All-Solid-State pH sensing material based on cysteic acid/graphene oxide nanocomposites

Lin Liu^a, Yuting Huang^b, Jing Zhao^a, Zhijie Zhu^c, Huaihao Zhang^a, Chengyin Wang^{a,*}

^a College of Chemistry and Chemical Engineering, Jiangsu Key Laboratory of environmental engineering and monitoring, Yangzhou University, 180 Si-Wang-Ting Road, Yangzhou 225002, China.

^b School of Environmental Science and Technology, Dalian University of Technology, 2 Liao-Ning Road, Dalian, 116024, China.

^c Yangzhou Educational Service Centre, 36 Jin-Zhong Road, Yangzhou, 225002, China.

*Corresponding Author: wangcy@yzu.edu.cn

Abstract

Novel cysteic acid/graphene oxide composite film on glassy carbon electrode has been developed through the electrochemical oxidation of *L*-cysteine (CySH) for constructing an all-solid-state pH sensor. Potentiometric pH response of the cysteic acid/graphene oxide modified electrode in Britton–Robinson buffers revealed a linear working range from pH 2 to 12 with a slope of about -50.2 mV pH^{-1} and fast response (less than 1 minute). The as-developed pH sensor also showed excellent reproducibility and high stability and had been successfully used to detect real samples with satisfactory results.

Keywords: graphene oxide, cysteic acid, *L*-cysteine, solid-state pH sensor.

1. Introduction

Graphene oxide (GO) was regarded as a two-dimensional-layer precursor for synthesizing graphene derivatives⁽¹⁾. GO containing various oxygen groups, such as epoxy, hydroxyl, and carboxyl groups can be easily dispersed in common organic solvents, which enables GO to form stable suspensions with biomolecules, polymers and solvents, and nanocomposite films⁽²⁾. These reactive oxygen groups also offer good active sites for functionalizing GO and immobilizing electroactive species⁽³⁾. Owing to its excellent electronic, thermal and mechanical properties⁽⁴⁾, GO has been widely applied in the electrochemical sensor⁽⁵⁾, nanoelectronics⁽⁶⁾, lithium battery⁽⁷⁾ and supercapacitor⁽⁸⁾. In recent years, many

studies have been focusing on preparation GO composite materials to construct electrochemical sensors. *L*-cysteine is known as an important amino acid for several biological equilibriums. It has been reported that cysteic acid can be obtained through electrochemically oxidizing *L*-cysteine⁽⁹⁾. Cysteic acid with carboxylate and sulfonated groups is referred to as a steady and biocompatible material for the fabrication sensors. Therefore, the cysteic acid/GO composite film would exhibit good mechanical properties and chemical reactivity owing to various functional groups for sensor applications.

As for pH value measurement, it is very important in many fields, such as food industries, environment monitoring, farming geonics, clinical and biological sciences⁽¹⁰⁾. It is crucial to choose a reliable method to analyze the acidity of aqueous solution. Although the traditional glass bulb pH electrode is a well established tool in the measurement of pH, it has a lot of disadvantages which cannot be avoided, such as mechanical fragility, instability, high-cost, high-resistance, special treatment before and after use⁽¹¹⁾. It can't be applied in some special applications, such as high-pressure, high-temperature or high-viscosity fluid environment. Since the use of a glass membrane electrode to determine the hydrogen ion concentration in aqueous solutions is frequent and necessary, great efforts has been made to develop all-solid pH sensors to avoid these drawbacks, and a variety of alternatives have been demonstrated. New techniques and methods have broadened the scope of pH detection. For examples, metal/metal oxide^(12, 13), ion sensitive field-effect transistors (ISFET)^(14, 15), fiber-optical techniques^(16, 17), and

sensing thin film materials have been extensively explored to fabricate the all-solid pH sensors.

In this paper, we fabricated a novel solid-state pH sensor based on cysteic acid/GO composite film. The cysteic acid was obtained from electrochemical oxidation of *L*-cysteine (CySH) on the surface of GO modified electrode. Owing to carboxylate and sulfonated groups in cysteic acid and GO with various oxygen containing functional groups, the proposed pH sensor achieved excellent electromotive force (emf) response with a wide linear range from pH 2 to 12 at 25 °C and high stability. We had successfully employed this proposed pH sensor to detect real samples and obtained satisfactory results. This novel GO/cysteic acid composite film could have great potential in various analytic applications.

