



Article WO₃-Nanocrystal-Modified Electrodes for Ultra-Sensitive and Selective Detection of Cadmium (Cd²⁺) Ions

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Abstract: The detection of heavy metal ions is becoming increasingly important for environmental monitoring and personal safety protection. Owing to their large surface area and suitable conductivity, metal oxide semiconductor nanocrystals have been utilized in chemically modified electrodes for the rapid and low-cost detection of heavy metal ions. However, their sensitivity and selectivity for cadmium ion (Cd²⁺) detection still remains a challenge. Here, a method of ultra-sensitive and selective Cd²⁺ detection based on WO₃-nanocrystal-modified electrodes is proposed and demonstrated. Colloidal WO₃ nanocrystals were synthesized via a solvothermal route and then deposited onto a carbon electrode using a spin-coating method, forming the modification layer at room temperature. The WO₃-nanocrystal-modified electrodes exhibit a remarkable signal transduction capability that converts Cd²⁺ adsorption into current output signals. The peak current was linear to the logarithm of the Cd²⁺ concentration from 1 nM to 10,000 nM when measured using the anodic stripping voltammetry method. The selectivity mechanism was studied and attributed to the high adsorption energy of cadmium on WO₃ compared to other heavy metal ions. Employment of WO₃ for a high-performance Cd²⁺-selective electrode opens many opportunities in portable ion-detection applications.

Keywords: cadmium ion detection; electrochemical sensor; chemically modified electrode; tungsten trioxide; colloidal nanocrystals

1. Introduction

Cadmium is one of the heavy metal ions that can cause irreversible damage to the kidneys, osteoporosis, and deformations if its concentration in the human body exceeds the normal standards [1,2]. Monitoring cadmium in the environment is crucial because cadmium present in nature enters the human body through the food chain [3]. The World Health Organization (WHO) suggests that the concentration of cadmium in drinking water should not exceed 27 nM.

Chemically modified electrodes (CMEs) for detecting heavy metal ions have many advantages such as fast speed, low cost and a simple operation process [4,5]. Strong adsorption capacity with the target ions and good charge transport capability are key parameters of CMEs to achieve high sensitivity and good selectivity. Various functional materials such as carbon [6,7], organic polymers [7] and biological materials [8] have been explored to modify the electrode surface and notable progress has been made for the detection of heavy metals in water.

Most of these materials have a large surface area and excellent catalytic activity, improving the detection sensitivity and range [9]. Porous activated-carbon-carrying palladium nanoparticles were modified onto glass carbon electrodes and measured with the square



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). wave anodic stripping voltammetry method [10]. This electrode showed good detection sensitivity for Cd^{2+} , Pb^{2+} and Cu^{2+} , and the limits of detection were 13.33 nM, 6.6 nM and 11.92 nM, respectively. The high sensitivity has been attributed to the large specific surface area of porous activated carbon and the excellent electrocatalytic performance of palladium nanoparticles. Graphene oxide/ κ -carrageenan/L-cysteine nanocomposite [11] was modified onto glass carbon electrodes to detect Cd^{2+} and Pb^{2+} with limit of detections of 0.58 nM and 1.08 nM, respectively. Nitrogen-doped graphene quantum dots [12] have been demonstrated as electrode modification materials for detecting trace Pb^{2+} , Cd^{2+} and Hg^{2+} . The defects introduced by nitrogen doping increased the adsorption energy of graphene quantum dots toward heavy metal ions.

Selectivity is another key parameter of CMEs for ion detection. Owing to their large surface area with suitable conductivity and chemical stability, metal oxide semiconductor nanocrystals have emerged as an alternative to electrode modification. Superior selectivity toward Hg^{2+} has been observed on both SnO_2 and ZnO semiconductor nanocrystal-modified electrodes. The high sensitivity and selectivity were attributed to the strong adsorption energy of Hg^{2+} on SnO_2 [13]. The thin ZnO layer coated on the electrode surface helps the migration of electrons between the redox-active analyte and electrode, leading to the enhanced electrochemical response toward Hg^{2+} [14]. However, the selective detection of Cd^{2+} remains a challenge for CMEs.

