Journal of Electroanalytical Chemistry 826 (2018) 90–95

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

# Fabrication of ZnO/rGO/PPy heterostructure for electrochemical detection of mercury ion

Yunpeng Zhuang[a], Minggang Zhao[a,*], Yan He[a], Frank Cheng[b], Shougang Chen[a,*]

[a] College of Materials Science and Engineering, Ocean University of China, 266100 Qingdao, PR China
[b] Department of Mechanical Manufacturing Engineering, University of Calgary, T2L1Y6, Canada

ARTICLE INFO

*Keywords:*
Heterostructure
Interface effects
Nanostructure
Electrochemistry
Mercury ion

ABSTRACT

The sensitive online detection technique for heavy metal ions present in ocean, while effectively eliminating the interference of other chemicals, has been lacking at the present time. We found that the interfacial barrier of ZnO/rGO/PPy heterostructure had powerful physical effects on electrochemistry, and the Schottky barrier driven electrochemical detection was further developed. As based on the interfacial physical barrier, it could avoid the existing problem of the traditional electrochemical sensing mechanism and apply in more interfering environment. The sensitive detection of trace mercury ion ($Hg^{2+}$) in actual seawater was achieved by employing the ZnO/rGO/PPy heterostructure. The interfacial barrier effect provides a chance to develop sensors used in more interfering environment.

## 1. Introduction

The ocean is the basic environment and important resource for the survival and development of mankind. Unfortunately, the pollution of the ocean has been increasing seriously. Contamination of seawater with heavy metals is one of the greatest challenges due to the huge threats to human health, marine organisms and ecosystem even at low concentrations [1,2], so it is necessary to develop effective methods for their detection in seawater. However, the presence of salts and organics in the marine environment interferes the performance of the sensors that have been developed in fresh water for heavy metal ions seriously [3,4]. The sensors working for detection of heavy metal ions in fresh water would malfunction in seawater, unless the complex pretreatment is carried out on the seawater, including physical and chemical. Therefore, it is desired to develop novel online sensing mechanism without interference by the environmental factors present in seawater.

Electrochemical techniques have been effective for the determination of heavy metal ions, due to the high sensitivity, low cost, fast response and simplicity [5–8]. As electrochemical methods are usually based on redox reactions, it is thus a challenge to eliminate the signals from interferents with similar redox characteristics. Unfortunately, most of them are interfered by other heavy metal ions and offer limited sensitivity [9]. Anodic stripping voltammetry (ASV) is one of the important and versatile techniques in electroanalytical methods and has been extensively used for metal ion determination [10]. However, it involves a pre-concentration step before analysis [11], making the process complex and not suitable for on-line detection. In addition, some researchers designed various electrochemical sensors based on the immune-recognition systems, such as antibodies [12], DNA zyme [13,14] and nucleic acid probes [15], to detected $Pb^{2+}$ [16], $Hg^{2+}$ [17], $Cu^{2+}$ [18], and so on. Although the sensors offer a high specificity, they suffer from high costs, rigorous fabrication conditions, poor reproducibility and critical operating conditions such as optimum temperature, pH and chemical instability, which limit their applications [19,20]. Moreover, most of the reported works forced on detection of heavy metal ions in buffer solutions or fresh water, to the sensors are rarely used directly determination of heavy metal ions in seawater due to the presence of various interference [3,21].

Recent advances demonstrated that the rational design of heterojunction interface could play a key role in the sensing process, and further research has good prospects. For example, zinc oxide (ZnO)–nickel oxide (NiO) nanowire based heterojunction exhibited a sensitive response to hemoglobin (Hb), resulting from the interfacial effects of p-n junction [22]. The p-p junction interface of NiO/polyaniline (PANI) could be used to distinguish dopamine (DA), uric acid (UA) and ascorbic acid (AA) [23]. It has been found that gas sensors based on Schottky junctions were able to realize supersensitive and fast response towards the gas phase analytes [24–27]. And the Schottky contact at the end of Metal-ZnO nanowires Field Effect Transistor (FET) device exhibited the enhanced sensitivity than ZnO nanowires with the