2. Experimental

2.1 Chemicals and apparatus

SP-1 natural graphite powders were obtained from Bay Carbon, MI, USA. *L*-cysteine (CySH) was purchased from Sigma-Aldrich Co., Ltd. Phosphoric acid, acetic acid, boric acid, sodium hydroxide and other reagents used in this experiment were all of analytical grade. All solutions were prepared with deionized water.

Cyclic voltammetry (CV) experiment was carried out on a CHI 660a electrochemical workstation (Shanghai Chenhua, China). We employed a conventional three-electrode system with a GO modified glassy carbon electrode (3.0 mm in diameter) as a working electrode, a platinum wire as an auxiliary electrode, and a saturated calomel electrode (with 2.0 mol/L KNO₃ salt bridge) as a reference electrode. Open-circuit potential (OCP) of the cysteic acid/GO modified electrode was measured as a function of pH value of the sample solutions by using CHI 660a electrochemical workstation. Field emission scanning electron microscope (FESEM) images were captured by S-4800 II FESEM (Hitachi High-Technologies Corporation, Japan) at an accelerating voltage of 15.0 kV.

2.2 Fabrication of cysteic acid/graphene oxide composite films

Firstly, the glassy carbon electrodes were polished with 1 μm and 0.05 μm α-alumina powders respectively, and then sonicated in 1:1 nitric acid, acetone and de-ionized water successively. Natural graphite powders were oxidized to GO using a modified Hummers method⁽¹⁸⁾. Graphene

oxide suspension was prepared by dispersing 3.0 mg GO in 20 mL THF under ultrasonication for 30 minutes. A 10 μL aliquot of the suspension was dropped directly on glassy carbon electrode surface and had it dried at the room temperature, and then obtained GO modified electrode. The cysteic acid/GO composite film electrodes were prepared by cycle scanning the electrodes between −0.8 V and +2.2 V (vs. SCE) at a scanning rate of 200 mV s^{−1} in 0.04 M HCl solution containing 2.5 × 10^{−3} M *L*-Cysteine (CySH) for 10 consecutive cycles, and the result was shown in Fig. 1. The SEM image of the as-obtained cysteic acid/GO composite film was shown in Fig. 2. The modified electrode was then electroactivated by cyclic scanning from 0 V to +1.5 V in the 0.5 M H₂SO₄ solution until a steady cyclic voltammogram was obtained.

Fig. 1. Cyclic voltammograms of the GO/GCE in 0.04 M HCl solution containing 2.5 × 10^{−3} M *L*-cysteine (CySH). Scan rate: 200 mV s^{−1}; Scan potential: −0.8 to +2.2 V; Consecutive cycle: 10.

Fig. 2. SEM image of cysteic acid/GO composite film.

3. Results and discussions

3.1 Electrochemical oxidation of *L*-cysteine and the mechanism of cysteic acid/graphene oxide for pH sensing

Electrochemical oxidation of CySH on GO/GCE was

investigated by the cyclic voltammetry. CySH can be adsorbed on the electrode by using voltammetric measurement or under high positive potential on the GCE electrode and further oxidized to cysteic acid⁽¹⁹⁾. A typical cyclic voltammogram from Fig. 1 shows that there is an irreversible oxidation peak at ca. +0.8 V, which implies that CySH is oxidized to *L*-cystine (CySSCy). And there is another irreversible oxidation peak at 1.3 V corresponding to the generation of CySO₃H. The detailed mechanism had been investigated in our previous study⁽²⁰⁾. GO are functionalized with oxygen containing functional groups proved to be effective to improve interfacial bonding between polymer and GO. Furthermore, the functional group -SO₃H of cysteic acid was confirmed to be strongly adsorbed at electrode through cyclic voltammetric and polarization measurements⁽²¹⁾. Therefore, the as-obtained cysteic acid/GO exhibited great stability and had good chemical reactivity owing to various functional groups.

Cysteic acid with carboxylate and sulfonated groups can be used as an electrode modifier due to its attractive ion-exchange characteristics. In addition, GO with a lot oxygen containing functional groups such as carboxyl, hydroxyl and phenol would be attributed to the good pH sensing. The cysteic acid/GO composite film had possessed the advantages of the above two materials and achieved excellent pH sensing performance.