In this work, we propose and demonstrate that WO₃-nanocrystal-modified electrodes are capable of ultra-sensitive and selective Cd^{2+} detection. Colloidal WO₃ semiconductor nanocrystals synthesized via a solvothermal route have excellent solution processability and can be easily deposited onto various substrates. The adsorption energy of different heavy metals on WO₃ was calculated and compared for the selectivity design. When measured using anodic stripping voltammetry (ASV), the WO₃ nanocrystal-modified electrodes exhibit remarkable signal transduction capability to convert the Cd^{2+} adsorption into current output signals.

2. Experiment

2.1. Synthesis of WO₃ Nanocrystals

WO₃ nanocrystals were synthesized via a one-step low-temperature solvothermal method. All the reagents were commercial products and used as-is. Deionized water (18.25 M Ω ·cm) was used to prepare all the aqueous solutions. The specific synthesis steps were as follows: 20 mL of oleic acid (OA, tech. Grade, 90%, Aladdin, Shanghai, China), 2.5 mL of oleamine (OLA, tech. Grade, 80–90%, Alfa Aesar, Haverhill, MA, USA) and 0.68 g of WCl₆ (Sigma, St. Louis, MO, USA) were added to a beaker and stirred while sonicating until WCl₆ was completely dissolved. Then, the beaker was placed in the reactor autoclave and stored in the oven at 180 °C for 3 h. After that, the reactor autoclave was submerged in cold water to cool down quickly. The product was cleaned by centrifugation and then dissolved in 12 mL of toluene to obtain WO₃ nanocrystals at a concentration of 33 mg/mL.

2.2. Preparation of WO₃-Modified Electrodes

The three-electrode was purchased from Zhejiang Nazhi Biotechnology Co., Ltd. (Zhejiang, China), in which polyethylene (PE) was used as the substrate of the modified electrode. Moreover, the working electrode (WE) and the counter electrode (CE) were made of carbon, and the reference electrode (RE) was Ag/AgCl. In total, 15 μ L of WO₃ colloidal nanocrystals were modified on the WE at 800 rpm by spin-coating, and the WO₃-modified electrode was obtained after natural drying. Figure 1 illustrates the schematic diagram of the electrode modification and detection process. The uniformly dispersed WO₃ nanocrystal solution was spin-coated on the WE of the carbon conducting layer, dried naturally, and kept in the Cd²⁺ standard solution for testing. The Cd²⁺ deposition and dissolution reactions occur under a certain voltage.



Figure 1. Schematic diagram of WO₃-modified electrode for Cd^{2+} sensor. (**a**) WO₃ nanocrystal solution; (**b**) The electrode modification process with WO₃ nanocrystals by spin-coating; (**c**) Ion adsorption and desorption process.

2.3. Characterization

The micromorphology and structure of WO₃ were characterized with a transmission electron microscope (TEM) (JEOL2100 from FEI, Shimadzu, Kyoto, Japan) and X-ray diffraction (XRD) (Maxima_XXRD-7000, Shimadzu). The modified layer structure and elemental distribution of WO₃ on the carbon electrode were analyzed with a scanning electron microscope (SEM) and energy dispersive spectrometer (EDS), using a field emission scanning electron microscopy (FE-SEM) device from GeminiSEM, Oberkochen, Germany. The electrochemical performance of the modified electrode was tested using the CHI660E electrochemical workstation (Shanghai Chenhua Company, Shanghai, China).

The Cd²⁺ concentration was tested using the ASV method, where the solutions to be tested were different concentrations of Cd²⁺ standard solution prepared from PBS solution with pH 5.5, with a deposition voltage of -0.7 V and a deposition time of 120 s. The starting value of the dissolution voltage was -0.7 V, and the termination voltage was 1 V. The ASV curve in PBS of pH 5.5 was used as the baseline current.

