaCl₂, KCl, Pb(NO₃)₂, ascorbic acid (Vc), and carotene (100-fold) were added into MBC solutions, respectively. As shown in Figure 10, almost all of the responses of peak current change less than 5%, indicating that the MoS₂ QDs@MWCNTs/GCE possesses a high selectivity in the detection of MBC. The long-term stability of the prepared sensor was evaluated by measuring the SWV response in 0.2 μmol·L⁻¹ MBC under optimized conditions. Above 95% of the original response was retained after being stored in a refrigerator at 4 °C for 30 days, showing that the proposed sensor has excellent long-term stability.

CONCLUSIONS

In summary, a novel nanohybrid material of MoS₂ QDs@MWCNTs was successfully fabricated via a facile sonication-assisted assembly method, and it was explored for the first time to quantitatively detect MBC in traditional Chinese medicines. The proposed sensor displayed a relatively wide linear range of 0.04–1.0 μmol·L⁻¹ with a low detection of 0.026 μmol·L⁻¹ owing to the synergistic effect occurred between MWCNTs and MoS₂ QDs. The proposed sensor has high sensitivity and selective response on MBC against various potential interferences. Moreover, the sensor enables efficient detection of MBC in typical traditional Chinese medicines with satisfactory recoveries and low RSD, which are in good agreement with the results of HPLC.

MATERIALS AND METHODS

Chemical and Reagents. Carbendazim (97%), Pb(NO₃)₂ (AR), carotene (AR), ascorbic acid (Vc, AR), KCl (AR), K₃[Fe(CN)₆]₃ (AR), and K₄[Fe(CN)₆]₄ (AR) were purchased from Aladdin Reagent Co., Ltd (Shanghai, China). MoS₂ QDs and MWCNTs-COOH (outer diameter, 20–30 nm; purity, 95 wt %) were obtained from Nanjing XFNANO Materials Tech Co., Ltd (Nanjing, China) and Chengdu Organic Chemicals Co., Ltd. (Chengdu, China), respectively. CaCl₂ (AR) and MgCl₂ (AR) were purchased from Shanghai Titan Scientific Co., Ltd. Absolute ethanol (≥99.7%) was acquired from Damao Scientific Co. Ltd (Tianjin, China). Phosphate buffer solutions (0.1 M) with different pH values were prepared by mixing Na₂HPO₄ (0.1 M) and NaH₂PO₄ (0.1 M) stock solutions at various ratios. Unless specified otherwise, other chemicals and reagents used in this study were of analytical grade. Ultrapure water (18.2 MΩ·cm) was used in all experiments.

Apparatus. All electrochemical experiments were performed on a CHI660E electrochemical workstation (Chenhua Instrument Co. Ltd., Shanghai, China) through a classical three-electrode system, in which bare and modified glassy carbon electrode (GCE, Φ = 3 mm) was used as the working electrode, and the saturated calomel electrode (SCE) and platinum wire electrode were used as the reference electrode and counter electrode, respectively. High-resolution transmission electron microscopy (HR-TEM, FEI-G20) was used to investigate the surface morphologies of materials. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB-250Xi X-ray photoelectron spectrometer (Thermo
Fisher Company). Thermogravimetric analysis (TGA) was performed on a thermal analyzer (NETZSCH STA 449 C, Germany) at a heating rate of 10 °C·min⁻¹ under an air atmosphere with a flow rate of 100 mL·min⁻¹ over a temperature range of room temperature to 1000 °C. Raman spectra were recorded on a micro-Raman spectrometer (Horiba Jobin Yvon HR800) with a 532 nm laser as the excitation source at room temperature. Chromatographic separations were obtained using C18 column (150 mm × 4.6 mm I.D., 2.7 μm, VanGuard). The mobile phase was the mixture of methanol and water solution (2:3, V/V) with a flow rate of 1.0 mL·min⁻¹. The injection volume was 10 μL, and the column temperature was 25 °C.

Preparation of Modified Electrodes. MWCNTs-COOH (2.00 mg) and MoS₂ QDs (4.00 mg) were dispersed in 2.0 mL of deionized water with ultrasonic treatment at 300 W for 1 h until uniformly mixed nanocomposites were obtained. Before modification, the bare GCE was polished with alumina slurry (0.05 μm) on chamois leather and then cleaned thoroughly with pure water under sonication, followed by drying process in air. The as-prepared nanocomposite suspension (5.0 μL) was dropped onto the surface of polished GCE and dried under an infrared lamp. The modified electrode was marked as MoS₂ QDs@MWCNTs/GCE. For comparison, other modified GCEs with MoS₂ QDs or MWCNTs were obtained via a similar process and named as MoS₂ QDs/GCE and MWCNTs/GCE, respectively.

Electrochemical Measurements. Electrochemical impedance spectroscopy (EIS) was used to characterize the conductivity property of electrodes, which was applied in a 5.0 mmol·L⁻¹ [Fe(CN)₆]³⁻/⁴⁻ probe solution containing 0.1 mol·L⁻¹ KCl and recorded in the frequency range of 10⁻¹−10⁸ Hz at an open-circuit potential with an amplitude of 5 mV. Chronocoulometry was used to evaluate the effective areas of various electrodes in the potential range of −0.2 to 0.6 V with a pulse width of 0.25 mV. Cyclic voltammetry (CV) and square-wave voltammetry (SWV) were performed in the potential range of 0.5–1.0 V.

Real-Sample Pretreatment and Recovery Experimental. Two typical TCMs samples, namely, platycodon grandiflorum and pear, were involved in the real-sample analysis. The juice of platycodon grandiflorum was prepared via the ethanol extraction method. In detail, 0.5 g of platycodon grandiflorum was immersed in 6 mL of absolute method for 24 h. After that, the extraction was centrifuged at 1000 rpm for 10 min to remove the solid impurities. The juice of pear was obtained via crushing 35 g of pear and then filtered with a Millipore filter (0.45 μm). The obtained juice or filtrate solution (pH 7.0; 0.1 M). The amount of MBC was determined by SWV according to the standard addition method.

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Notes
The authors declare no competing financial interest.

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