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Polydopamine@electrochemically reduced graphene oxide-modified electrode for electrochemical detection of free-chlorine

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ABSTRACT

This paper describes the electropolymerization of dopamine on an electrochemically reduced graphene oxide (ERGO) surface that was utilized successfully for the electrocatalytic detection of free chlorine (free-Cl). ERGO was fabricated on a glassy carbon (GC) electrode by the reduction of graphene oxide (GO) using cyclic voltammetry (CV). Subsequently, the electrode (ERGO/GC) surface was electropolymerized using dopamine for 30 cycles and a polydopamine-modified electrode (PDA@ERGO/GC) was obtained. The PDA@ERGO/GC-modified electrode was characterized by field emission scanning electron microscopy, X-ray photoelectron spectroscopy, electrochemical impedance spectroscopy, and CV. The surface coverage concentration (τ) of the PDA@ERGO/GC electrode was 1.70×10^{-10} mol cm^{-2}. The presence of quinone functional groups on the electrode surface offers excellent electrocatalytic ability for the determination of free-Cl. The calculated kinetic parameters of the fabricated electrode confirmed its facile performance towards the determination of free-Cl with a rate constant (ks) and charge transfer coefficient (α) of 3.38 s^{-1} and 0.75, respectively. Under the optimal conditions, the reduction current of free-Cl is proportional to its concentration range, 9.9–215.2 μM, with a correlation coefficient of 0.998 and a sensitivity and detection limit (LOD) of 0.0071 μA μM^{-1} and 44 nM, respectively. Furthermore, PDA@ERGO/GC was used for the real sample determination of free-Cl from swimming pool water with satisfactory recoveries obtained in the range of 102.4% to 103.0%.

1. Introduction

Sodium hypochlorite (NaOCl) is a widely used disinfectant in water treatments, such as in drinking water purification, wastewater management, swimming pool water disinfection, and chemical industries [1–3]. In general, a 2–3 mg L^{-1} chlorine concentration gives excellent disinfection activity, and the tolerable amount of chlorine is 5 mg L^{-1} [4]. If the level of chlorine concentration is too low, it will be ineffective for disinfection; an overdose of free chlorine may lead to the formation of trihalomethanes [5]. Trihalomethanes are suspected carcinogens to humans; hence, regular monitoring of the free chlorine in water is necessary and challenging [6]. Chlorine (dissolved gas) and NaOCl are hydrolyzed in water (acid base pH 7.5) in the form of hypochlorous acid (HOCl) and hypochlorite ions (OCl^-), and these are called the free chlorine (free-Cl).

$$Cl_2\,(g) + 2H_2O \rightarrow 2HOCl + 2H^+ + 2e^- \quad (1)$$

$$NaClO \rightarrow Na^+ + ClO^- \quad (2)$$

$$HClO \leftrightarrow ClO^- + H^+ \quad (3)$$

Equations (2) and (3) are pH sensitive; at values of pH less than 7.5, the dominant species is HOCl. The $HClO/ClO^-$ ratio fluctuates at the range of pH 6–9. Several methods have been developed for free chlorine determination in water, such as spectrophotometry [7], potentiometry [8], colorimetric methods [9], chromatography coupled to mass spectrometry [10], chemiluminescence [11], and electrochemical methods [2,4,12–14]. Among the proposed techniques, electrochemical methods offered attractive features, of time consuming, simple procedure, and easy handling. A range of electrochemical methods have been reported for the determination of free chlorine, which is mostly overlapped with the dissolved oxygen reduction potential of free chlorine, making it complex. Salazar et al. fabricated a surfactant-assisted modified Prussian blue film electrode for free chlorine determination with a working potential