3. Results and Discussion

3.1. Structure and Morphology of the WO₃ Nanocrystals and Modified Layers

WO₃ nanocrystals were synthesized using a solvothermal method. Figure 2 shows the morphology of WO₃ nanocrystals and the modified electrode. The TEM diagram of WO₃ (Figure 2a) shows that the particle size of WO₃ was less than 5 nm, and the lattice was 0.370 nm, corresponding to the (200) crystal face. The structure of WO₃ nanocrystals was analyzed using XRD (Figure 2b) and diffraction peaks were found at 24°, 33°, 48° and 55°, corresponding to the crystal faces of (200), (220), (400) and (420), respectively. Moreover, no other evident peaks were visible, indicating the high purity of the nanocrystal. Figure 2c,d show SEM images of the carbon electrodes before and after modification with WO₃, respectively. As shown in Figure 2c, the surface of the carbon electrode was loose and porous before modification with WO₃, the micropores were distributed in various sizes, and the carbon particles were relatively large.

3.2. Performance Optimization of the WO₃-Modified Electrodes

The CV curve of the WO₃-modified carbon electrode was first tested in PBS solution with a Cd²⁺ concentration of 10 μ M and pH = 5.5 under the following test conditions: the starting and ending voltage was 0 V, the highest voltage was 1.5 V, the lowest voltage was -1.5 V, and the scanning speed was 0.05 V/s. The test result is shown in Figure 3. From the results it can be seen that the reduction peak appeared at -0.7 V, so -0.7 V was used as the deposited potential.

The number of WO₃-modified layers and the pH value of the Cd^{2+} standard solution were optimized for optimum detection. The electrochemical reaction of the WO₃-nanocrystal-modified carbon electrode for heavy metal ions detection is controlled by three fundamental processes: ion diffusion in solution, electrochemical reaction and electron transmission on the electrode surface. All three processes are related to the modified material, and are reflected in the electrochemical properties of the electrode. The equivalent circuit is shown in Figure 4a. The arc radius in the high-frequency region of the electro-

chemical impedance spectrum (EIS) represents the electron transmission ability (R_{ct}) on the electrode surface. The ability to transmit electrons on the electrode surface decreases with increasing arc radius. The line in the low-frequency region represents the ion diffusion ability, namely, the capacitance characteristic (C_d). Theoretically, increasing the electron transmission and ion diffusion ability can improve the electrode's sensitivity. The electron transmission ability is directly related to the conductivity of the modified electrode. In addition to the distribution of the double-electric layer on the electrode surface, the ion diffusion ability depends on the ion diffusion characteristics of the test solution. Therefore, the modification parameters of the electrode can be optimized by the size of R_{ct} in the equivalent circuit.



Figure 2. The characterization of material and electrode micromorphology. (**a**) TEM image of WO₃ nanocrystals; (**b**) XRD diagram of WO₃ nanocrystals; (**c**) SEM image of the unmodified carbon electrode; (**d**) SEM image of WO₃-modified electrode; (**e**) Cross-sectional SEM image of the modified electrode; (**f**-**h**) The W-element (**f**), C-element (**g**), and O-element (**h**) distribution mapping of the electrode's cross-section.



Figure 3. The CV curve of the WO₃-modified electrode in the Cd²⁺ standard solution.



Figure 4. Optimization of WO₃-modified electrodes. (**a**) The equivalent circuit of the electrochemical system; (**b**) The EIS (inset) and R_{ct} of the modified electrode with different numbers of layers of WO₃ nanocrystals in the KKS solution; (**c**) The EIS (inset) and R_{ct} of the modified electrode with different numbers of layers of WO₃ nanocrystals in the KKS and Cd²⁺ mixture solution; (**d**) Dissolution peak currents of WO₃-modified electrodes in Cd²⁺ solutions with different pH values.

