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 $\mu\text{mol}\cdot\text{L}^{-1}$, a low detection limit of $2.6 \times 10^{-8} \text{ mol}\cdot\text{L}^{-1}$, 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

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agriculture residues with advantages such as high portability, easy operation, and high efficiency.^{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.^{26–30} Among various nanomaterials, molybdenum disulfide (MoS_2) has been evidenced to be effective in the development of advanced electrochemical sensors owing to its unique structure and prominent electrocatalytic activity.^{31,32} Compared to the nanosheet counterpart, MoS_2 quantum dots (QDs) possess a higher surface area with more unsaturated terminal atoms, which are helpful in electrochemical reactions.³³ Therefore, MoS_2 QDs show a more interesting prospective as sensor materials. For example, MoS_2 QD-based sensors show a wide detection range (0.01–5.57 mM) and a low detection limit (1.90 μM) in the detection of H_2O_2 .³⁴ However, MoS_2 QDs are randomly accumulated, resulting in a decrease of electronic catalytic activity.³⁵ Hybridization with other conductive components such as carbon nanotubes³⁶ and graphene³⁷ is an effective method to improve their electrochemical catalytic performance.

Based on the aforementioned considerations, a 0D/1D nanohybrid MoS_2 QDs@MWCNT was fabricated by integrating metallic 1T-phased MoS_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. HRTEM was employed to characterize the size and microstructure of obtained samples. Obviously, MoS_2 QDs have uniform size with an average diameter of about 2.18 ± 0.64 nm (Figure 1a,b). A highly paralleled and ordered lattice fringe with a d -spacing of 0.25 nm can be indexed to the (103) faces of MoS_2 crystals (Figure 1a, inset).³⁸ No common (002) lattice plane of crystalline MoS_2 was observed as MoS_2 QDs contain very few layers.³⁹ Figure 1c presents the typical TEM images of MoS_2 QDs@MWCNTs, which is observed that the MoS_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_2 QDs and the MWCNT surface.⁴⁰ Figure 1d shows that MoS_2 QDs keep the initial crystal structure after the nanohybrid preparation process. Figure 1e shows the TG analysis of MoS_2 QDs and MoS_2 QDs@MWCNTs. The MWCNTs exhibit one mass loss stage at the initial temperature of about 617 $^\circ\text{C}$, corresponding to the calcination of MWCNTs. As for the MoS_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 $^\circ\text{C}$. The onset temperature of MWCNT calcination in the MoS_2 QDs@MWCNTs sample is about 100 $^\circ\text{C}$ lower than that of the MWCNT sample, showing that the MWCNTs get more individualized after anchoring of MoS_2 ,⁴¹ in good accordance with the TEM results (Figure 1c). Evidently, the well-dispersed MWCNTs and the MoS_2 QDs lead to enhanced surface area of MoS_2 QDs@MWCNTs, which will be further proved by the

Figure 1. (a) HR-TEM image and the highly crystallized lattice (inset) of MoS_2 QDs. (b) Histogram of particle size distribution of MoS_2 QDs. HR-TEM image (c) and highly crystallized lattice (d) of MoS_2 QDs@MWCNTs. (e) TG profiles of MWCNTs and MoS_2 QDs/MWCNTs. (f) Raman spectra of MWCNTs (curve a), MoS_2 QDs (curve b), and MoS_2 QDs@MWCNTs (curve c).

