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First Eurasian Conference on Nanotechnology, Baku, Azerbaijan
**Photoelectrochemically-Assisted Bioanode Constructed by Ru-
Complex and g-C₃N₄ Coated MWCNT Electrode**

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Abstract

In this study, a novel photobioanode was constructed using a Ruthenium complex (Ru-complex) sensitized graphitic carbon nitride (g-C₃N₄) nanomaterial deposited on multi-walled carbon nanotubes (MWCNT). g-C₃N₄ coated MWCNT bearing Ru-complex acts as a platform for the immobilization of flavin adenine dinucleotide dependent glucose dehydrogenase (FADGDH). The formed photosensitive bioanode showed an enhancement in glucose oxidation current under visible light irradiation. The electrocatalytic current increase for in glucose oxidation are possibly due to the good electrical contacting of the immobilized FADGDH on the electrode surface and utilization of light energy. The spectroscopic properties of g-C₃N₄ and Ru-complex in dimethylformamide (DMF) were determined by UV-visible absorption spectra demonstrating the characteristic absorption peaks in the visible light region. Upon visible light illumination, the enzymatic photoanode revealed a prompt rise in photocurrent (ca. 1.44 μA cm⁻²) compared to the photoelectrode without enzyme (0.65 μA cm⁻²). Light irradiation of the bioanode improved the overall performance of the electrode as glucose oxidation was reinforced by photoelectrochemical (PEC) process.

Keywords: MWCNT; FADGDH; g-C₃N₄; Ru-complex; Photoelectrochemical bioanode; Glucose oxidation

Introduction

Solar energy is the most abundant renewable energy resource on earth. To take more advantage of such huge amount of energy, tremendous researches on harnessing of solar energy have been carried out. The biofuel cells (BFC) can convert chemical energy directly into electricity [1]. Combining sunlight harnessing materials with BFCs enables us to achieve dual-directional energy conversion *viz.* light and chemical energy to electricity and can lead to further improvement in BFC performances [2]. Nowadays, the direct generation of electrical energy from sunlight and a biofuel by using a photoelectrochemical biofuel cell (PEBFC) is a hot topic [3]. PEBFCs have been constructed with an efficient photon-to-electron approach to boost the energy conversion efficiency. Accordingly, photoanodes and photocathodes have been constructed for the assembly of PEBFC [4].

In this study, a photoelectrochemical bioanode was fabricated by using an electrode composed of Ru-complex and g-C₃N₄ deposited MWCNT nanomaterial, and the electrochemical response was enhanced under visible light irradiation.

Materials and Method

For the synthesis of cis-(Bpy-Py₂)₂RuCl₂·2H₂O (Ru-complex) [5] [6], RuCl₃·hydrate (6.18 g, 29.8 mmol), 4,4'-bis(4-pyrenyl-1-ylbutyloxy)-2,2'-bipyridine (42.3 g, 60.0 mmol), and LiCl (8.4 g, 2 mmol) were refluxed in reagent grade DMF (5 mL) for 8 h. After cooling down to room temperature, 250 mL of reagent grade acetone was added and the resultant solution was kept at 0 °C overnight. The suspension was then filtrated, washed successively with deionized water (DW) and diethyl ether, and then dried in vacuum (yield: 62%). UV/Vis (DMF) : $\lambda_{\text{max}} / \text{nm}$ ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$) = 385 (2880), 440 (1280), 490 (960). g-C₃N₄ was obtained from our previous study [7]. The MWCNT coated glassy carbon electrodes (GCE) were obtained by drop-casting 25 μL of a sonicated MWCNT dispersion in (N-Methyl-2-pyrrolidone) NMP (5mg mL⁻¹) and dried in vacuum. Then 5 μL of g-C₃N₄ in NMP (1 mg mL⁻¹) was coated and dried in vacuum. 10 μL of Ru-complex solutions in DMF (0.6 mM) were applied on the electrode and dried in vacuum. After complex deposition, the electrodes were rinsed several times with DW to remove unbound complexes. FADGDH was immobilized by dropping 20 μL enzyme solution in phosphate buffered saline (PBS) pH 7 (5 mg mL⁻¹) on the electrode surface and left at 4 °C overnight. The modified GCE was rinsed with PBS to remove the loosely bound FADGDH. Finally, Nafion in methanol (0.5%) was applied on the electrodes and the resulting PEC bioanodes (designated as GCE/MWCNT-g-C₃N₄-Ru (Bpy-Py₂)₂ Cl₂-FADGDH) were stored at 4 °C.

Results and discussion

Characterization of Ru-complex

Schematic illustration of assembly of the PEC bioanode was given in Figure 1. Only a single-monolayer of Ru-complex in a good contact with g-C₃N₄ meet the need for photo-induced electron transfer, and the high surface area of porous MWCNT structure can provide an enhanced sunlight harvesting. Also, MWCNT plays a pivotal role as an efficient electron

acceptor for the light sensitive entity and improve the photocurrent generation [8][9].