The distribution of WO_3 on the electrode surface will directly affect the electron transmission ability of the electrode and the double-electric layer on the electrode surface. The EIS curve of the electrode modified with different layers of WO₃ nanocrystals were tested in 0.05 M K₃[Fe(CN)₆]/K₄[Fe(CN)₆] and 0.1 M KCl mixed solution (KKS), and in KKS and 10 μ M of cadmium ions (Cd²⁺) mixed solution (KKS/Cd²⁺) (Figure 4b,c, respectively). The results show that R_{ct} first decreases and then increases with the increased number of modified layers in the KKS solution and KKS/Cd²⁺ mixed solution after modification with WO₃ nanocrystals. This may be attributed to the conversion of electronic transmission from carbon to WO_3 and carbon joint transmission. In addition, the electrical conductivity of WO₃ is weaker than that of carbon, which decreases the electron transmission ability and increases R_{ct} . As the amount of WO₃ increases and covers the electrode surface, the electron transmission on the electrode surface changes from WO_3 and carbon joint transmission to WO₃ transmission. Owing to the large number of unsaturated suspension bonds, WO₃ nanocrystals can adsorb metal ions in the solution and conduct electrochemical reaction on their surface. When the charge caused by the electrochemical reaction accumulates a higher potential, it causes a sudden current release, which enhances the conductivity of the electrode. Consequently, the R_{ct} in the equivalent circuit is reduced. As the number of WO₃modified layers and their thickness increase, the effective adsorption of Fe²⁺/Fe³⁺ only occurs on the limited atomic layers in the surface, while the deeper WO₃ cannot positively affect electron adsorption and electrochemical reaction. As a relatively poor-conductivity semiconductor material, WO3 nanocrystals become resistant to electronic transmission, thereby increasing the R_{ct} in the equivalent circuit. The addition of Cd²⁺ did not affect the ion adsorption and the electrochemical reaction, so the change in R_{ct} in the mixture solution of KKS/ Cd^{2+} is consistent with the conditions in the KKS solution. With the increased number of modified layers, the Rct first increases and then decreases. The results show that R_{ct} is minimal when the number of modified layers is three. Meanwhile, the

equivalent circuit and the EIS results of three-layer WO₃ nanocrystals in KKS/Cd²⁺ mixture solutions showed that R_Ω, R_{ct} and C_d can also be calculated as R_Ω = 253 Ω, R_{ct} = 8176 Ω and C_d = $3.788 \times 10^{-7} \mu$ F/cm², respectively.

The optimal pH value was selected with the optimal number of three modified layers. The bar graph of the ASV peak current of WO₃-modified electrodes in 10 μ M of Cd²⁺ solution at different pH values is shown in Figure 4d. As the pH value increases from 4.5 to 7.0, the peak current increases and then decreases. When the pH value of the solution is 5.5, the modified electrode has the highest sensitivity to Cd²⁺. This is because the products generated by the oxidation of the Cd at the working electrode are mainly Cd²⁺ in the weakly acidic environment with a pH value of 5.5, and the dissolved oxygen on the CE is reduced and bound to H⁺ in the solution into water. The corresponding reactions on the WE and the CE are as follows:

$$WE: 2Cd \rightarrow 2Cd^{2+} + 4e^{-} \tag{1}$$

$$CE: O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
 (2)

According to the Nernst equation:

(

$$\varphi = \varphi^{\theta} + \frac{0.0591}{n} \lg \frac{\left[C(O_x)/C^{\theta}\right]^{b}}{\left[C(R_{ed})/C^{\theta}\right]^{a}}$$
(3)

where the electrode potential for the CE is:

$$\varphi(O_2/H_2O) = \varphi^{\theta} + \frac{0.0591}{4} \lg C(O_2) / [C(H^+)]^4$$
(4)

The above equation shows that the reactants in the electrochemical reaction on the CE contain H⁺, and the H⁺ concentration in the solution affects the electrode potential (φ) of the CE. The electrode potential affects the reaction process and the output current, so the solution's pH has an optimal value for Cd²⁺ detection and pH 5.5 was selected.