---

* Corresponding authors.
*E-mail addresses:* zhaomg@ouc.edu.cn (M. Zhao), sgchen@ouc.edu.cn (S. Chen).

https://doi.org/10.1016/j.jelechem.2018.08.016
Received 31 July 2018; Received in revised form 15 August 2018; Accepted 16 August 2018

ohmic contact in protein detection [28,29]. The Schottky junction is a heterogeneous junction formed by metal and semiconductor, and the photoelectric properties can be significantly improved by changing the junction area state [30]. A potential barrier exists in the Schottky interface, hindering the electronic transmission in certain directions. Since electrochemical detection involves reactive electron transfer in certain directions, it is assumed that the barrier possesses a strong effect on electrochemical reactions. Furthermore, if the analyte can induce the change of the Schottky barrier, direct electrochemical response would be driven to generate.

In this work, we proposed a Schottky barrier driven electrochemical sensing mechanism considering the effect of interfacial barrier on electrochemistry. A sensing model of detecting $Hg^{2+}$ was established by using ZnO/reduced graphene oxide (rGO) Schottky barrier as the driving factor and polypyrrole (PPy) as the selective adsorption factor. In this system, the adsorption of $Hg^{2+}$ trapped electrons from Schottky junction, leading to changes of barrier height to drive electrochemical detection. It broke the bottleneck of the seawater interference and achieved the sensitive $Hg^{2+}$ detection in seawater. Different from traditional electrochemical strategies, the interfacial barrier effect on electrochemistry plays a unique role.

## 2. Experimental

### 2.1. Synthesis of the ZnO nanomaterials

Prior to use, fluorine-doped tin oxide (FTO) conductive glass (10 mm × 5 mm × 2 mm) was carefully cut and cleaned by sonication in acetone, ethanol, and deionized water for 15 min each case, respectively, and then dried at 60 °C. Take 0.416 g $Zn(NO_3)_2{\cdot}6H_2O$ to dissolve into 38 mL deionized water. After magnetically stirring for 10 min, 2 mL $NH_3{\cdot}H_2O$ was added in the prepared $Zn(NO_3)_2$ solution drop by drop, which was then magnetically stirred for 10 min. The FTO was immersed into the solution, which was installed in an autoclave kept at 95 °C for 6 h. The substrate was removed from the solution, rinsed with ethanol and deionized water, and dried at 60 °C for 6 h.

### 2.2. Synthesis of the ZnO/rGO Schottky interface

The grapheme oxide (GO) prepared by modified hummer method [31] was well dispersed in deionized water to make a suspension. The suspension was sonicated until obtaining well-dispersed GO solution. The electrodeposition of reduced grapheme oxide (rGO) was carried out in 1 mg/mL GO solution at −1.2 V for 90 s. A three-electrode system was used, where a platinum plate was used as counter electrode, an Ag/AgCl electrode as reference electrode and the FTO/ZnO as working electrode. The products were washed and dried at 60 °C for 6 h.

### 2.3. Synthesis of the ZnO/rGO/PPy hierarchical structure

For electrochemical polymerization of pyrrole, 0.15 M sodium dodecylbenzene sulfonate (SDBS) was added to the deionized water to obtain the actual electrolyte solution. Electropolymerization was carried out in 0.1 M pyrrole monomer by cyclic voltammetric on a three-electrode system. After rinsed in ethanol and deionized water, the ZnO/rGO was served as working electrode, while a Pt foil and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. The potential scanning was from −0.5 V to 2 V at a potential scan rate of $100\ mV{\cdot}s^{-1}$. The loading amount of polypyrrole (PPy) was controlled by the number of potential scan cycles. After deposition, the working electrode was washed with deionized water, and then dried in vacuum at 60 °C for 6 h.

