

**NANOCOMPOSITE ELECTRETS ELECTROCHEMICAL SENSORS FOR
TRIPTOLIDE**

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ABSTRACT

Triptolide, a diterpenoid triepoxide, is the key biological component of *Tripterygium wilfordii* Hook. It has been used in traditional Chinese medicine for centuries to treat autoimmune diseases including proapoptotic, and oncolysis activity in different types of cancer cells, angiogenesis, psoriasis, other immune-mediated inflammatory diseases, membranous nephropathy, diabetic cardiomyopathy, arthritis and rheumatism. Triptolide shows potent activity in inflammation, nephritis, immune modulation, and diseases of the central nervous system as well. It has documented antiproliferative, immunosuppressive, anti-inflammatory, antifertility, and chronic lymphatic thyroiditis effects. Studies on its synergistic effects with other therapies have led to its precise molecular targets in the biochemical systems. Metabolite profiling, identification and determination of triptolide has been reported on various investigative tools.

Pure and metal oxide (nano) doped PVDF-PVK polymer blend-nanocomposites have been investigated for charge transfer effects in electrochemical sensors. Cyclic voltammetry was employed to test electronic interface activity of the modified polymers. Electrode reactions of the intermediates and the products formed during the forward scan have been studied for Triptolide Drug. Comparative electro activity of the PVDF-PVK polymer blend-nanocomposite electrets electrode with the glassy carbon electrode was studied.

Keywords:PVDF, PVK, CV

INTRODUCTION

Sensitive sensor materials have been developed with pure and nanoZnO doped Poly vinylidene fluoride – Poly (9vinyl carbazole) polymer blend nanocomposite electrets for use as electrodes. Decrease in charge transfer resistance in modified polymer sensors have been reported through thermally stimulated discharge current [1,2] studies. The electrochemical behaviour of Triptolide drug was studied at pure and nanoZnO doped PVDF-PVK polymer blend nanocomposite electret electrodes by cyclic voltammetry (CV). Analyte reduction current peak was observed in Britton- Robinson (BR) buffer. Diffusion controlled nature of the electrode process was observed.

Electrochemical sensors have chemical characteristics and physical construction of the material suitable for charge transfer processes.[3–5] Problem of electrode fouling, limiting their long-term stability and requiring frequent polishing/disposal occur with time-honoured carbon-based conventional electrodes. Smart materials with wider potential window, low background current, chemical inertness and desired mechanical stability have been the area of active research.[6-16] Proven efficacy of modified polymer blends needs proper explanation of the charge injection and carrier migration process.

In the present work, charge transfer properties of the modified polymer for electrochemical sensitivity of Triptolide Drug using cyclic voltammetry have been studied.

The amorphous configuration of PVDF- PVK composites, pure as well as doped with nano ZnO was modified by poling the polymer composite at elevated temperatures and steady functional voltage. The polymer composite upon cooling to room temperature under constant applied voltage, gets its heterojunctions set to furnish the required electrets. In the nano blends, the mechanically robust polymer lattice substituted with ZnO nanoparticles modifies electrical conductivity. Their biocompatibility provides resources suitable electrode material for various applications.

EXPERIMENTAL**Apparatus**

Autolab potentiostat-galvanostat 302N (Netherlands) with software NOVA 1.8 was used for electrochemical measurements. Electrodes were PVDF- PVK blend electrets, bare as well as doped with nanoZnO as working electrodes, graphite rod as the auxiliary electrode and Ag/AgCl (1M KCl) as reference electrode. All pH measurements were made on a Decible DB-1011 digital pH meter. Pure nitrogen gas was purged into all solutions to eliminate dissolved oxygen, after which a blanket of pure nitrogen gas was maintained over the

