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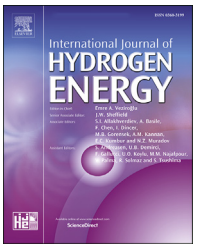

Optimization of MnO_2-Graphene/polythioaniline (MnO_2-G/PTA) hybrid nanocomposite for the application of biofuel cell bioanode

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ABSTRACT

This study reports the synthesis of a nanocomposite comprised of graphene (G) supported manganese dioxide (MnO_2) incorporated into the network of polythioaniline (MnO_2-G/PTA). The hybrid composite was applied as an electrode material for the development of a bioanode. The bioanode was fabricated by the electrochemical entrapment of ferritin (Frt) as mediator and glucose oxidase (GOx) enzyme in the matrix of the as-synthesized MnO_2-G/PTA deposited on glassy carbon electrode (GCE) surface. The structural features and electrochemical behaviour of the modified electrodes were investigated by Fourier transform infrared spectroscopy (FTIR), cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). The results unfolded that the hybrid electroactive support (MnO_2-G/PTA) employed for the immobilization of the enzyme (GOx) established an appropriate electrical cabling between the redox enzyme (GOx) and the electrode surface with the assistance provided by the biocompatible mediator (Frt) working to enhance the electrical signals. The developed GCE/MnO_2-G/PTA/Frt/GOx bioanode attained a maximum current density of 3.68 $mAcm^{-2}$ at 35 mM glucose concentration at a scan rate of 100 mVs^{-1}. Thus, the MnO_2-G/PTA/Frt/GOx modified electrode possesses high potential and good biocompatibility for bio-electricity production from glucose.

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Introduction

Over the past few decades, there has been a paradigm shift in the technology of conventional fuel cells that are currently witnessed as biofuel cells. This shift predominantly emerged due to the prime concern of energy associated with fossil fuels which are on the verge of their extinction. The chief advantage of enzymatic biofuel cells (EBFCs) is that they are a renewable and non-corrosive source of energy along with their inherent biocompatible and bio-implantable characteristics. In EBFCs, enzymes are employed for the catalytic conversion of the chemical energy of specific substrates (biofuels like glucose) to electrical energy and this is what makes EBFCs explicitly renewable as well as biocompatible [1]. With this splendid change in fuel cell technology, the tremendous upsurge in the discipline of implantable medical devices has been noticed, evidenced by the escalating interest in research targeted towards the development of cost-effective yet high-power and high-energy-density electrochemical power generating devices so as to stand the quest of growing energy need [2]. Glucose has reserved a separate zone in biofuel cells assigned to its abundance in nature from where it can be easily extracted. It has been extensively used in the development of glucose based biofuel cells because of its odourless, non-flammable, non-toxic and renewable nature unlike other alcohols such as methanol and ethanol. These favourable properties of glucose drive it to be a fascinating fuel for a broad spectrum of applications, especially for portable electronic and miniaturized medical devices [3–5]. In spite of carrying such attractive advantages, glucose fuel cells are still struggling to realize their practical applications. Incomplete oxidation of glucose at the anode is one of the principal challenges that is required to be addressed while dealing with the manufacturing of glucose biofuel cells. Literature unveils that glucose oxidase [6,7] and glucose dehydrogenase [8–10] are efficient biological catalysts to carry out glucose oxidation, and thus, have been greatly employed in the development of enzymatic glucose biofuel cells (EGBFCs).

The establishment of appropriate electrical cabling between the redox enzymes and the electrode is a fledgeling research field, approaching towards the upgradation of EGBFCs [3,11,12]. Several attempts have been made to develop the required electrical communication by coupling the electroactive relay to redox active proteins [13–15] or by the immobilization of the redox enzymes in the complex network of electroactive polymers [16–18]. For further amplification in the charge transfer process, various types of redox mediators which are fundamentally charge carrier systems, have been utilized in biofuel cells [17,19,20]. Unlike the reported non-biocompatible redox mediators, ferritin (Frt) has been unfolding as an enthralling protein on the basis of its interesting redox activity, biocompatibility and eco-friendly characteristics which are primarily taken into consideration while dealing with BFCs for their proper functioning in biological fluids [12,16,21].

Generally, those approaches are worth considering that involve the factors of feasibility and cost-effectiveness of the electrode with high catalytic activity towards glucose oxidation. A great deal of noble metal-based catalysts, such as, Pt [22], nanoporous gold (NPG) [23,24], bi-metallic catalysts of Ag-Au [25–28], Pd-Pt [29,30], Pt-Au [31–33], and Pd-Ni [34,35], as well as Pt-Pd-Au [36] and Ni-Cr-Co ternary catalysts [37] have made their contribution in the discipline of glucose biofuel cells. But the current research is mainly focused on developing noble-metal free/low quantity noble metal-based electrode materials with high catalytic performance and good stability at low expense. In this context, hybrid materials have earned considerable attention due to their synergistic behaviour that results from the combined merits of both pseudo-capacitive materials such as conducting polymers (CPs) [38] and transition metal oxides [39] and double layer capacitive materials involving graphene, CNTs and their other derivatives. For instance, an economically feasible cuprous oxide (Cu_2O) based catalyst was prepared for the successful implementation in direct methanol fuel cells (DMFCs). The electrocatalyst composite consisting of cuprous oxide (Cu_2O) nanoparticles upheld in graphene oxide (GO) and polypyrrole (PPy) matrix demonstrated a remarkable elevation in current density alongside greater stability [40]. It was reported that the Cu_2O/PPy–GO hybrid system showed superior performance over Pt–Ru/C electrode towards DMFCs. Conducting polymers such as polyaniline (PANI), polythiophene (Ptp) and PPy are usually taken into consideration as electrode materials for catalytic applications due to their pseudocapacitive trait. An electrodeposited PANI/multiwalled carbon nanotubes (MWCNT) glazed on the surface of pencil graphite electrodes (PGEs) was studied for the immobilization of laccase enzyme (Lac) [41]. The study unveiled that the PANI/MWCNT/Lac modified PGEs have the larger number of active sites for the higher loading of the enzyme on the electrode surface which in turn enhanced the biocatalytic activity of the enzyme. The developed electrode caused about 80% improvement in the electrochemical performance of the EBFC and also exhibited considerable stability of the immobilized enzyme. Another conducting polymer-based bioelectrode for the purpose of EBFCs was fabricated using electrochemically synthesized Ptp film on a glassy carbon electrode [42]. GOx was entrapped within the conducting network so as to develop a ferritin (Frt) mediated GCE/Ptp/Frt/GOx modified bioanode. This electrode resulted in fast electron transfer and high catalytic efficiency due to the increased surface area of the electrode. The increment in the active surface area was attributed to the network structure of Ptp film that allowed high loading of the enzyme. Further, extensive work has been carried out to synthesize promising hybrid electrode materials integrating both pseudo-capacitive substrates and double layer capacitive materials. It has been reported that various types of capacitive and conducting polymers were combined to form composites with tailor-made properties for hybrid supercapacitors/biofuel cells [43].

Osgood et al. [44] synthesized a composite material using a transition metal ion-chelating ordered mesoporous carbon and multi-walled carbon nanotubes (TM-OMC/CNT). The observed enhanced surface area of the composite material indicates its potential applications in achieving substantial oxygen reduction reaction activity with high stability. A Pt/TiO_2/carbon fuel cell electrocatalyst has also emerged as a prospective hybrid material in extensively improving the electrochemically active surface area of the electrode [45]. The study explored that significantly higher oxygen reduction

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