It is clear that the absorption of ruthenium complex ranges from 350 nm to 550 nm, mainly in visible light regions (Figure 2). The complex exhibits the first transition at 385 nm (3.22 eV) with a sharp band edge absorption and the second transition at 440 nm (2.82 eV) and third transition at 490 nm (2.53 eV) in the visible range, which can be attributed to the metal to ligand charge transfer band[10]. Ru-complex also reveals band edge emissions at 460 nm (2.70 eV) and 490 nm (2.53 eV), which can be attributed to excimer of pyrene[10].

According to the decay curve of transient absorption, the charge-separated state occurs within 3.66 ns, which indicates that the electron injection into g-C₃N₄ occurs on a sub-microsecond timescale (Figure 3).

The one electron redox system of the complex is observed at $E_{1/2} = 0.065$ V vs Ag/AgCl (scan rate, 2 mV s⁻¹) in argon saturated 0.1 M PBS pH 7.0 with a peak-to-peak separation (ΔE_p) of 0.13 V (Figure 4). It can be concluded from the cyclic voltammogram that the synthesized Ru complex has a redox potential in a suitable range for mediated electron transfer with FADGDH when taking into consideration of the redox potential of FAD in glucose oxidizing enzymes at ca. -0.45 V vs Ag/AgCl at pH 7.0 [11]. For the driving force of fast and efficient electron transfer, an appropriate potential difference is needed between the mediator and the FAD unit. The higher this difference is, the electron transfer efficiency will increase but will be detrimental in terms of the final cell voltage of a biofuel cell. The choice of mediator is therefore always a compromise.

Photo-generated charge convey through the bio-anode

Upon visible light illumination, Ru-complex and g-C₃N₄ are excited to charge separation, and can generate photocurrent in the presence of an electron donor. Herein, glucose was oxidized by the photoelectrochemically-assisted bioanode and gives two electrons to Ru-complex mediator. The injected electrons to the electrode surface migrate through an external circuit to a counter electrode. FAD serves as the electron acceptor in glucose oxidation catalysed by FADGDH, thereby regenerating FADH₂ after the enzymatic oxidation of glucose. The enzyme catalyzed, and Ru complex mediated electron transfer between glucose and the photoanode are reminiscent of a bioanode operation in an enzymatic BFC [8]. All in all, during the photoelectrochemically-assisted glucose oxidation, chemical energy and light energy are both converted into electricity. Under the light illumination, the photocurrent response of GCE/MWCNT-g-C₃N₄ photoanode poised at 0 V vs. Ag/AgCl was found to be 0.4 $\mu\text{A cm}^{-2}$ and the photocurrent increased to 0.65 $\mu\text{A cm}^{-2}$ for GCE/MWCNT-g-C₃N₄-Ru (pyrene)₂ Cl₂ photoelectrode. The photocurrent reached to 1.44 $\mu\text{A cm}^{-2}$ for GCE/MWCNT-g-C₃N₄-Ru (pyrene)₂ Cl₂-FADGDH bioelectrode in 170 mM glucose (Figure 5) by yielding the most enhanced value.

Photoelectrocatalytic activity of the bioanode

The high activity of FADGDH and good catalytic activity toward light driven glucose oxidation give way to the development of efficient photosensitive electrode. Figure 6 displays the effect of visible light irradiation on anodic bioelectrocatalysis of glucose. The optimum glucose

concentration was chosen as 170 mM according to the reported study, in which concentration enzymatic reaction velocity and electron transfer turned out to be the limiting factor rather than substrate concentration [1]. Under irradiation, the increment in the glucose oxidation current by 4.9% at 0.2 V vs Ag/AgCl verified that the electron transfer kinetics between Ru complex and electrode was improved.

Conclusion

In summary, a visible light driven bioanode was constructed. The Ru-complex sensitizer was attached to g-C₃N₄ by π - π interactions. The findings from cyclic voltammetry confirmed that the synthesized Ru complex has a suitable redox potential for mediated electron transfer and the electron transfer kinetics between Ru complex and electrode has improved under irradiation. The PEC bioanode generated improved photocurrent under illumination, which could be attributed to efficient light energy utilization along with good electrical contacting between immobilized enzyme and the electrode surface. The PEC bioanode couples the photogenerated charge separation to the FADGDH-catalyzed glucose oxidation. The energy to drive these processes is provided both by incident photons and by solar energy stored in the chemical bonds of glucose. By choosing a cathode with a large reduction potential, the fabricated bioanode can be used in a biofuel cell to boost the overall performance of BFC. The bioanode displayed fast and stable PEC response towards the visible light illumination, which proves its feasibility for the mass production of a new kind of photo-driven biofuel cell by providing an extending insight beyond the conventional biofuel cell.