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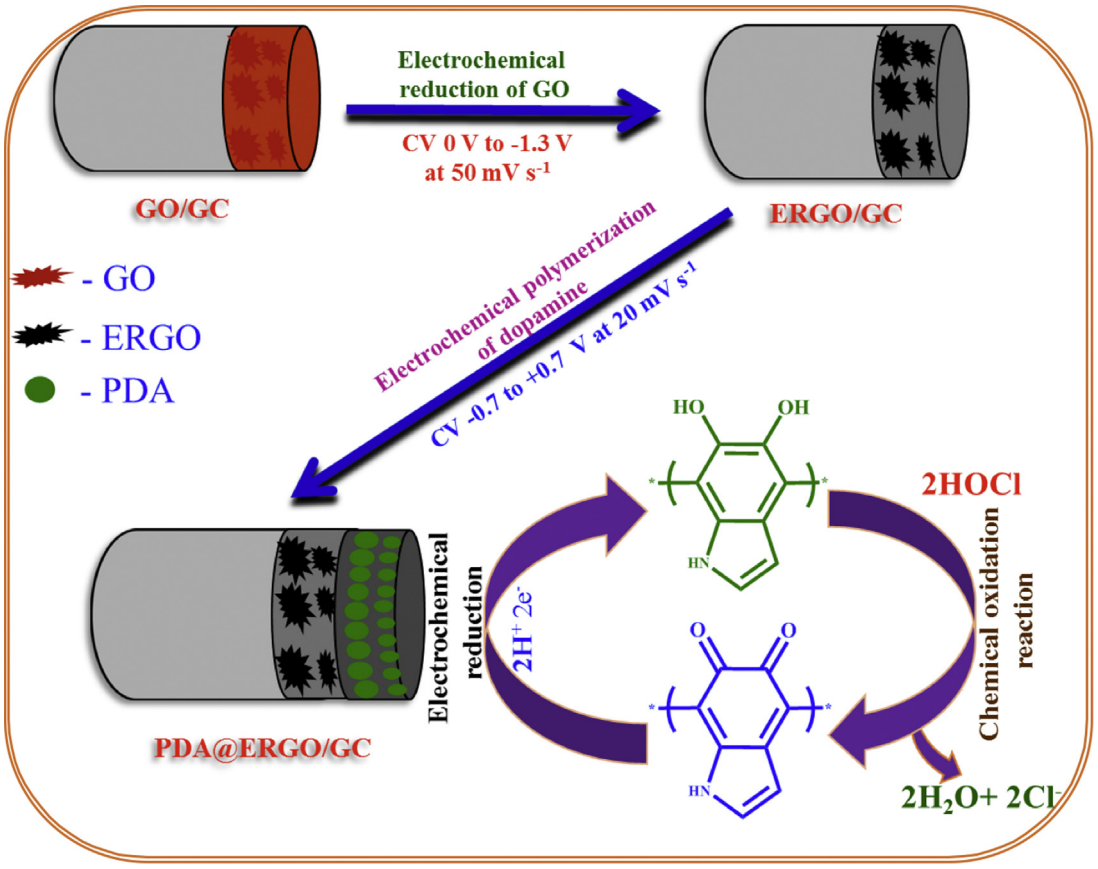

Scheme 1. Schematic diagram of the electrode preparation and PDA@ERGO/GC-modified electrode free-Cl determination by the EC' mechanism.

of −0.2 V [12]. To avoid problems of dissolved oxygen reduction potential overlapping with free-Cl reduction potential, Campo et al. used silicon chips coated with gold thin-films as the working electrode with an operating potential of +0.15 V, but the electrode materials are expensive [2]. A boron-doped diamond electrode has been applied for free chlorine detection with a working potential of +1.1 V, which is a higher operating potential [4]. Senthilkumar et al. utilized a polymelamine-modified screen printed carbon electrode for electrocatalytic free chlorine detection [15]. Therefore, the electroactive redox polymer probe for free chlorine determination is a reliable and extensive interest. The polydopamine (PDA)-modified glassy carbon electrode, as an electrocatalytic (EC) mechanism probe has not been used for free chlorine determination, which might be suitable for real sample applications.

PDA is an eumelanin polymer; its attractive adhesive properties have versatile applications, such as thin film coating materials [16], antifouling high-flux membranes [17], nanoparticle stabilization [18], protein immobilization [19], biomineral formation [20], and electrochemical biosensor [21–24]. The polymerization of dopamine (DA) occurs mostly by chemical methods [25] and it is facile to polymerize; however, it is difficult to control its surface morphology and layer thickness. In addition, the utilization of PDA as an electrocatalytic probe should be done at the desired conductivity. Also, PDA is a catecholamine, which easily oxidize by electrochemical-chemical-electrochemical reactions series to form polymer on the electrode surface [26,27]. Loget et al. reported that the electrodeposition of PDA leads to passivated multilayers, which decrease the anodic and cathodic peak currents, limiting its applications as an electrocatalytic probe electrode material [27]. The electrochemical redox couple activity of PDA can be extended by conductive carbon-based composite materials.

Recently, graphene/polymer composites have been reported to be excellent electrode materials for supercapacitors, batteries, and electrochemical biosensors [29–31]. In addition, reduced graphene oxide supports polymer growth by the increased polymer nucleation rate, which has large internal surface areas, unique properties of the polymers, and the good conductivity of graphene with a large surface area [29]. Graphene-modified electrodes have potential electrochemical sensing applications. Each atom of the graphene layer contains surface atoms that have effective molecular interactions, leading to electron transport over graphene, and making it quite sensitive to adsorbed analytes [32]. Therefore, graphene-based composites have attracted great attention for electrochemical biosensors. Numerous methods have been exposed for graphene production; among these, the chemical reduction of graphene oxide (GO) obtained from the Hummers' method [33] is a convenient method for obtaining a good yield. On the other hand, chemicals that are used for GO reduction, such as hydrazine hydrate, require a high temperature treatment, need multiple washing steps, and are labor and time consuming. To avoid these problems, the electrochemical reduction of GO has been developed [34,35], which is interesting for graphene thin layer formation owing to the fast, simple, and green method. This paper reports the electrocatalytic reduction of free chlorine based on a quinone redox couple of PDA. Using the optimized PDA@ERGO composite, a better catalytic reduction current could be obtained by the ERGO support.

2. Experimental

2.1. Reagents and chemicals

Graphite, sodium hypochlorite, disodium hydrogen phosphate (Na_2HPO_4), and monosodium hydrogen phosphate (NaH_2PO_4)