### 2.4. Detection of $Hg^{2+}$

The detection of $Hg^{2+}$ experiments were carried out in 0.1 M phosphate buffer solution (PBS) or seawater use differential pulse voltammetry (DPV) method at room temperature. The PBS pH = 7.0, the seawater was collected from the Yellow Ocean at the Qingdao Shilaoren beach (Shandong province, China), the pH = 8.0. The potential scanning was from 0 V to 0.5 V at a sensitivity of $10^{-4}$ A/V. Obtain a DPV curve by adding mercury ions of different gradient concentrations.

### 2.5. Characterization and electrochemical measurement

The morphologies of prepared specimens were characterized using ULTRA 55 Field-Emission Scanning Electron Microscope (FESEM) and a HITACHIH-7650 Transmission electron microscope (TEM). The X-ray diffraction (XRD) patterns of the specimens were obtained using a Bruker D8 ADVANCE X-ray diffractometer with a Cu Kα radiation over the 2θ range from 20° to 80° at the scanning speed of 4°/min. Energy-dispersive X-ray spectrum (EDS) was measured with a Phenom ProX SEM. The Raman spectroscopies were obtained with LabRAM HR Evolution (532 nm).

The electrochemical experiments were performed using a CHI600E workstation (Shanghai Chenhua) on a conventional three electrode system which consisted of a platinum electrode as counter electrode, a Ag/AgCl electrode as reference electrode and the prepared specimen as working electrode. All electrochemical measurements were carried out in 0.1 M phosphate buffer solution (PBS) or seawater at room temperature.

## 3. Results and discussion

### 3.1. Characterization of the ZnO/rGO/PPy hierarchical structure

Fig. 1 shows the SEM and TEM images of the prepared ZnO/rGO and ZnO/rGO/PPy, respectively. From Fig. 1a–b, it is seen that the ZnO/rGO nanostructure had a uniform structure, and a few of ZnO nanorods were bridged by rGO thin films. In Fig. 1c, the surface of ZnO exhibited a typical wrinkled texture since it was wrapped by rGO. The wrapping characteristic was further confirmed by TEM image in Fig. 1e, where the thickness of the rGO was about 4 nm, corresponding to the rGO with five or six layers based on the theoretical value of 0.78 nm for single layer graphene [32]. From Fig. 1d, it is seen that the surface of rGO became rougher and less transparent, indicating the presence of PPy layers. It is further confirmed in Fig. 1f that the rGO films were surrounded by PPy.

Fig. 2 showed the XRD, Raman and EDS data of the prepared ZnO/rGO/PPy, respectively. The XRD pattern in Fig. 2a showed the intensive peaks correspond to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), (2 0 1), (0 0 4), and (2 0 2) crystalline planes, suggesting a good crystallinity of ZnO. The additional diffraction peaks corresponding to $SnO_2$ were resulted from the FTO substrate. The structural characterization by Raman spectra in Fig. 2b showed Raman spectra of GO, ZnO/rGO/PPy composite. The Raman spectra of GO included the high intensity of G band at 1591 $cm^{-1}$ and D band at 1344 $cm^{-1}$. The Raman spectrum of ZnO/rGO/PPy includes the peaks at 576 $cm^{-1}$, 956 $cm^{-1}$, 1042 $cm^{-1}$, 1344 $cm^{-1}$ and 1591 $cm^{-1}$. Particularly, the peak at 576 $cm^{-1}$ was attributed to ZnO in the composite. There was no shift of the peak position between GO and ZnO/rGO/PPy, but the intensity ratio of D band over G band (ID/IG) increased from 0.96 to 1.07 in the ZnO/rGO/PPy hierarchical structure, indicating the reduction of GO [33,34]. The atomic percentage of the ZnO/rGO/PPy hierarchical structure was determined by EDX in Fig. 2c. The results demonstrated the existence of O (from ZnO and rGO), Zn (from ZnO), C (from rGO and PPy) and N (from PPy), and the atomic percentage of each element was also given. The typical current voltage (I-V) curve of the ZnO/rGO in air was shown in Fig. S1 (Supporting information), the nonlinear behavior implied the formation of Schottky barrier [35].