3.3. Electrochemical Performance of WO₃-Nanocrystal-Modified Electrodes

The ASV method was used to detect Cd^{2+} under the optimal WO₃ modification layer number and pH value of the measured solution. Figure 5a,b compare the ASV curves in different Cd^{2+} concentration solutions before and after modification. The carbon electrode without WO₃ has no significant dissolution peaks, and the carbon electrode modified with WO₃ has a considerable dissolution peak current in the Cd^{2+} solution. The peak current increases with increasing the Cd^{2+} concentration. The potential of the dissolution peak is approximately -0.5 V. This may occur when a specific voltage is applied to WO₃, where Cd^{2+} is first reduced to zero valence Cd at the potential of -0.7 V and then to Cd^{2+} at the reverse linear scanning voltage while releasing charges and forming the dissolution peak current. The greater the Cd^{2+} concentration, the greater the current generated by oxidation. Figure 5c further analyzes the ASV curve of the Cd²⁺ concentration from 0 nM to 10 nM, showing that by further refining the concentration range of Cd²⁺, WO₃-modified electrodes can still clearly distinguish the Cd²⁺ concentration and achieve a fine detection. It can also be found that the stripping peak potential position differs with the Cd²⁺ concentration. According to the Nernst Equation (3):

$$\varphi(Cd^{2+}/Cd) = \varphi^{\theta}(Cd^{2+}/Cd) + \frac{0.0591}{2} lg[C(Cd)/C(Cd^{2+})]$$
(5)



Figure 5. Electrochemical performance of the WO₃-modified electrodes. (**a**) ASV curve of the unmodified electrodes in different concentrations of the Cd^{2+} solution; (**b**) ASV curve of WO₃-modified electrodes in high concentrations of the Cd^{2+} solution (inset: linear fitting curve of the dissolution peak current of WO₃-modified electrodes in different concentrations of the Cd^{2+} solution); (**c**) ASV curve of WO₃-modified electrodes in low concentrations of the Cd^{2+} solution (inset: linear fitting curve of the dissolution peak current of WO₃-modified electrodes in low concentrations of the Cd^{2+} solution (inset: linear fitting curve of the dissolution peak current of WO₃-modified electrodes in low concentrations of the Cd^{2+} solution); (**d**) Comparison of the dissolution peak current of different heavy metal ions (the concentration of Cd^{2+} was 1 μ M, and the other interfering ions were 25 times that of Cd^{2+}); (**e**) Comparison of ASV and ICP methods in different water samples; (**f**) Normalized fitting curve for the ASV method and the ICP method.

With the increasing concentration of Cd^{2+} , the electrode potential of Cd^{2+}/Cd moves in a negative direction, in agreement with the results shown in Figure 5c. As the Cd^{2+} concentration further increases, Cd²⁺ may accumulate on the electrode surface. The electrode potential approaches the electrode potential of Cd^{2+}/Cd again. The inset in Figure 5b,c extracts the peak current of the ASV curve in the range of 0–10,000 nM and 0–10 nM. It was discovered that the Cd^{2+} concentration C is linear to the logarithm of the peak current I in the range of 1–10,000 nM and satisfies the linear equation I = 0.778 lgC + 6.296, with linear correlation coefficient $R^2 = 0.975$. In the range of Cd^{2+} concentrations from 0 to 10 nM, the Cd^{2+} concentration C is linear with the peak current I and satisfies the linear equation I = 0.190C + 4.633 with linear correlation coefficient R² = 0.934. From the results of the linear fitting, it can be seen that the detection sensitivity of the modified electrode is $0.190 \,\mu\text{A/nM}$. To study the reproducible detection ability of the modified electrode to Cd²⁺, the above test process was repeated five times. The error bars were added in the inset of Figure 5b,c. The relative error was less than 0.43, suggestive of good repeatability. The limited of detection (LOD) of the modified electrode for Cd^{2+} was calculated as 0.029 nM using the 3SD_{blank}/slope [15]. Table 1 compares the detection effects of Cd²⁺ reported in the literature. The results reveal that the WO₃-nanocrystal-modified electrode for Cd^{2+} detection in this article has a wider detection range and lower LOD.

