



Development of multi-walled carbon nanotubes modified pencil graphite electrode for the electrochemical investigation of aceclofenac present in pharmaceutical and biological samples

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ABSTRACT

A sensitive and novel chemically modified multi-walled carbon nanotubes modified pencil graphite electrode (MCPGE) has been developed for the electrochemical investigation of aceclofenac (ACF). MCPGE was characterized by scanning electron microscopy (SEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Phosphate buffer solution (PBS) of pH 7.0 was used as a suitable electrolytic medium, in which aceclofenac (ACF) exhibited a sensitive adsorption controlled oxidation peaks at +0.12, +0.32 and +0.51 V and a reduction peak at −0.26 V (vs Ag/AgCl). The experimental conditions were optimised by means of investigating the dependence of peak current on solution pH, concentration and scan rate etc. The electrochemical parameters such as surface concentration (Γ), electron transfer coefficient (α) and the standard rate constant (k_s) were investigated at MCPGE. The oxidative peak currents were varied linearly with concentration in the range between 1×10^{-6} to 60×10^{-6} M with a detection limit of 2.6×10^{-9} M. The UV–Vis absorption spectrum of ACF gave the λ_{\max} at 272–273 nm and is attributed to the presence of ACF. The applicability of the MCPGE was illustrated by the determination of ACF present in pharmaceutical and human urine samples.

1. Introduction

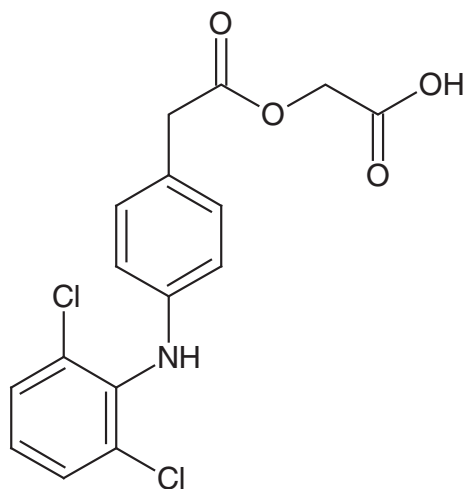
Non-steroidal anti-inflammatory drugs (NSAIDs) have a heterogeneous group of organic acids which possess analgesic, antipyretic, anti-inflammatory and platelet inhibitory actions [1]. The mechanism of action of NSAIDs involves the inhibition of cyclooxygenase, which is a key enzyme in the inflammation cascade [2,3]. The ACF is one of the most effective non-steroidal anti-inflammatory drugs, which directly blocks the prostaglandin synthesis and exhibits anti-inflammatory, analgesic and antipyretic properties. ACF has less gastrointestinal complications and is highly recommended drug in the symptomatic treatment of rheumatoid arthritis, osteoarthritis and ankylosing spondylitis [4,5]. ACF has shown better gastric tolerance when compared to other NSAIDs [6]. The acute gastric ulcerogenic activity of ACF is found to be 2 fold less than naproxen, 4 fold less than diclofenac and 7 fold less than indomethacin [7]. ACF shares structural similarities with another NSAID such as diclofenac [8]. Indeed, the ACF is a well established NSAID in clinical use as the therapeutic index of ACF is reported to be four times greater than that of diclofenac. Although ACF is similar to other NSAIDs in terms of efficacy, superior tolerability and compliance, which clearly indicates the possible economic consequences [9] (Scheme 1).

From past few decades, drugs analyses have great importance in many aspects. Along with it, the developments of new selective and sensitive methods for the analyses of drugs have become important. Numerous methods have been reported for the estimation of ACF, such as titrimetric [10], densitometric [11], colorimetric [12], polarographic [13], stripping voltammetric [14], spectrofluorimetric [15], high-performance liquid chromatographic [16–18], liquid chromatography-tandem mass spectrographic [19], methods. But most of these methods involve laborious, time-consuming and tedious liquid-liquid extractions or solid phase extractions [20–27]. Therefore, in recent years, the uses of electrochemical techniques have gained importance to determine the drugs in pharmaceutical and real samples, because of its experimental simplicity, high selectivity and sensitivity [28–31].

Nowadays, the developments of novel and sensitive modified electrodes using nanoparticles have attracted large interest in the field of drug determinations. This is because of their good catalytic activities and potential applications in various analyses [32–35]. The nanoparticles are different from their of bulk materials and these nanoparticles, as modifiers, have unique properties, such as good conductivities, outstanding electro-catalytic activities, optical and magnetic properties etc. Therefore, the development of electrodes

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Scheme 1. Chemical structure of Aceclofenac (ACF).

modified with nanoparticles have many advantages, such as easy fabrication, low-cost, eco-friendly, high sensitivity, better reproducibility, etc. [36]. Hence, the developments of nanoparticles modified electrodes are receiving significant importance in recent years [37–39].

Recently, the multi-walled carbon nanotubes (MWCNTs), because of their good electrical conductivity and high mechanical strength, find extensive and impressive research applications in electro-analytical chemistry, especially in electrode modification towards the electrochemical oxidation and reduction of organic molecules. Therefore, MWCNTs have been extensively used in the preparation of electrochemical sensors [40–42].

