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Electrocatalytic oxidation of thiourea on graphene nanosheets–Ag nanoparticles hybrid ionic liquid electrode

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ABSTRACT

A simple, selective and sensitive graphene nanosheets–Ag nanoparticles hybrid ionic liquid electrode (GNSs–AgNPs/ILE) was used for the electrochemical determination of thiourea (TU). Cyclic voltammogram of TU showed two well defined oxidation signals at the potentials of -0.2 and 0.1 V vs. Ag/AgCl. Amperometric method was used for quantification of TU in the range of 1.0 – 3000 μM . The theoretical detection limit was obtained as 0.7 μM . The sensor was successfully applied for TU determination in orange juice and waste water.

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1. Introduction

Thiourea (TU) is known to be a serious environmental organic pollutant, with harmful effects on mammalian species and nitrifying bacteria [1,2]. It is a carcinogenic [3] and allergenic [4] substance. Furthermore, TU causes the disturbance of carbohydrate metabolism [5], induce hypothyroidism [6] and inhibits nitrification in soil and water [7]. However, it has a widespread use in various fields of science and technology such as electroplating industry [8], rubber industry [9], photography [2], analytical chemistry [10], agriculture [11] and for induction of early ripening in several fruits [12]. Thus, a convenient, selective, sensitive, rapid and cost-effective method is demanded for the analysis of this hazardous material in waste water and environment.

Several analytical methods have been reported for determination of TU such as titrimetry [13], piezoelectric method [14], high performance liquid chromatography (HPLC) [15], Fourier transform infrared (FT-IR) spectrometry [16], chemiluminescence [10], flow injection methods [11], UV–vis spectrophotometry [17,18] and electrochemical methods [1,8,19–24]. Compared with other methods, electrochemical techniques have some advantages including simplicity, rapidity, high selectivity and sensitivity.

The unique electronic, catalytic and optical properties of metal nanoparticles make them attractive for potential applications in

the electrochemical and optical sensors [25,26]. Recently, several metal nanoparticles modified electrochemical sensors have been reported for the determination of different important analytes [26–30]. In the case of electrochemical sensors, the important functions provided by metal nanoparticles include the catalysis of electrochemical reactions and the enhancement of electron transfer [25].

Graphene nanosheets (GNSs), a new member of carbon materials has become a hot topic of interest in different fields of chemistry owing to its unique nanostructure and its extraordinary electronic, mechanical and catalytic properties [31]. In recent years, GNSs has attracted tremendous attention as a new support of metal nanoparticles mainly due to its chemical stability, high electrical conductivity and the high surface to volume ratio [32–35]. Metal nanoparticles-embedded GNS hybrids display special features in sensors, catalysis and electrical applications [32–35]. Recently, a facile and rapid one-step procedure has been reported in our research group for the preparation of graphene nanosheets–Ag nanoparticles hybrid (GNSs–AgNPs) [35]. GNSs–AgNPs/ILE was prepared using GNSs–AgNPs as the conductive phase and octylpyridinium hexafluorophosphate (OPFP) as a binder [35]. OPFP was introduced for the first time in our research group as a very suitable binder for preparation of carbon ionic liquid electrode (CILE) [36,37]. It shows an excellent performance compared to conventional organic binders due to high conductivity, high thermal stability, wide electrochemical window, non-volatility and non-inflammability [36,37]. CILE exhibits highly desirable features such as simple preparation, renewable surface, low background current,

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wide potential window, resistivity toward fouling and high rates of electron transfer. There are many reports on using CILE as a high performance electrode for the determination of wide range of analytes [37–42].

The direct electro-oxidation of TU at different carbon based electrodes such as conductive diamond [8], graphite [22] and pencil graphite electrodes [21] has been investigated and large overpotentials have been reported. To the best of our knowledge, this is the first report on TU determination using carbon nanocomposite electrodes based on graphene supported metal nanoparticles. In this work, the electrocatalytic performance of the GNSs-AgNPs/ILE was studied by amperometric measurements. Electrochemical experiments show that the GNSs-AgNPs/ILE has excellent catalytic activity.

2. Experimental

2.1. Apparatus

Voltammetric and amperometric measurements were performed using an Autolab electrochemical system (Eco-Chemie, Utrecht, The Netherlands) equipped with PGSTAT-12 and GPES software (Eco-Chemie) and a three electrode electrochemical cell: an Ag/AgCl/KCl (3 M) reference electrode (Metrohm) and a platinum disk as a counter electrode. The applied working electrode in this study was a GNSs-AgNPs/ILE (1.8 mm diameter). 0.1 M NaOH solution was used as the supporting electrolyte in all of the experiments. Argon was used to deaerate the working solutions.

2.2. Reagents

TU, silver(I) acetate ($\text{AgC}_2\text{H}_3\text{O}_2$, 98%) and NaOH were obtained from Merck. Graphite powder (particle size $<100\ \mu\text{m}$, purity 99.9%) was supplied by Fluka. The GNSs-AgNPs was synthesized as described elsewhere [35]. The IL, octylpyridinium iodide was synthesized using a reported procedure [43]. OPFP was obtained by anion exchange of octylpyridinium iodide with ammonium hexafluorophosphate.