The selectivity of modified electrodes is important for detecting heavy metal ions. Figure 5d shows the peak current extracted from the ASV curve in the presence of different heavy metal ions. The Cd²⁺ concentration was 1 μ M; 25 times that concentration of Hg²⁺, Pb²⁺ and Cu²⁺ were successively added to the Cd²⁺ solution and their ASV curves at the deposition voltage of -0.7 V were tested. The dissolution peak current of the ASV curve showed that adding Hg²⁺ and Pb²⁺ did not significantly change the dissolution peak current, indicating that the WO₃-modified carbon electrode had a good anti-interference ability with Hg²⁺ and Pb²⁺. After the addition of Cu²⁺, the dissolution peak current increased slightly, probably because the ionic radius of Cu²⁺ (0.73 Å) is smaller than that of

 Cd^{2+} (0.95 Å). It is easy to deposit on the WO₃ surface and combine with the suspension bond. Then, Cu^{2+} is reduced at the reduction potential of -0.7 V to form a Cd–Cu–W alloy, causing a dissolution peak current due to oxidation. Thus, Cu^{2+} has some cross-interference with the detection of Cd^{2+} [16], but the dissolution peak potential of Cu^{2+} is significantly different from that of Cd^{2+} . Therefore, the interference of Cu^{2+} can be addressed by the position of the dissolution peak current.

Figure 5e compares the Cd^{2+} concentrations of several real water samples detected with the WO₃-modified electrode and the Inductive Coupled Plasma (ICP) method [17]. The results show that the Cd^{2+} concentration tested with the two methods were basically consistent and lower than the WHO standard requirements in drinking water, indicating that the WO₃-modified electrode has some practical value in detecting Cd^{2+} in real water. Figure 5f normalizes the test results using ASV and ICP methods, with a slope of 0.813. The closer the slope of the curve is to 1, the more consistent the results are. The test results showed that the modified electrode method was basically consistent with that of ICP.

Table 1. Comparison of Cd²⁺-detection performance of electrodes modified with different chemicals.

Modification Material	Method	Detection Range	Detection Limit	Reference
RGO/g-C ₃ N ₄ /BiTF	SW-ASV	180–4050 nM	90 nM	[18]
Graphene Oxide/k-carrageenan /L-cysteine nanocomposite	SW-ASV	550 nM	0.58 nM	[10]
Pd@PAC/GCE	SW-ASV	25,500 nM	13.3 nM	[11]
Sb ₂ O ₃ /MWCNTs	LASV	715,625 nM	100 nM	[19]
AC/MGPE	ASV	452,678 nM	500 nM	[20]
Bismuth/GCE	DP-ASV	9–135 nM	0.81 nM	[21]
zinc ferrite/GCE	DP-ASV	89–1160 nM	22.5 nM	[22]
WO ₃ nanocrystals	ASV	1–10,000 nM	0.029 nM	This work

3.4. Analysis of the Sensitive Mechanism of WO₃-Modified Electrodes

To investigate the mechanism of Cd^{2+} detection using WO₃-modified carbon electrodes, different stages of adsorption and electrochemical reaction were studied. Firstly, the effective active area of the electrode was analyzed via the CV curves in the KKS solution before and after WO₃ modification at different scan speeds, as shown in Figure 6a,b. The oxidation peak currents at different scan speeds were extracted and plotted against the scan speed v^{1/2} to obtain Figure 6c. The effective area of the electrode before and after WO₃ modification was calculated according to the Randles–Sevcik formula [23]:

$$i_p = 2.69 \times 10^5 A n^{\frac{3}{2}} D_0^{\frac{1}{2}} C_0^* v^{\frac{1}{2}}$$
(6)

where i_p is the peak current of the CV curve; *A* is the electroactive area; n is the electron number of reaction-transfer (n = 1); D_0 is the diffusion coefficient of the reactants $(D_0 = 7.6 \times 10^{-6} \text{cm}^2 \text{s}^{-1})$; *v* is the scan speed; and C_0^* is the initial concentration of the reactants $(C_0^* = 5 \text{ mM})$ [24].