chronocoulometry technique in the **Electrochemical Characterization** section. Moreover, the total weight loss ratio of MoS_2 QDs@MWCNTs is about 65.23%, lower than that of MWCNTs sample, further evidencing that MoS_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} .⁴² 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.⁴³ The I_D/I_G band intensity ratio in MWCNTs is 0.496, which then decreases to 0.433 after anchoring of MoS_2 QDs, showing that the defect sites are reduced, which is possibly because the defect sites of MWCNTs were masked by the MoS_2 QDs. As for the MoS_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_2 , respectively, while the other three peaks at 280, 379, and 402 cm^{-1} are ascribed to the E_{2g}^1 , E_{2g}^2 , and A_{1g} modes from 2H-phase MoS_2 , respectively.^{44,45} The existence of 1T-phase structure endows MoS_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.⁴⁶ In addition, the thickness of MoS_2 QDs

can also be estimated by the difference value between E_{2g}^1 and A_{1g} modes.⁴⁷ The difference value is 24 cm^{-1} in this case, showing that MoS₂ QDs are four-layer thick. Commonly, very few layered structures of MoS₂ 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

Figure 2. XPS survey spectra of MoS₂ QDs and MoS₂ QDs@MWCNTs (a); high-resolution XPS spectra of O 1s (b), Mo 3d (c), and S 2p (d) in MoS₂ QDs and MoS₂ QDs@MWCNTs.

the MoS₂ QDs@MWCNTs hybrid, indicating that MoS₂ QDs were successfully anchored on the MWCNTs. In addition, the appearance of the C element in the nanomaterial of MoS₂ QDs is attributed to the absorption of CO₂ from air. The high-resolution Mo 3d spectra of the MoS₂ QD and MoS₂ QDs@MWCNT 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 Mo⁴⁺ from 2H-phase MoS₂, while the peaks centered at 229.3 and 232.64 eV reveal the existence of 1T-phase MoS₂. The multipeak curve fitting results reveal that the percentage of 1T phase is 54%, suggesting the metallic property and high conductivity of the obtained MoS₂ QDs.⁴⁹ The peak at 235.98 eV is ascribed to Mo⁶⁺, generated from the slight oxidation of Mo edges during the exfoliation process.⁵⁰ Figure 2c presents the high-resolution spectra of S 2p of the two samples. For the MoS₂ QDs, the peaks at 161.76 eV (S 2p_{3/2}) and 163.38 eV (S 2p_{1/2}) represent the 1T-phase MoS₂, and the peaks at 162.64 eV (S 2p_{3/2}) and 164.2 eV (S 2p_{1/2}) represent the 2H-phase MoS₂. The curve fitting results reveal that the percentage of 1T phase is 54%, in good agreement with that of Mo 3d XPS. No S 2p signal peak was found in hybrid samples, suggesting that the S 2p peak was masked by the presence of MWCNTs, which is in accordance with a previous report.⁴⁰ Figure 2d shows the high-resolution spectra of O 1s of the two samples. The peaks at 533.4 and 532.2 eV are assigned to the C–O and C=O, whereas the peak at 530.7 eV is corresponding to the Mo–O bond, which are also consistent with ref 40. In a word, physical characterizations

reveal that the prepared 1T-phased MoS₂ QDs can anchor onto the MWCNTs via van der Waals forces and the anchoring of MoS₂ QDs makes the MWCNTs more dispersed. At the same time, the MWCNTs prevent the aggregation of metallic MoS₂ QDs.

Electrochemical Characterization. The electron-transfer ability of bare and modified electrodes was characterized by electrochemical impedance spectroscopy (EIS) (Figure 3a).

Figure 3. Nyquist diagrams (a) and Bode plots (b) of various electrodes in 5.0 mmol·L^{−1} K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1) containing 0.1 mol·L^{−1} KCl; Q–t (c) and Q–t^{1/2} (d) plots of bare GCE (curve a), MWCNTs/GCE (curve b), MoS₂ QDs/GCE (curve c), and MoS₂ QDs@MWCNTs/GCE (curve d).

