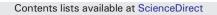
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# Journal of Molecular Liquids





## Voltammetric determination of dopamine in the presence of ascorbic acid and uric acid at sodium dodecyl sulphate/reduced graphene oxide modified carbon paste electrode

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#### ARTICLE INFO

Article history: Received 30 March 2015 Received in revised form 8 June 2015 Accepted 4 July 2015 Available online xxxx

Keywords: Reduced graphene oxide Sodium dodecyl sulphate Dopamine Voltammetry

#### ABSTRACT

In this work, the electrochemical behaviour of dopamine in the presence of various surfactants via sodium dodecyl sulphate (SDS), cetyltrimethylammonium bromide (CTAB) and Tween-20 was examined. It is found that in anionic surfactant, SDS enhanced electrochemical response at reduced graphene oxide modified carbon paste electrode (R-GO/MCPE). The electrochemical parameters, such as heterogeneous rate constant and number of electron transfer were calculated and the overall sweep rate effect shows that the electrode process was diffusion and adsorption controlled. The detection limits were 0.26 and 0.35  $\mu$ M for DA and UA respectively. Differential pulse voltammetric technique was used for the simultaneous determination of dopamine (DA), ascorbic acid (AA) and uric acid (UA). The separation of the oxidation peak potentials for DA-AA and DA-UA by SDS/R-GO/ MCPE was 178 and 114 mV, respectively. The experimental results suggest that the modified electrode showed good sensitivity and selectivity for dopamine.

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#### 1. Introduction

Graphene, a single layer of graphite, has been paying attention in research due to their fascinating properties [1–3]. It contains a twodimensional layer of sp<sup>2</sup> hybridized carbon atoms bound in a hexagonal lattice structure [4]. It is a zero-gap semiconductor, which has become an interesting material not only used in sensor application but also in solar cells, hydrogen storage, fuel cells and photocatalysis [5–7]. The above mentioned applications draw the attention of effective graphene preparation methods. Graphene itself does not occur naturally, a number of techniques such as electric arc discharge, solution-based chemical reduction, epitaxial growth, and chemical vapour deposition, have been exploited [8–12]. However, the above mentioned methods could not meet the demand of large scale production of graphene, preventing its utilization in number of fields. Graphite oxide and graphene oxide are alternative graphene materials that can meet efficiently these large scale demands with their advantageous characteristics [13–15].

There is a vast interest surrounding the use of carbon based nanoparticles (CNT and graphene) as an electrode material for the detection of electroactive compounds i.e. dopamine (DA), uric acid (UA) and ascorbic acid (AA) [16–18]. DA and AA are compounds of great biomedical interest, playing significant roles in the functioning of the human metabolism, central nervous and renal systems [19]. DA is an important monoamine neurotransmitter in central nervous system of mammalians [20]. The low levels of DA are related to neurological disorders such as Parkinson's disease, schizophrenia and HIV infection [21,22]. Similarly, AA is an essential vitamin known as vitamin C; the lack of vitamin C in human can cause bleeding gums and weak bones [23]. UA is another essential biological molecule in our body that an abnormal level leads to several diseases such as pneumonia, fatal poisoning, toxaemia of pregnancy and Lesch-Nyan disease. DA usually coexists with UA and AA in body fluids [24]. At bare carbon paste electrode these molecules have almost same oxidation potentials and often suffer from a fouling effect, which result in rather poor selectivity and reproducibility. Therefore, developing nanoparticle modified electrode is very important for the determination of electroactive compounds.

Surfactants play an important role in micelle formation, which leads to solubilisation [25]. It is well known that cationic, anionic and nonionic surfactants not only endow the electrode solution interface with different electrical properties, but also adsorb at electrode surface or aggregate into super molecular structures to change electrochemical process [26–29]. Swamy et al. previously reported immobilisation of surfactant on the surface of electrode to improve the electrochemical response of some bioactive molecules. The results showed that the electrochemical responses of these compounds were greatly enhanced in the presence of trace amount of surfactants [30–35]. Hu and Bard have characterized the adsorption of sodium dodecyl sulphate (SDS) on both charge regulated and hydrophobic substrates by atomic force microscopy measurement [36]. They found that the interaction between SDS and the positively charged electrode surface was a strong function of SDS concentration.