In this electrochemical system, n = 1, $D_0 = 7.6 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ and $C_0^* = 5 \text{ mM}$. Therefore, the slope of the above formula is only correlated with the effective electroactive area A of the electrode. It can be obtained that the effective electroactive area was 0.672 cm² and 0.451 cm² before and after WO₃ modification, respectively. The effective electroactive area decreases after modification with WO₃ nanocrystals, which is consistent with the SEM analysis before and after modification with WO₃ nanocrystals, indicating that the effective area of the electrode is not the primary reason for improving the detection performance of Cd²⁺.



Figure 6. Comparison of the CV curves at different scan speeds. (**a**) CV curve of the unmodified electrodes at different scanning speeds in the KKS solution; (**b**) CV curve for WO₃-modified electrodes at different scanning speeds in KKS solution; (**c**) Linear fitting curve of the oxidation peak current and $v^{1/2}$ before and after electrode modification at different scanning speeds.

The adsorption energy of heavy metal ions on the surface of WO₃-modified electrodes was analyzed using the density functional theory (DFT). The simulation was performed with VSAP in the Materials Studio system. Heavy metal ions were found to have the following adsorption surfaces on the WO₃-modified carbon electrode (Figure S1): WO₃ surface, WO₃-C interface and C surface. Each adsorption surface had the following adsorption sites of O-, W-O, W-, C, and C-C, respectively. Their adsorption energies and bond lengths are shown in Table 2. The table reveals that the O- adsorption site of Cd²⁺ at the WO₃-C interface had the largest adsorption energy of -2.054 eV and the minimum bond length of 2.651 Å. Compared with the adsorption energy at C and C-C positions, WO₃-C interface sites had the maximum adsorption energy. Therefore, the electrode modified with WO₃ has a better performance than the unmodified electrode because of the greater adsorption energy of O-sites.

Table 2. Adsorption energy and bond length of Cd^{2+} at different adsorption sites on the surface of WO_3 -nanocrystal-modified electrode.

Sites	Items	0	W-O	W	C-C	С
WO ₃ surface	E _{ads} (eV)	-1.373	-0.671	-0.394		
	Length (Å)	2.861	2.713	3.295		
WO ₃ –C interface	E _{ads} (eV)	-2.054	-1.663	-0.617		
	Length (Å)	2.651	2.741	3.013		
C surface	E _{ads} (eV)				-0.855	-1.066
	Length (Å)				3.269	3.054

Table 3 compares the adsorption energy of heavy metal ions such as Cd^{2+} , Pb^{2+} , Hg^{2+} and Cu^{2+} at the WO₃–C interface. The results demonstrate that Cd^{2+} has the largest adsorption energy and the shortest bond length. Therefore, WO₃ has a good selectivity for Cd^{2+} .

Table 3. Adsorption energy of different heavy metal ions on the WO₃-modified electrode surface.

Sites	Items	Cd	Pb	Hg	Cu
0	E _{ads} (eV)	-2.054	-1.371	-0.751	-0.573
	Length (Å)	2.651	2.763	2.968	2.967
W-O	E _{ads} (eV)	-1.663	-0.811	-0.423	-0.217
	Length (Å)	2.741	2.861	3.154	3.051
W	E _{ads} (eV)	-0.617	-0.185	-0.159	-0.413
	Length (Å)	3.013	3.261	3.369	2.975

In addition to the strong adsorption capacity of the ions on the electrode surface, the electrons should also be transmitted efficiently. Figure 7a,b present the schematic diagrams

of the adsorption sites and electron transfer of Cd^{2+} on the WO₃ surface, as analyzed using the DFT theory. With the absorption of Cd^{2+} on the O-bond of the WO₃ surface, the redistribution of the electron motion trajectory is caused by the overlap of the electron cloud. The blue part in Figure 7b is the electron dissipation region, and the yellow part is the electron accumulation area. Due to the strong electronegativity of the oxygen atoms, the electron cloud shifts to the oxygen atoms overall, forming the accumulation and dissipation regions of the electrons.