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 MoS₂ QDs and MWCNTs films, respectively, revealing that both MoS₂ QDs and MWCNTs have better electrochemical conductivity. The high conductivity of MoS₂ QDs is attributed to that the 1T-phased structure of MoS₂ 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 MoS₂ QDs@MWCNTs, revealing the synergy between MoS₂ 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–t^{1/2} by the following equation

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

where A is the electrode effective area, n presents the transferred electron number, F is the faraday constant, c expresses the concentration of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$, D is the diffusion coefficient of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution ($7.6 \times 10^{-6}\text{ cm}^2/\text{s}$), and Q_{dl} and Q_{ads} present the double-layer charge and faradic charge, respectively. According to the linear regression equation of Q–t^{1/2} (Figure 3d), the effective areas of MoS₂ QDs@MWCNTs/GCE, MoS₂ QDs/GCE, MWCNTs/GCE, and bare GCE are calculated to be 0.13837, 0.07766, 0.06394, and 0.04028 cm², respectively.

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 electro-

Figure 4. Electrochemical behaviors of 1.0 $\mu\text{mol}\cdot\text{L}^{-1}$ MBC at GCE, MoS₂ QDs/GCE, MWCNTs/GCE, and MoS₂ QDs@MWCNTs/GCE in 0.1 $\text{mol}\cdot\text{L}^{-1}$ phosphate buffer solution (pH = 7.0) characterized by CV (a) and SWV (b), respectively.

chemical oxidation peak is observed for various modified electrodes, showing that the oxidation process is a quasi-reversible process (Figure 4a).⁵¹ 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.³⁵ 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 ϵ is almost constant in the same aqueous system.⁵² Therefore, the largest 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,^{53–55} 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 $\text{mg}\cdot\text{mL}^{-1}$) was explored. As shown in Figure 5a, the peak current response attains the maximum when the concentration of MoS₂ QDs is 2 $\text{mg}\cdot\text{mL}^{-1}$. 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

Figure 5. Cyclic voltammetry response of 1 $\mu\text{mol}\cdot\text{L}^{-1}$ MBC to (a) different ratios of MoS₂ QDs and MWCNTs (MoS₂ QDs:MWCNTs: 4:1, 3:1, 2:1, 1:1, 1:2) and (b) different volumes (3, 4, 5, 6, 7 μL) of nanohybrid-modified electrode under phosphate buffer solution (pH = 7.0; 0.1 M).

decreased electrode surface. Therefore, a 2:1 mass ratio between MoS₂ QDs and MWCNTs was used in the following experiments.

The influence of the amount of hybrid material on the electrode response to 1.0 $\mu\text{mol}\cdot\text{L}^{-1}$ MBC is 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 nanocomposite 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.⁵⁶ 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

Figure 6. (a) Cyclic voltammetry response of 1 $\mu\text{mol}\cdot\text{L}^{-1}$ MBC in the pH range of 5.0–9.0 at the MoS₂ QDs@MWCNTs/GCE. (b) Influence of pH on the peak.

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.,⁵⁷ 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 (E_{pa}) and pH follows the regression equation of E_{pa} (V) = $-0.0549 \text{ pH} + 1.147$ ($R^2 = 0.9930$), 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 $\text{mV}\cdot\text{s}^{-1}$) on the detection of MBC (1.0 $\mu\text{mol}\cdot\text{L}^{-1}$) at the MoS_2 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: $I_{\text{pa}} (\mu\text{A}) = -0.4938 \nu^{1/2} (\text{mV}/\text{s})^{1/2} + 2.5479$ ($R^2 = 0.9968$), revealing a typical diffusion-controlled electrochemical reversible reaction process. The relationship between the peak potentials and the natural logarithm of the scan rates is shown in Figure 7d, following the equation E_{pa}

Figure 7. (a) Cyclic voltammograms of MoS_2 QDs@MWCNTs/GCE in 0.1 M phosphate buffer solution (pH 7.0; 0.1 M) containing 1.0 $\mu\text{mol}\cdot\text{L}^{-1}$ MBC at scan rates of 50, 75, 100, 150, 200, 250, 300, 350, 400, and 450 $\text{mV}\cdot\text{s}^{-1}$. (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 scan rate ($\ln \nu$).