2.3. Electrode preparation

The electrode preparation was described in our previous work [35]. Briefly, the GNSs/ILE was prepared using GNSs and OPFP with a ratio of 50/50 (w/w). GNSs-AgNPs/ILE was prepared using GNSs-AgNPs (50%) containing different percentages of AgNPs (10%, 20%, 30% and 40%) and OPFP. A portion of the resulting paste was packed firmly into the cavity (1.8-mm i.d.) of a Teflon holder. In order to have a better uniformity in the composite and lower background current, the electrode was heated in an oven to a temperature higher than the melting point of OPFP (mp 65°C). It was then left to cool to room temperature. The electrical contact was established via a stainless steel wire.

3. Results and discussion

3.1. Electrocatalytic properties of GNSs-AgNPs/ILE toward oxidation of TU

The electrochemical response of TU at GNSs-AgNPs/ILE was investigated in Britton–Robinson buffer solution at a wide pH range. Some cyclic voltammograms are shown in Fig. 1. The oxidation of TU just occurred at pH above 9. By increasing the solution alkalinity, the oxidation current and the oxidation potential of TU were improved (Fig. 1). Moreover, the adsorption and the oxidation mechanism of TU at Ag electrodes in alkaline media were reported

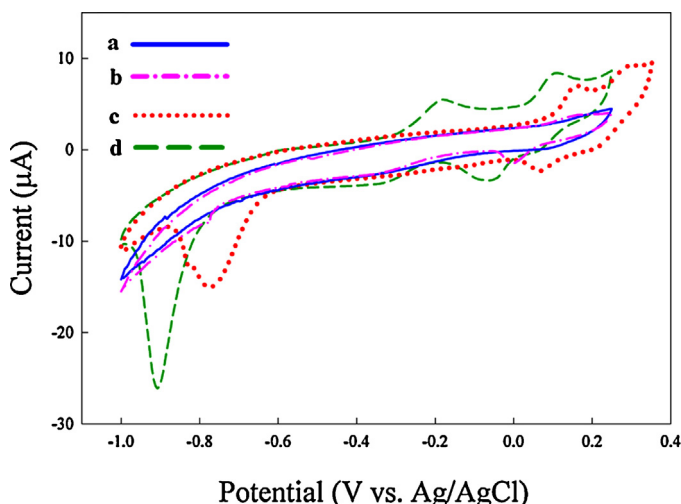


Fig. 1. Cyclic voltammograms of a solution containing 0.5 mM TU at GNSs-AgNPs/ILE in Britton–Robinson buffer solution with pH of (a) 2, (b) 7, (c) 9, and (d) 12. Scan rate $50\ \text{mV s}^{-1}$.

previously [44,45]. So, 0.1 M NaOH was selected as an appropriate electrolyte for the determination of TU at GNSs-AgNPs/ILE.

As reported previously, two anodic peaks (at -0.12 and $0.10\ \text{V}$ vs. SCE) and one reduction peak (at -0.76 vs. SCE) were observed for the oxidation of TU at the Ag disk electrode in alkaline media [44]. Based on the reported mechanism, the two oxidation peaks and one reduction peak can be related to sulfide (S^{2-}) and disulfide formation and S^{2-} reduction, respectively [44]. Therefore, the two observed anodic signals in this work at -0.2 and $0.1\ \text{V}$ correspond to S^{2-} and disulfide formation, respectively. The cathodic signal at $-0.92\ \text{V}$ corresponds to S^{2-} reduction (curve d in Fig. 1) which confirms the proposed mechanism. It was previously reported that the oxidation of TU at the Ag disk electrode in alkaline media is irreversible [44]. However, the reduction peak at $-0.08\ \text{V}$ (curve d in Fig. 1) revealed that the oxidation of TU at $0.1\ \text{V}$ is quasi reversible at GNSs-AgNPs/ILE.

To investigate the electrocatalytic behavior of GNSs-AgNPs/ILE compared to GNSs/ILE, cyclic voltammograms of TU at GNSs/ILE and GNSs-AgNPs/ILE were recorded in 0.1 M NaOH at $50\ \text{mV s}^{-1}$ (Fig. 2). GNSs/ILE did not show any detectable signal for TU whereas

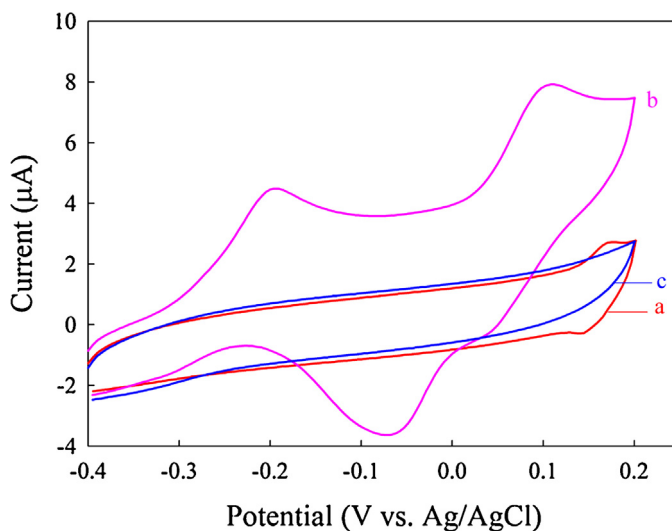


Fig. 2. Cyclic voltammograms of 0.1 M NaOH solution (a) in the absence of TU at GNSs-AgNPs/ILE and in the presence of 0.5 mM TU at (b) GNSs-AgNPs/ILE and (c) GNSs/ILE. Scan rate $50\ \text{mV s}^{-1}$.

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