Figure 7. The adsorption of Cd^{2+} on the WO₃ surface and the transfer of the electron. (a) The adsorption site of Cd^{2+} on the WO₃ surface; (b) The electron transfer at the interface after the adsorption of Cd^{2+} .

The Cd^{2+} reaction process on the WO₃-modified carbon electrode surface may be as follows:

Deposition :
$$Cd^{2+}+2e^- \rightarrow Cd$$
 (7)

Dissolution :
$$Cd \rightarrow Cd^{2+} + 2e^{-}$$
 (8)

 Cd^{2+} initially diffuses from the solution to the electrode surface under the electric field before being adsorbed on the electrode surface. The concentration of the solution is very low, and the diffusion coefficient of Cd^{2+} in the solution is a constant ($D = 7.2 \times 10^{-6} cm^2 s^{-1}$). Therefore, the speed of the reaction process is mainly determined by the deposition speed of Cd^{2+} on the electrode surface and the electrochemical dissolution reaction speed. The adsorption of cadmium ions on the WO₃ surface causes the offset of the electron cloud and the compact electrode structure of WO₃ and carbon permeate each other, giving it a good electron transport capability, facilitating the electrochemical reactions and charge transfer, and thus improving the detection of Cd^{2+} .

The detection efficiency of Cd^{2+} based on the WO₃-modified electrode is analyzed in Figure 8. According to the scanning speed (50 mV/s) and the ASV curves with different Cd^{2+} concentrations (Figure 5b), the current-time curves of Figure 8a can be obtained, which integrate the current into the time to achieve the dissolved charge Q₂. The deposited currents at different concentrations of Cd^{2+} were tested and multiplied by the deposition time of 120 s to yield the deposited charge Q₁ (Figure 8b). The detection efficiency η of Cd^{2+} was obtained by Q₂/Q₁. Figure 8c shows the detection efficiency at different concentrations of Cd^{2+} . The results demonstrate that when the concentration of Cd^{2+} is low (≤ 10 nM), its detection efficiency is relatively high. With the increase in Cd^{2+} concentration, its detection efficiency is high. With the increase in Cd^{2+} concentration of Cd^{2+} , so the detection efficiency is high. With the increase in Cd^{2+} concentration, although the dissolution current increases, the proportion of the dissolution sites to the adsorption sites decreases, thus reducing the reaction efficiency.



Figure 8. Analysis of the detection efficiency for Cd^{2+} . (a) The relationship of dissolution current and scanning time; (b) The relationship of deposition current, deposition charge, dissolution charge and Cd^{2+} concentration; (c) The relationship between Cd^{2+} concentration and detection efficiency.

4. Conclusions

In this paper, WO₃ nanocrystals were spin-coated on the carbon electrode surface for Cd^{2+} detection. The number of WO₃ modification layers and pH value of the measured solution were determined to be optimal at three and 5.5, respectively. The ASV method was used to detect Cd^{2+} concentrations in the range of 1–10,000 nM, and the limit of detection was 0.029 nM. Meanwhile, the WO₃-modified electrode has a better selectivity for Cd^{2+} than other heavy metal ions, which may be attributed to the strong adsorption energy to Cd^{2+} and remarkable signal transduction capability, which convert the Cd^{2+} adsorption into current output signals. The excellent Cd^{2+} -detection ability and convenient electrode preparation process indicate that the WO₃-nanocrystal-modified electrode has strong application prospects for Cd^{2+} detection.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/chemosensors11010054/s1, Figure S1: Schematic diagram of the adsorption sites of heavy metal ions on the modified electrode surface.

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