3.2 Selection of the optimal operation conditions

The pH response of the cysteic acid/GO was affected by the amount of the GO loaded on the electrode surface. The same volume (10 μ L) of the suspensions with different concentrations (0.05, 0.1, 0.15, 0.20, 0.25 mg mL⁻¹) of the GO was used to seek the optimal amount of GO during the preparation process. After the cysteic acid film was formed on the GO/GCE electrode by electrooxidation of CySH, the potentiometric responses of the pH sensors based on as-obtained composite film for the detection pH values from 2.0 to 12.0 was recorded. With the increment of the GO concentration, the potentiometric response increased accordingly and the slope of pH value was closed to Nernstian slope, indicating that the sensitivity increases with the loading of GO on the electrode. However, the peak current didn't increase when the GO concentration was beyond 0.15 mg mL⁻¹, which could be attributed to the decrease of electrical conductivity due to excessive GO loaded on the electrode. Therefore, an optimum GO concentration of 0.15 mg mL⁻¹ was selected for the

fabrication of the cysteic acid/GO composite modified electrodes in this work.

The potentiometric responses of the pH sensors should also be concerned with the amount of cysteic acid adsorbed on the electrode. When the GO/GCE was swept by the cyclic voltammetry, the more cycles swept, the more cysteic acid molecules would be produced onto the surface of the GO/GCE electrode. Owing to more cysteic acid with more active groups, the potentiometric responses gradually increased with the sweep cycles performed on the electrode. But more cysteic acid would reduce the conductivity of the composite film. We finally chose 10-sweep-circle under the cyclic voltammetry as optimized condition for electrochemical oxidation of *L*-cysteine in the present experiment.

3.3 Calibration curve, response time and stability

Under the optimum detection conditions, the emf response of the pH sensor based on cysteic acid/GO to pH changes was investigated using a Britton-Robinson (BR) buffer solution and performing simultaneous pH control employing a calibrated standard glass pH electrode dipped into the same solution. We found that the potentiometric response was proportional to the pH value in the range of 2.0 - 12.0 with a near-Nernstian slope of 50.2 mV/pH unit. Fig. 3 showed the linear relationship between pH values of testing solution and their corresponding potentials from which a linear equation can be established as: E (V) = 0.4215-0.0502(V/pH) *pH*. The correlation coefficient R^2 = 0.997 can also be deduced.

The response time of the proposed electrode was determined from step changes of pH in BR buffer solution after injections of HCl or NaOH solutions. The response time was about 5 s at the pH of around 7.0. The response times of the pH sensor in solutions of different pH values were detected in the same way, and the results are in the following: 28 s at pH 2, 23 s at pH 4, 10 s at pH 6, 8 s at pH 8, 21 s at pH 10, 58 s at pH 12. Therefore, the response times of the proposed pH sensor can be used for practical application.

The test stability of the pH sensor was carried out in a 0.1 mol L⁻¹ phosphate buffer solution of pH 5.0 for 11 hours without interruption, at a temperature of 25 $^{\circ}$ C. The results demonstrated that the stability of the proposed pH sensor was excellent with a relative deviation standard of 0.80 %. The repeatability proved to be good when the pH sensor was repeatedly transferred between the solution of pH 4.0 and pH 5.0, and the relative standard deviation is

0.51 %. The lifetime of the cysteic acid/GO/GC electrode had also been examined, and it demonstrated that the proposed electrode can retain 98.2 % of its initial response after one-month-storage. This stability should be acceptable for most practical applications.

Fig. 3. Calibration curve of potentiometric response versus pH of cysteic acid/GO/GC electrode.

3.4 Application of pH measurement in real samples

The developed sensor for the pH detection was applied to test real samples including Coca Cola and tap-water, and then the result was shown in Table 1. The relative deviations were 1.6 % and 0.7 %, respectively. It can be seen that the proposed pH sensor can be used in detecting real aqueous samples.

Table 1. Detection of pH in real samples.

Real samples	Detected by glass bulb electrode	Detected by the proposed pH sensor	Relative deviation (%)
Coca Cola	3.87	3.81	1.6
Tap-water	6.81	6.86	0.7

4. Conclusions

We had developed a novel solid-state pH sensor based on the cysteic acid/GO composite film. The proposed pH sensor possessed a sensitivity of 50.2 mV/pH, high stability (over a month) and a linear working range from pH 2 to12 at 25 °C. The measurements of some real samples demonstrated that the proposed pH sensor is suitable for pH determination in real aqueous samples. The method also provides a potential to miniaturize pH sensor.

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