solutions throughout the CV experiments. Glassy carbon electrode was polished with fine grade emery paper followed by polishing alumina (0.5 μ m) and subsequently activated by triangular voltage sweeps from +1.0 to –1.0 V at the scan rate of 5 to 200 mV/sec. for 5 minutes. The activity of the electrode was checked for ferricyanide-ferrocyanide system in 0.1 M KCl. Coulometric measurements were performed in the potentiostatic mode with platinum foil of large surface area as the working electrode, Ag/AgCl as the reference electrode and platinum wire as the auxiliary electrode. From the decrease in current or increase in coulombs with time, the number of electrons transferred was calculated. Progress of electrolysis was monitored by recording cyclic voltammograms at different time intervals until the reduction peak completely disappeared. UV-Visible double beam spectrophotometer Systronic 2101 was used for spectral studies during electrolysis.

Reagents and chemicals

ZnO nanopowder (90–250 nm, 99.89% purity) was procured from Fischer Scientific (USA). All other chemicals were of analytical grade and used without further purification. Triptolide (99%) was procured from *Biopurity*.

Analytical procedure

Standard solution of the Triptolide drug (1mg/mL) was prepared by dissolving the analyte sample in dimethylformamide+ dioxin (1,1) and further dilutions were made with BR buffer to get final concentration in the working range (20–250 μ g/mL). A series of Britton-Robinson (BR) buffer (2.0–12 pH) was prepared in ultra-pure water. For electrochemical measurements, a known volume of the analyte sample was added in voltammetric cell and total volume made up to 10 mL with 1 M KCl as supporting electrolyte. The solution was deoxygenated with pure nitrogen gas for 120 s. The voltammograms were recorded at room temperature by applying potential scan from -1500 to -100 mV, frequency 50 Hz, pulse amplitude 50 mV/s and scan increment 10 mV/s.

Fabrication of ZnO - PVDF- PVK blend electrets electrode

0.3 μ m alumina slurry and deionised water were used to polish the bare glassy carbon electrode. The cleaned electrode was gently blown under a nitrogen stream on the surface and dried at room temperature. Solution cast technique was employed to fabricate the blends of polymer with nanoZnO. Modified composites were cast on the glassy carbon electrode surface and the coated surface was cleaned after physical measurements followed by polishing with 0.3 μ m alumina slurry and ultrasonic cleaning for 2 minutes. The electron transfer behaviour of the modified electrodes was investigated using thermally stimulated depolarization current (TSDC) studies. The poling field and temperature dependent TSDC thermograms for pure PVDF, PVK, blended PVDF-PVK and the blends doped with nano ZnO have been studied. The modified polymer electrets electrodes with their lower charge transfer resistance indicated superior electroactivity facilitating the electro-reduction of the analyte.

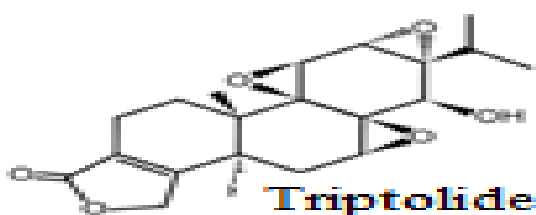


Fig 1: Structure of Triptolide.

RESULT AND DISCUSSION

The electrochemical behaviour of Triptolide at PVDF-PVK blend and PVDF-PVK/nanoZnO electrets electrode exhibited a well defined reduction peak at the glassy carbon electrode (Fig. 1). The electroanalytical performance of PVDF-PVK/nanoZnO electrets electrode was better over that experimental at the bare PVDF-PVK blend. The cyclic voltammograms of the analyte showed 72.6% enhancement in the reduction peak current at PVDF-PVK/nanoZnO electrets electrode.(Fig. 2,curve c) as compared to a bare PVDF-PVK blend electrode . (Fig. 2, curve b). At modified electrode, peak potential shifted towards negative side as the electron transfer kinetics was facilitated at the PVDF-PVK/nanoZnO electrets electrode.