(V) = $0.0125 \ln \nu (\text{mV}/\text{s}) + 0.7557$ ($R^2 = 0.9856$). The relationship between E_{p} and $\ln \nu$ can be expressed as the Laviron equation⁵⁸

$$E_{\text{p}} = E^0 + \frac{RT}{\alpha nF} \ln \frac{RTk^0}{\alpha nF} + \frac{RT}{\alpha nF} \ln \nu \quad (2)$$

where T represents the temperature (298 K), F is the Faraday constant ($96480 \text{ C}\cdot\text{mol}^{-1}$), R is the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}$), and α 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,⁵⁹ 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 $\text{N}+\text{O}$ —proceeding with two electrons and two protons.^{60–63} 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 MoS_2 QDs@MWCNTs/GCE under optimum conditions. As shown in Figure 9a, the peak current increases linearly with the

Figure 9. (a) SWV response of various concentrations of MBC (0.04, 0.07, 0.1, 0.3, 0.5, 0.7, 1.0 $\mu\text{mol}\cdot\text{L}^{-1}$) at MoS_2 QDs@MWCNTs/GCE in 0.1 M phosphate buffer solution (pH 7.0; 0.1 M). (b) Linear relationship between peak current and MBC concentration.

increase of MBC concentration in the range of 0.04–1.00 $\mu\text{mol}\cdot\text{L}^{-1}$. The linear regression equation is expressed as $I_{\text{pa}} = -12.0171 (\pm 0.3775) c + 0.284 (\pm 0.0328)$ ($R^2 = 0.9951$). The limit of detection (LOD) is calculated to be 0.026 μM according to the equation $3S_{\text{d}}/K$, where K is the slope of the linear regression equation and S_{d} is the standard deviation of K ($n = 3$). Compared to other previously reported works as shown in Table 1,^{61,64–67} the sensor developed in this work

Table 1. Comparison of Different Modified Electrodes for the Determination of Carbendazim

modified electrode	linear range ($\text{mol}\cdot\text{L}^{-1}$)	LOD ($\text{mol}\cdot\text{L}^{-1}$)	references
GO-MWNT/GC	1.0×10^{-8} – 4.0×10^{-6}	5.0×10^{-9}	61
ZMCPEs	1.0×10^{-7} – 2.35×10^{-6}	3.5×10^{-9}	64
SiO_2 /MWCNT/GCE	2.0×10^{-7} – 4.0×10^{-6}	5.6×10^{-8}	65
NP-Cu/RGO/GCE	5.0×10^{-7} – 3.0×10^{-5}	9.0×10^{-8}	66
Ce-doped ZnWO_4 /CPE	1.0×10^{-8} – 5.5×10^{-6}	3.3×10^{-9}	67
MoS_2 QDs@MWCNTs/GCE	4.0×10^{-8} – 1.0×10^{-6}	2.6×10^{-8}	present 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 MoS_2 QDs

Figure 8. Scheme of the suggested electro-oxidation mechanism of MBC at the MoS_2 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		
	added ($\mu\text{mol}\cdot\text{L}^{-1}$)	found ($\mu\text{mol}\cdot\text{L}^{-1}$)	recovery (%)	RSD (%)	found ($\mu\text{mol}\cdot\text{L}^{-1}$)	recovery (%)	RSD (%)
platycodon grandiflorum	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
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

increases the van der Waals interaction between the side wall of MWCNTs, and meanwhile, the MWCNTs provide support to the MoS_2 QDs, which prevent the aggregation of MoS_2 QDs, leading to the high exposed surface area of nanohybrid MoS_2 QDs@MWCNTs. In addition, the conductivity of MoS_2 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 grandiflorum 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 $0.2 \mu\text{mol}\cdot\text{L}^{-1}$. 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 MoS_2 QDs@MWCNTs/GCE for MBC detection. MgCl_2 , CaCl_2 , KCl , $\text{Pb}(\text{NO}_3)_2$, 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 MoS_2 QDs@MWCNTs/GCE possesses a high selectivity in the detection of MBC. The long-term stability of the prepared sensor was evaluated by

