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Enhancement of photovoltaic performance of photoelectrochemical biofuel cells by β-functionalized porphyrin sensitizers

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HIGHLIGHTS

- A calculation is used to analyze series of porphyrins as sensitizers.
- Photoelectrochemical biofuel cells were fabricated with the above porphyrins.
- The haematoporphyrin showed the best performance of the series of porphyrins.
- The theoretical calculation was consistent with the experimental results.

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ABSTRACT

Extending excited-state of sensitizer that absorbs visible photon and produces charge separation is of importance for a photoelectrochemical biofuel cell (PEBFC). In the present work, the dependence of series of porphyrins functionalized at β-positions as sensitizers' structures on their excited-state are analyzed with the density functional theory and time-dependent density functional theory. The calculated results expect that the radiative lifetime decreases in the order of haematoporphyrin > protoporphyrin IX > H_2-mesoporphyrin IX. The designed PEBFCs with the above porphyrins as sensitizers are assembled, in which the photocurrent action spectra testifies that the order of the radiative lifetime is consistent with that of the incident photon-to-collected electron conversion efficiency (IPCE) value based on the series of porphyrins. All the experimental characteristics show that the porphyrin with ethanol group (−CHOH−CH_3) at β-positions can enhance the photovoltaic performance of the PEBFC as expected.

1. Introduction

A photoelectrochemical biofuel cell (PEBFC) that combines a dye-sensitized solar cell (DSSC) [1–4] with an enzyme-catalyzed biofuel cell (BFC) [5–9] has attracted increasing research enthusiasm since Moore and co-workers have developed the new type cell (Fig. 1) [10]. The PEBFC relies upon charge separation at a dye-sensitized semiconductor photoanode, which is in close analogy with DSSC. Following photoinduced charge separation, the sensitizer cation is reduced by β-nicotinamide adenine dinucleotide (β-NADH), ultimately generating β-nicotinamide adenine dinucleotide (β-NAD^+), the oxidized form of the mediator. β-NAD^+ can serve as an electron acceptor and obtain electrons from β-D-glucose in the electrolyte under the catalysis of the glucose dehydrogenase (GDH). For the PEBFC, β-NAD^+ is not reduced at either the cathode or the photoanode, in contrast, the oxidized species, I_3^-, is reduced at the photoanode, leading to energy-wasting recombination reactions and loss of efficiency for the DSSC, and hence, charge recombination does not occur as DSSC does. In addition, for the enzyme-catalyzed BFC the efficiency is related to the stability and the immobilization of the enzyme on the electrode while for the PEBFC the enzyme is in the electrolyte and stable. Although the PEBFC has many advantages compared to the DSSC and BFC, but photovoltaic performance of the PEBFC is poor [10–19]. Amao et al. used chlorophyll or its derivative zinc chlorin-e_6 as sensitizers to construct the PEBFC which showed that short-circuit current (I_{sc}) and the open-circuit potential (V_{oc}) were 9.0 μA cm^{-2} and 415 mV, respectively. And the peaks in the photocurrent action spectrum were observed at 400 and 800 nm and the incident photon-to-collected electron conversion efficiency (IPCE) values at 400 and

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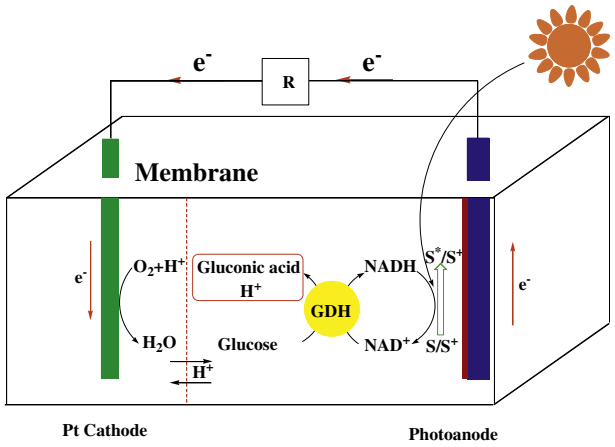

Fig. 1. Schematic diagram of the oxidation-reduction for the photoelectrochemical biofuel cell.

800 nm were estimated to be ca. 17.3% and 10.6% [16,17]. Gust et al. reported the PEBFC with 5-(4-carboxyphenyl)-10, 15, 20-*tris*(4-methylphenyl)porphyrin as a sensitizer. The PEBFC with porphyrin exhibited more performance than that with chlorophyll. The I_{sc} and V_{oc} were 55 μA cm^{-2} and 1.10 V, respectively for the PEBFC with porphyrin.