To the best of our knowledge, there are no previous reports on the usage of a pencil graphite electrode (PGE) modified with MWCNTs for the determination of ACF in pharmaceutical formulations and in physiological samples. The PGE's modified by using catalysts/modifiers will appreciably improve the electro-analytical performance of the electrode [43]. In recent years, the applications of modified pencil graphite electrodes have provide better performance in the electrochemical investigation of biologically important molecules [44–47].

Therefore, in the present work, MCPGE has been developed for the sensitive electrochemical determination of ACF by cyclic voltammetry and differential pulse voltammetry.

2. Experimental

2.1. Instrumentation

The electrochemical measurements were performed using electrochemical workstation (CHI660D, CH instruments, USA) and all the experiments were conducted in a standard three-electrode assembly incorporating PGE or MCPGE as working electrode, platinum wire as auxiliary electrode and Ag/AgCl as reference electrode. The UV–Vis spectroscopic analysis was carried out using UV–Vis spectrophotometer [Model: USB 4000 Ocean Optics, USA]. The surface morphology of the modified electrode was analysed by field emission scanning electron microscope [Model: FE-SEM Carl Zeiss AG-ULTRA 55]. The compound was characterized by ^1H Nuclear magnetic resonance spectroscopy (NMR) [Model: BRUKER AV 400].

2.2. Chemicals and reagents

ACF was purchased from Sigma-Aldrich and used as received without purification. A stock solution of 1 mM ACF was prepared in PBS of pH 7. The tablets containing ACF, AC-100 and AC-200 were purchased from local pharmaceutical shops. The chloroauric acid,

potassium dihydrogen phosphates and di-potassium hydrogen phosphate were procured from Merck, Mumbai, India. Potassium ferricyanide was procured from Merck, Darmstadt, Germany. All the chemicals used were of analytical grade. The 0.1 M phosphate buffer solution was prepared and the pH of the solutions were adjusted either by using H_3PO_4 or NaOH. Double distilled water was used for the preparation of all the reagents.

2.3. Fabrication of multi-walled carbon nanotubes modified pencil graphite electrode (MCPGE)

The working electrodes MCPGE was prepared with 2B pencil graphite lead (Kokuyo Camlin Ltd.) and MWCNTs (Sigma-Aldrich). The MWCNTs of 1 mg mL^{-1} were dispersed in distilled water and ultrasonicated for 2 h to get homogeneous solution. On the other side, one end of the pencil graphite lead was connected to a copper wire to establish an electrical contact and was inserted in a small Teflon tube of 1 mm of inner diameter and a height of 6 cm, filled with epoxy resin. After 24 h, the anterior end of the electrode was cut using a sharp knife, polished with alumina slurry, sonicated and finally washed with millipore water. Then about 10 μL (optimised concentration) of MWCNTs solution was drop casted on the PGE surface to obtain MCPGE. The modified PGE was allowed to dry at room temperature for about 12–16 h. After that, the dried PGE was gently washed to remove the loosely attached MWCNTs. The obtained modified electrode was used as working electrode for electrochemical analyses.

3. Results and discussion

3.1. Scanning electron microscopy (SEM) characterization of PGE/MCPGE

The surface morphologies of PGE and MCPGE were characterized by scanning electron microscopy (SEM). Fig. 1 shows the surface morphology of unmodified PGE and modified PGE. The SEM images of unmodified PGE (Fig. 1A) shows uniform smooth surface, whereas SEM images of MCPGE (Fig. 1B) clearly demonstrates the adsorption of thread like structures of MWCNTs on the surface of PGE. This kind of arrangement of carbon nanotubes on PGE increase the surface area of the electrode and also improves the electron transfer rate between the electrode surface and bulk analytical solution. The increased performance of MCPGE towards the electron transfer activity has been confirmed by the electrochemical studies of potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$).

3.2. Electrochemical characterization of PGE/MCPGE

$[\text{K}_3[\text{Fe}(\text{CN})_6]]$ is one of the most valuable and convenient probe to distinguish the electrochemical performance of unmodified and modified electrodes. The unmodified PGE and MCPGE were used as working electrodes for the investigation of voltammetric response of $[\text{K}_3[\text{Fe}(\text{CN})_6]]$. Fig. 2A illustrates the, cyclic voltammograms of 1 mM $[\text{K}_3[\text{Fe}(\text{CN})_6]]$ in 0.1 M KCl at PGE and MCPGE. The cyclic voltammograms of PGE (a) and MCPGE (b) shows a peak to peak separation (ΔE_p) of 0.138 V and 0.090 V, respectively. The decreased ΔE_p at MCPGE has clearly indicates a better reversible charge transfer process on MCPGE when compared to that of PGE [48,49]. The results clearly indicated that the MCPGE has got nearly four-fold enhancement in redox peak current than that of PGE. Therefore, the increase in peak current with a subsequent decrease in ΔE_p proves that MCPGE has a better electrocatalytic activity on MCPGE. This is attributed to the presence of MWCNT on the surface of PGE which increases the electrochemical active surface area (EASA) and hence, the rate of charge transfer reaction on the electrode increased [50,51].

Voltammograms at different scan rates corresponding to 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ in 0.1 M KCl were used for the determination of the EASA of the electrodes. For reversible electrode processes, the following

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