Figure 10. SWV response of $0.2 \mu\text{mol}\cdot\text{L}^{-1}$ MBC in the absence and presence of 100-fold ascorbic acid, MgCl_2 , CaCl_2 , KCl , $\text{Pb}(\text{NO}_3)_2$, and carotene ($n = 3$) at the MoS_2 QDs@MWCNTs/GCE under phosphate buffer solution (pH 7.0; 0.1 M).

measuring the SWV response in $0.2 \mu\text{mol}\cdot\text{L}^{-1}$ 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 MoS_2 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 $0.04\text{--}1.0 \mu\text{mol}\cdot\text{L}^{-1}$ with a low detection of $0.026 \mu\text{mol}\cdot\text{L}^{-1}$ owing to the synergistic effect occurred between MWCNTs and MoS_2 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%), $\text{Pb}(\text{NO}_3)_2$ (AR), carotene (AR), ascorbic acid (Vc, AR), KCl (AR), $\text{K}_3[\text{Fe}(\text{CN})_6]$ (AR), and $\text{K}_4[\text{Fe}(\text{CN})_6]$ (AR) were purchased from Aladdin Reagent Co., Ltd (Shanghai, China). MoS_2 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. CaCl_2 (AR) and MgCl_2 (AR) were purchased from Shanghai Titan Scientific Co., Ltd. Absolute ethanol ($\geq 99.7\%$) was acquired from Damao Scientific Co. Ltd (Tianjin, China). Phosphate buffer solutions (0.1 M) with different pH values were prepared by mixing Na_2HPO_4 (0.1 M) and NaH_2PO_4 (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 ($18.2 \text{ M}\Omega\cdot\text{cm}$) 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, $\Phi = 3 \text{ mm}$) 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 ESCLAB-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 $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under an air atmosphere with a flow rate of $100\text{ mL}\cdot\text{min}^{-1}$ over a temperature range of room temperature to $1000\text{ }^{\circ}\text{C}$. Raman spectra were recorded on a micro-Raman spectrometer (Horiba Jobin Yvon LabRAM HR800) with a 532 nm laser as the excitation source at room temperature. Chromatographic analysis was carried out on a high-performance liquid chromatography (HPLC) device (Waters e2695). Chromatographic separations were obtained using C18 column ($150\text{ mm} \times 4.6\text{ mm I.D.}$, $2.7\text{ }\mu\text{m}$, VanGuard). The mobile phase was the mixture of methanol and water solution (2:3, V/V) with a flow rate of $1.0\text{ mL}\cdot\text{min}^{-1}$. The injection volume was $10\text{ }\mu\text{L}$, and the column temperature was $25\text{ }^{\circ}\text{C}$.

Preparation of Modified Electrodes. MWCNTs-COOH (2.00 mg) and MoS_2 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 ($0.05\text{ }\mu\text{m}$) on chamois leather and then cleaned thoroughly with pure water under sonication, followed by drying process in air. The as-prepared nanocomposite suspension ($5.0\text{ }\mu\text{L}$) was dropped onto the surface of polished GCE and dried under an infrared lamp. The modified electrode was marked as $\text{MoS}_2\text{ QDs@MWCNTs/GCE}$. For comparison, other modified GCEs with MoS_2 QDs or MWCNTs were obtained via a similar process and named as $\text{MoS}_2\text{ QDs/GCE}$ and MWCNTs/GCE , respectively.

Electrochemical Measurements. Electrochemical impedance spectroscopy (EIS) was used to characterize the conductivity property of electrodes, which was applied in a $5.0\text{ mmol}\cdot\text{L}^{-1}$ $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe solution containing $0.1\text{ mol}\cdot\text{L}^{-1}$ KCl and recorded in the frequency range of 10^{-1} – 10^5 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 film ($0.45\text{ }\mu\text{m}$). The obtained juice or extraction was adjusted to pH 7.0 with phosphate buffer 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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