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Electrochemical studies of two diphenols isomers at graphene nanosheet–poly(4-vinyl pyridine) composite modified electrode

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ABSTRACT

A voltammetric sensor for hydroquinone (HQ) and catechol (CC) was developed. This was realized by modifying a glassy carbon electrode with composite film of graphene nanosheet and poly(4–vinylpyridine) (GR–P4VP/GCE). The smaller peak potential separation (ΔE_p) of the GR-P4VP/GCE indicates the electrode process is very reversible as a result of increase in kinetics of electron transfer as and when P4VP was present in the modified electrode as compared to the GR/GCE and bare GCE. The proposed electrode has displayed a synergistic effect of P4VP and GR on the electrocatalytic oxidation of CC and HQ in sodium sulphate buffer solution (pH 2.5). The anodic peak potential, E_{pa}, of both were clearly resolved in either cyclic voltammetry or differential pulse voltammetry which made simultaneous determination of both compounds possible. The GR–P4VP/GCE has exhibited excellent sensitivities in the measurement of HQ and CC with detection limits of 8.1 nM and 26 nM, respectively. The GR–P4VP/GCE developed was not interfered by traditional interferences, viz. phenol, nitrophenol, aminophenols, bisphenol A and chlorophenols. The GR–P4VP/GCE was successfully applied for simultaneous detection of spikes HQ and CC in tap water and lake water with encouraging results.

1. Introduction

The simultaneous determination and isolation of phenolic compounds is of interest in many fields, such as medical, food and environmental controls [1–3]. Hydroquinone (HQ) and catechol (CC) are two isomers of diphenols. They are toxic to humans and difficult to degrade [3]. Furthermore, the simultaneous detection of HQ and CC is highly desirable as they usually coexist in products due to their similarities in structures and properties [2,3]. Therefore, it is necessary to develop rapid and simple analytical methods for sensitive and selective determination of HQ and CC.

Graphene (GR) has been used extensively in electrochemical sensors because of its excellent conductivity, high specific surface area; high mechanical, thermal and chemical stabilities compared with graphite and carbon nanotubes [4–6]. Its unique crystal structure makes it extremely attractive as a support material to promote the electrochemical reactivity of molecules on the modified electrode surface [7,8]. In spite of all these, functionalization and dispersion of graphene sheets are also crucial in their applications. The functionalized and defective graphene sheets are more hydrophilic and can be easily dispersed in solvents with long-term stability [6,9]. In addition, appropriate chemical functionalization of graphene for example by conventional acid treatment method, for formation of–COOH and–OH groups, prevents the agglomeration of single layer graphene and aggregation can also be reduced by the attachment of other small molecules or polymers to the graphene sheets [6,10,11]. Meanwhile, non-covalent functionalization, e.g., co-dispersion with polymers has proven successful in solubilizing graphene nanosheet [1].

At present, a number of methods have been developed to determine CC and HQ, such as chromatography [12], spectrophotometry [13], capillary electrophoresis [14], chemiluminescence [15], pH based-flow injection analysis [16] and electrochemical methods [17–19]. The electrochemical methods have their advantages in various aspects such as excellent sensitivity, high accuracy, good reliability and low cost of instrumentation compared to the other modern techniques. Thus, they become more desirable methods for environmental and industrial analysis of CC and HQ [2,20]. However, the application of conventional electrodes has its drawback in that the overpotential for oxidation of CC and HQ is high, detection