Typical sensitizer of the PEBFC is porphyrin compounds because they possess an intense Soret band at 400–450 nm and moderate Q-bands at 500–650 nm. The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of porphyrin match well with the conduction band of TiO_2 molecule. We have reported the PEBFCs based on H_2-mesoporphyrin IX which exhibited the I_{sc} of 395 μA cm^{-2}, the open-circuit potential (V_{oc}) of 767 mV and meso-tetrakis (4-carboxyphenyl) porphyrin (TCPP) which exhibited I_{sc} of 69 μA cm^{-2}, V_{oc} of 740 mV [19]. The above result that the difference of the sensitizer leads to the difference of the I_{sc} and V_{oc} shows that the structure of the sensitizer has an important influence on the performance of the PEBFC. In addition, Gust et al. employed TiO_2 rather than SnO_2 as the wide band gap semiconductor of the PEBFC, which represent a significant increase in cell performance [10,11]. When the PEBFC operates with the platinum cathode under anaerobic conditions, hydrogen produces under the catalysis of the Clostridium acetobutylicum [FeFe]-hydrogenase HydA [14].

The study on the PEBFC is extensively reported [10–19], however there is no report on sensitizer structure – cell function relationship. Long excited-state of sensitizer plays an important role of injecting electrons into the conduction band of titania (TiO_2) for the PEBFC. It is obvious that the structure of sensitizer is of importance for its excited-state. In this paper, series of porphyrin compounds as sensitizers (H_2-mesoporphyrin IX, protoporphyrin IX and haematoporphyrin as shown in Fig. 2) were analyzed using the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) [20–22]. With the aid of DFT and TD-DFT calculations, the HOMO, the LUMO, the energy difference between the HOMO and LUMO (ΔE_{H-L}), radiative lifetime (τ) were obtained, and the radiative lifetime decreased in the order of haematoporphyrin > protoporphyrin IX > H_2-mesoporphyrin IX [23]. The longer radiative lifetime is advantageous to injecting the electron into the conduction band of TiO_2, which is expected to enhance the photovoltaic performance of the PEBFC [23]. The experimental results showed that compared with the reported PEBFC based on H_2-mesoporphyrin IX, the PEBFCs sensitized by protoporphyrin IX or haematoporphyrin sensitizers showed much higher IPCE and better photovoltaic performance. The short-circuit current (I_{sc}) and the open-circuit potential (V_{oc}) values of the PEBFCs based on the series of sensitizers decreased in the order of haematoporphyrin > protoporphyrin IX > H_2-mesoporphyrin IX as expected. Thus, the function at β-position of the porphyrin is an important factor that must be considered for the development of the efficient PEBFC.

2. Experimental

2.1. Materials

H_2-mesoporphyrin IX, protoporphyrin IX and haematoporphyrin were purchased from J&K CHEMICAL LTD. β-NADH was purchased from Sigma–Aldrich Company. Perfluorinated sulfonic acid proton-exchange membrane Nafion 117 (thickness: 80 μm, exchange capacity: 1.0 ± 0.02 mM g^{-1}) was purchased from Shandong Dongyue Shenzhou New Material Co, Shandong China. The trishydroxylaminomethane (Tris) was obtained from J&K Chemical Ltd. GDH was obtained from Toyobo Co., Ltd. The enzyme activity was assayed following a protocol provided by the manufacturer. β-D-glucose, *N*, *N*-dimethyl formamide (DMF) and potassium chloride (KCl) were obtained from Beijing Chemical Company (Beijing, China). 3α, 7α-dihyroxy-5β-cholic acid (cheno) was obtained from Fluka. One unit of GDH activity is defined as the amount of enzyme consumed per minute that reduced 1.0 mmol NAD^+ to NADH by glucose.

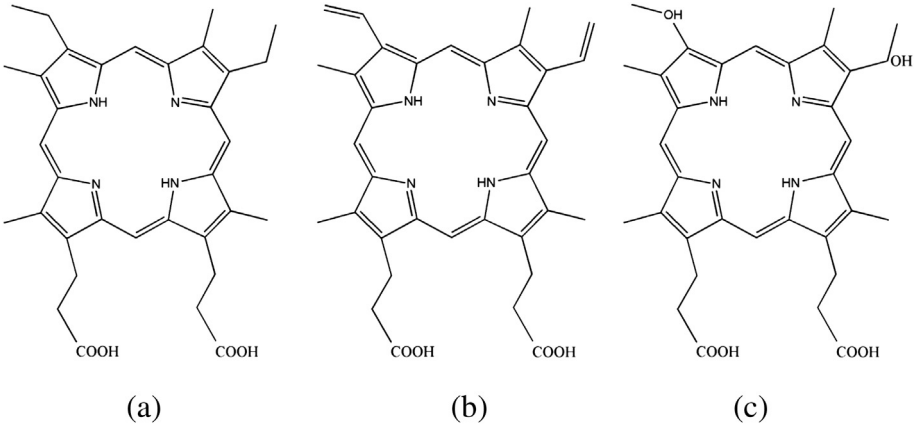

Fig. 2. Molecular structures of (a) H_2-mesoporphyrin IX, (b) Protoporphyrin IX and (c) Haematoporphyrin sensitizers.