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The main objective of the present work is to increase the sensitivity and current signals of oxidation and reduction of analytes at reduced graphene oxide/modified carbon paste electrode (R-GO/MCPE) in the presence of surfactants namely SDS, CTAB, and Tween-20. Among these SDS an anionic surfactant showed significant increase of the peak current compared to CTAB and Tween-20. The Structure of (a) SDS, (b) CTAB, and (c) Tween-20 is shown in Scheme 1. [52].

The ability of the modified electrode to recognize DA in the presence of excess of AA and UA is enhanced with the faster electron transfer process inherent with the R-GO electrode interface.

#### 2. Experimental

### 2.1. Reagents and materials

DA, AA, UA, CTAB and SDS were obtained from Himedia Chemicals. Sodium hydroxide, perchloric acid, sodium dihydrogen orthophosphate dihydrate, and di-sodium hydrogen phosphate anhydrous were obtained from Merck. Graphite powder and Tween-20 were acquired from Lobo Chemical.  $25 \times 10^{-4}$  M DA,  $25 \times 10^{-3}$  M AA, and  $25 \times 10^{-4}$  M UA stock solutions were prepared by dissolving in 0.1 M perchloric acid solution, double distilled water and 0.1 M NaOH, respectively. All other reagent solutions were prepared in double distilled water. All chemicals are of analytical grade quality and were used without further purification.

#### 2.2. Apparatus

Electrochemical measurements were carried out with a CHI Model 660c Electrochemical Workstation connected to a personal computer for control and data storage. All electrochemical experiments were performed in a standard three-electrode cell. The bare carbon paste electrode or the electrode modified with the R-GO was used as a working electrode. The counter electrode was platinum wire and the reference electrode was a saturated calomel electrode (SCE). All potentials reported are with respect to the SCE.

#### 2.3. Synthesis of R-GO

The synthesis of R-GO has been reported in our previous work [37]. In brief, 10 mg of graphite oxide was dispersed in 50 mL of water, and then AA was added. Here AA used as a reducing agent for the reduction of Graphite oxide. The above mixture was stirred at 70 °C. The formation of black colour indicates the completion of synthesis reaction of R-GO.

#### 2.4. Preparation of CPE

The carbon paste electrode was prepared by hand-mixing graphite powder and silicon oil at a ratio of 70:30 (w/w) in an agate mortar for about 30 min to get homogeneous carbon paste. The paste was then packed into the cavity of a Teflon tube electrode (3 mm diameter). Before the measurement, the electrode was smoothened on a piece of transparent paper to get a uniform, smooth and fresh surface.

#### 2.5. Preparation of SDS/R-GO/MCPE

The SDS/R-GO/MCPE was prepared by adding 20 mg R-GO to the graphite powder and silicon oil at a ratio of 70:30 (w/w) in an agate mortar for about 30 min to get homogeneous carbon paste. The prepared modified paste was tightly packed into a PVC homemade cavity and then smoothened on a piece of transparent paper. Later R-GO/MCPE was further modified by immobilizing the SDS solution on the R-GO/MCPE surface by using micropipette and was incubated. The electrode was later thoroughly rinsed with water to remove unabsorbed modifier and dried in air at room temperature. The electrical contact was provided by a copper wire connected to the paste at the end of the tube.

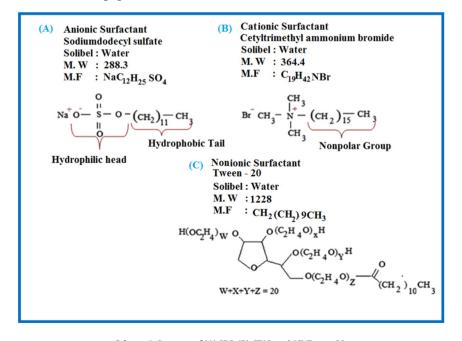
#### 2.6. Electrochemical measurements

Electrochemical determination of DA, AA and UA was carried out in a voltammetric cell with is 0.2 M phosphate buffer as a supporting electrolyte. The standard stock solution of DA, AA and UA was added to the cell according to the requirement. The cyclic voltammograms were recorded at the given scan rate of 100 mV s<sup>-1</sup> for the determination of DA, AA and UA at room temperature at pH-7.4.

#### 3. Results and discussion

#### 3.1. Effect of various surfactants on the electro-oxidation of dopamine

The effect of various surfactants on the electrooxidation of dopamine at R-GO/MCPE was explored in Fig. 1 It is well known that surfactants can be adsorbed on solid surfaces to form surfactant film [38,39]



Scheme 1. Structure of (A) SDS, (B) CTAB, and (C) Tween-20.

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