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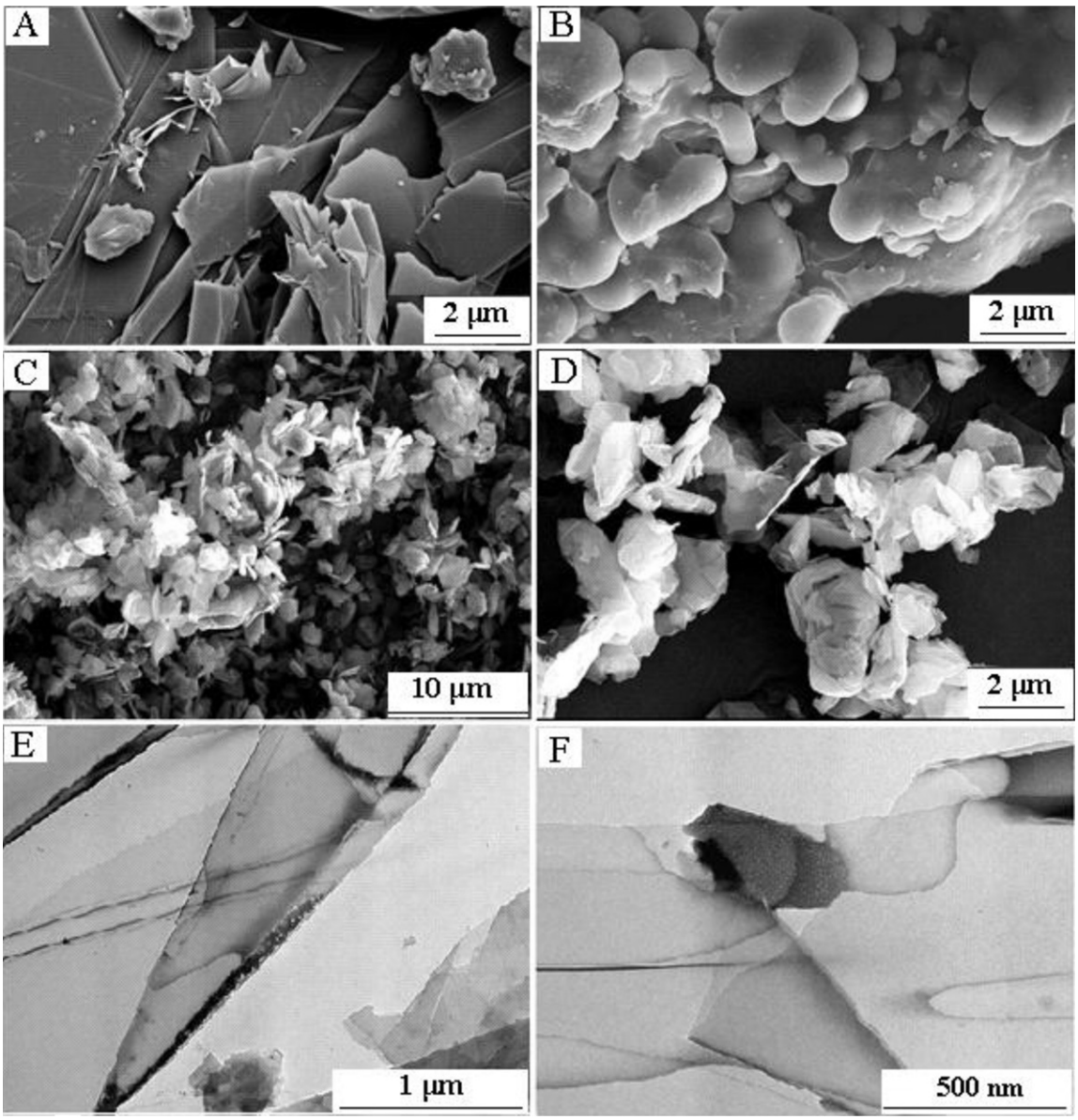

Fig. 1. SEM images of (A) GR nanosheet (B) P4VP and GR–P4VP/GCE in (C) low-magnification and (D) high-magnification, EF-TEM images of GR–P4VP/GCE in (E) low-magnification and (F) high-magnification.

selectivity is poor and also redox peaks of the two phenol isomers are, in many cases, highly overlapped [2,19,21]. Hence, much effort has been focused on utilizing advance materials as electrodes modifier, for the purpose of achieving sensitive and selective detection of CC and HQ [2,22].

On the other hand, using of conducting polymers such as poly(4-vinyl pyridine) (P4VP) and polypyrrole to improve the electrocatalytic activity, electron transfer kinetics and stability of the modified electrodes have been reported [23–27]. P4VP is a hydrophobic polymer in a polar solvents and in aqueous is cationic polyelectrolytes at low pH [27]. It has been reported [28–30] that non-covalent and covalent modifications of the carbon-based nanomaterials, e.g. carbon nanotubes (CNTs) and GR, with polymers or biomolecules are aimed at improving their dispersions and orientations in aqueous solutions. The flexible chains of P4VP may act as a stabilizing agent when wraps around the GR, preserving its intrinsic electrical and mechanical properties [27]. Besides, high electrical conductivity and good redox mediator are among the analytical advantage of P4VP in polymer nanocomposite electrodes [23,29,30].

To the best of our knowledge there has been no report yet on the usage of GR nanosheet–P4VP composite modified glassy carbon electrode (GCE) in the monitoring of these diphenols (CC and HQ). In this study, we report on the combination of GR nanosheet and P4VP as a modifier in the fabrication of modified GCE for the simultaneous determination of the CC and HQ. A favorable electrode performance is described in the following sections.

2. Experimental

2.1. Instrumentation

Electrochemical measurements were carried out on electrochemical workstation BAS Epsilon (Bio analytical system, USA). A conventional three-electrode system including a platinum wire as an auxiliary electrode and an Ag/AgCl (3 M NaCl) as a reference