Supporting electrolytes like KCl, phosphate buffer, acetate buffer, citrate buffer, and BR buffers were tested, BR buffer excelled with respect to signal enhancement and the symmetric peak shape. Effect of varying pH

(2.0–12) of BR buffer was studied for the peak current of the analyte at various concentrations. Rise in pH decreasing the peak current indicates the involvement of protons in the electrode process.

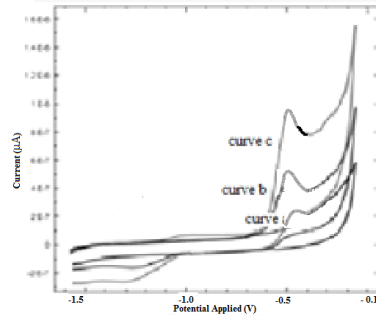


Fig 1: Cyclic voltammograms of Triptolide analyte at pH 4.75, at various scan rates 80 to 160 v/s at glassy carbon electrode

Voltammograms of Triptolide (100 µg/mL) were recorded at various scan rates in the range 10–240 mV/s. Triptolide at the PVDF-PVK/nanoZnO electrets electrode exhibited a single, well defined reduction peak at 5.50 V (vs. Ag/AgCl). Electrode process was irreversible in nature as no current was observed in the reverse scan.

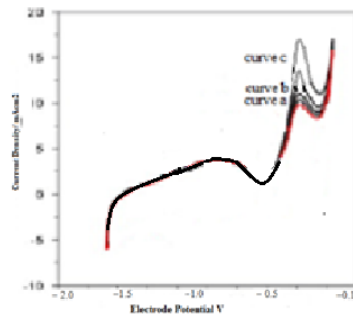


Fig2: Cyclic voltammograms of Triptolide analyte at pH 4.75, scan rate 160 v/s at PVDF-PVK/nanoZnO electret electrode (curve c), at bare PVDF-PVK blend electret electrode (curve b) and blank (curve a).

The peak potential shifted towards right-hand with increase in the scan rate also confirmed the irreversible nature of the reduction process, which can be expressed by the equation,

$$E_p = E^0 + RT(1-\alpha)nF \{ \ln(ks/D^{1/2}) - 0.5 \ln[(1-\alpha)nFv/RT] - 0.78 \} \quad (1)$$

Where, E^0 is the standard electrode potential, D is the diffusion coefficient, v is the scan rate, F is faraday constant, R is gas constant and T is room temperature.

A linear plot of current (i_p) vs. square root of scan rate ($v^{1/2}$) is obtained when the process is diffusion controlled, whereas the adsorption controlled process results in a linear plot of i_p vs. v . In the present experiment a linear relationship between i_p and $v^{1/2}$ is obtained suggesting the diffusion of the analyte at the surface of PVDF-PVK/nanoZnO electrets electrode, which can be expressed by the following equation:

$$z i_p / \mu A = 0.5035 v^{1/2} (\text{mV/s}) - 1.3768, r^2 = 0.9935 \quad (2)$$

Again a linear relationship was observed between $\log i_p$ and $\log v$, corresponding to the equation,

$$\log i_p = 0.5066 \log v - 0.3730, r^2 = 0.9988 \quad (3)$$

The slope of 0.5056 is close to the expected value of 0.5 for a purely diffusion controlled irreversible reaction.

CONCLUSION

A simple method for determination of Triptolide, a diterpenoid triepoxide at PVDF-PVK/nanoZnO electrets electrode is presented. The PVDF-PVK blend with nanoZnO and upon poling significantly enhanced the performance of the quasiaelectrets electrode due to reduction of charge transfer resistance. Enhancement assessment was performed using CV technique. PVDF-PVK/nanoZnO electrets electrode showed 72.6% current enhancements when compared with the simple PVDF-PVK blend quasiaelectrets electrode. Calibration plot reveals linearity within the range of 20–220 µg/mL with correlation coefficient of 0.9752. Lower limit of

detection (10.26 µg/mL) proved the sensitivity of the proposed method. Voltammetric study of the analyte at different scan rates revealed the irreversible and diffusion controlled reaction process.

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