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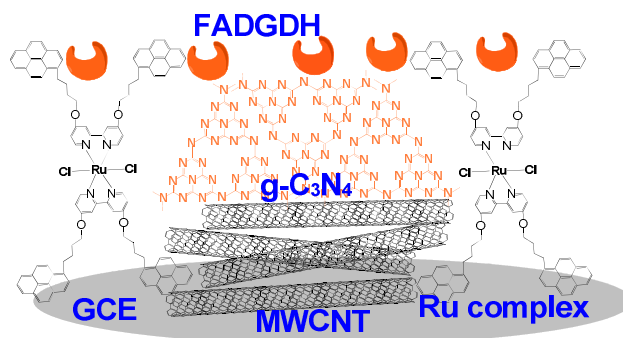


Figure 1. Assembly of GCE/MWCNT-g-C₃N₄-cis (Bpy-Py₂)₂RuCl₂

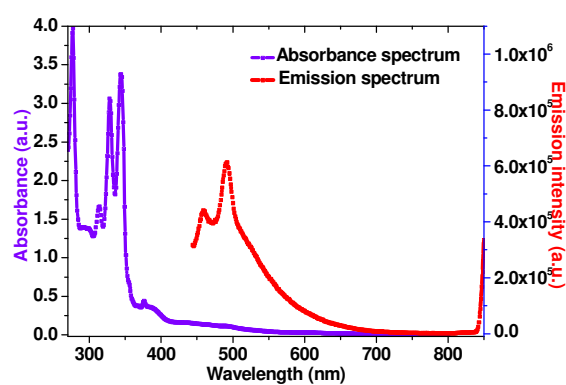


Figure 2. Absorbance and fluorescence spectra of Ru-complex (in DMF, excitation wavelength: 430 nm)

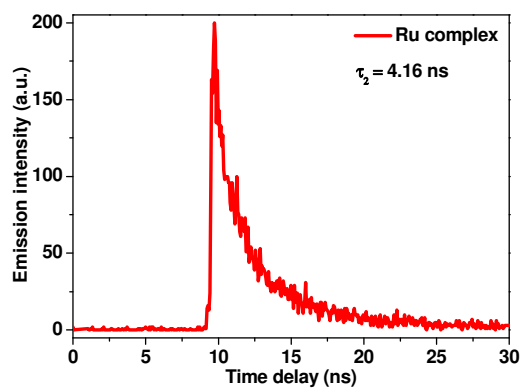


Figure 3. Luminescence decay curve after laser excitation at 490 nm recorded for Ru complex in deoxygenated DMF ($1.25 \cdot 10^{-4}$ M).

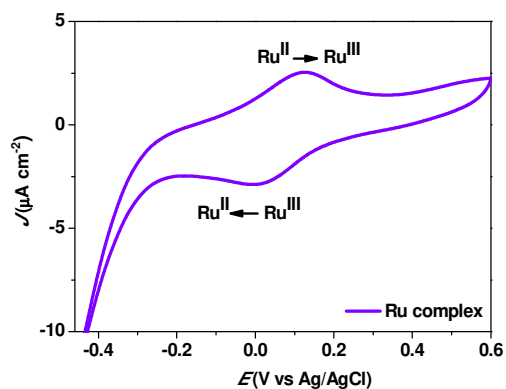


Figure 4. Cyclic voltammogram of GCE/MWCNT-g-C₃N₄- cis-(pyrene)₂RuCl₂ in argon saturated 0.1 M PBS (pH 7.0) (scan rate, 2 mV s⁻¹)

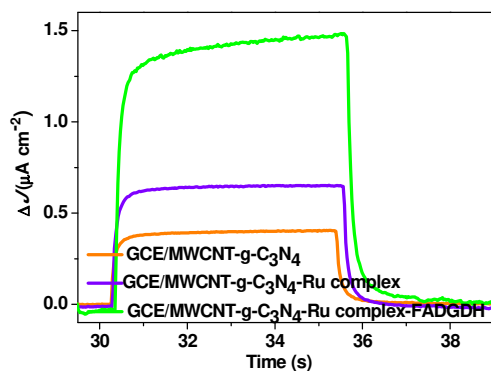


Figure 5. The photocurrent generation for the photoelectrodes in argon saturated 170 mM glucose in 0.1 M PBS (pH 7.0) at 0 V vs Ag/AgCl

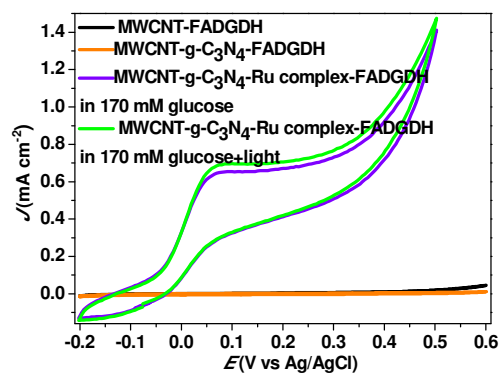


Figure 6. Glucose oxidation for the photoelectrodes in argon saturated 0.1 M PBS (pH 7.0) (scan rate, 2 mV s⁻¹)