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Short communication

Tris(hydroxymethyl)aminomethane photooxidation on titania based photoanodes and its implication for photoelectrochemical biofuel cells

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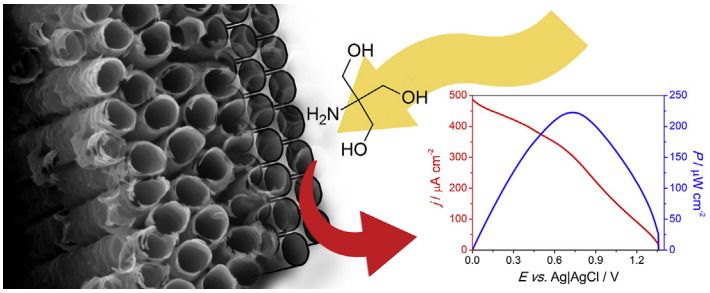
HIGHLIGHTS

- TRIS can be photoelectrooxidized on titania nanotube (TNT) anodes.
- A TNT anode was combined with an airbreathing biocathode to a photo-biofuel cell.
- TRIS can act as fuel in a photo-electrochemical biofuel cell.
- Care needs to be taken when using TRIS as buffer in photobiofuel cells.

GRAPHICAL ABSTRACT



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ABSTRACT

In many photoelectrochemical biofuel cells tris(hydroxymethyl)aminomethane (TRIS) is used a buffer. We show that TRIS can be readily photooxidised on titania electrodes. Combining a titania nanotube photoanode in a TRIS buffer with an air-breathing enzymatic biocathode we construct a relatively efficient photoelectrochemical biofuel cell using the TRIS buffer as fuel. This shows both the prospect of using air-breathing bio-cathodes in this kind of cells, but more importantly, shows the need for caution when using TRIS as buffer in photoelectrochemical applications.

1. Introduction

After Grätzel's and O'Regan's report about dye-sensitized solar cells in 1991 [1] a new era of converting solar energy to electricity started. The concept of dye-sensitized solar cells is quite simple; in their case, since the semi-conductor (TiO_2) photoanode adsorbed light only in the UV range, a dye was introduced allowing the photoanode to capture less energetic photons. This research was the first report of O'Regan's high surface area nanostructured titania being employed with Grätzel's ruthenium dye. However, a problem lied in regenerating the dye – it could be easily destroyed in aqueous solutions due to the presence of oxygen radicals generated *in situ*. O'Regan's and Grätzel's answer to this problem was to use an organic iodide electrolyte [1]. Lately, an alternative idea is to mimic living organisms by employing a whole new

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regenerating system [2]. In this system, the dye is being regenerated by reduced nicotinamide adenine dinucleotide (NADH), which is then regenerated by an NADH-dependent dehydrogenase (*e.g.* glucose dehydrogenase) while oxidizing the corresponding fuel (usually glucose [2–12]). The main advantage of this system is that it allows the use of highly deoxygenated aqueous solutions. There are several articles where this second regenerating system is combined with an enzyme-based cathode to form an enzyme-based photoelectrochemical biofuel cell (PECBFC) [2]. This system achieves simple and direct coupling of the two complementary processes, combines some of the advantages of each approach in a single unit, and can in principle provide more power than either process working independently [2]. The results from many of these reports look very promising. In most cases (*e.g.* Refs. [2–4,6,9,13]) the enzyme based regeneration system is immersed in an aqueous tris(hydroxymethyl)aminomethane (TRIS) buffer, which is commonly used in biochemical applications. In the photocatalytic research community it is well-known that amines can be photooxidized on titania [14,15] (TRIS has even been used as a probe for investigating photocatalysis on titania [16]). However, in the articles on PECBFCs TRIS is treated simply as a passive buffer. In the present work, we show that TRIS does not play only the role of a buffer but that it also can be efficiently photoelectrooxidized and acts as a fuel for the photoelectrochemical cell. We have chosen to use a TiO_2 nanotube (TNT) based photoanode because TNTs have been shown to be efficient both for PECBFCs [13,17] and for photooxidation [18,19]. Moreover, we combined this photoanode with an air-breathing biocathode described recently [20] to show that the photoelectrochemical biofuel cell can give a similar output as other reported PECBFCs, but in pure TRIS buffer in the absence of any other fuel.

2. Experimental

2.1. Materials and methods

If not stated otherwise, all chemicals were of analytical grade. 1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt hydrate (PTSA, ≥97.5%), Tris(hydroxymethyl)aminomethane (TRIS, TRIZMA base, ≥99.9%), phosphoric acid, ethanol, methanol and titanium foil (99.7%) was purchased from Sigma Aldrich. Acetic, hydrochloric, nitric and sulphuric acids were provided by Chempur, and hydrofluoric acid was bought from POCh. Bilirubin oxidase (BOD) from *Myrothecium* sp. (EC 1.3.3.5) with an activity of 2.10 U/mg was donated by Amano Enzyme Inc. Toray Teflon Treated Carbon Paper TGP-H-090 (with 5% wet proofing) was purchased from the Fuel Cell Store, Colorado. Methyltrimethoxysilane (MTMOS) from ABCR, and ethylene glycol (EMSURE, purity ≥99.5%) from Merck (Netherlands). Single-walled carbon nanotubes, SWCNTs were purchased from Elicarb (UK). Deionised water obtained from an ELIX system (Millipore) was used for the preparation of all solutions.

2.2. Instrumentation and electrochemical measurements

All amperometric experiments were carried out at ambient temperature (22–24 °C) with Autolab or μAutolab III potentiostats (Metrohm Autolab). Impedance spectroscopy was measured using an Ivium Compactstat.e bipotentiostat. Where a 3-electrode cell configuration was used, platinum wire (d = 0.5 mm, length ca 2 cm) or platinum net was used as counter electrode and Ag|AgCl|KCl(3M) as reference electrode. Scanning electron microscope (SEM) images were taken using a FEI Nova NanoSEM system. Illumination was provided by a xenon arc lamp (100 mW/cm^2) from Instytut Fotonowy (Poland) with an AM1.5 filter from Sciencetech (Canada).

2.3. Photoelectrochemical cell preparation

The titania nanotubes were prepared by anodizing a titanium foil in a HF solution. The titanium foil was cut in 1.2 × 1.2 cm squares and polished electrochemically for 1 min (3.15 mA/cm^2 in a solution of concentrated acids – CH_3COOH: H_2SO_4: HF, ratio 60:15:25) and chemically for 30 s (in a solution of concentrated acids – HF:HNO_3, ratio 1:3). This procedure was described earlier [21]. The originally matte surface became mirrorlike after this two-step polishing.

The titanium foil was anodized for 1 h at 100 V in a 0.75% v/v HF solution in ethylene glycol (H_2O content 9.985% v/v). The counter electrode, placed 1.5 cm from the anode, was a platinum net). Then, after abundant rinsing with ethanol, the titania nanotubes were annealed in a tube furnace for 3 h at 450 °C [22]. This resulted in tubes with an inner diameter of *ca* 120 nm and outer diameter of 140–160 nm. The length of the tubes was *ca* 5 μm (see Fig. S1 in supplemental materials).

The biocathode preparation was described before [20]. Briefly, PTSA functionalised SWCNTs [23], in a solution containing a sol–gel silicate precursor and the enzyme bilirubin oxidase (BOD), were drop-coated onto a Toray paper electrode. The exposed area of each electrode *ca* 0.2 cm^2 (*i.e.* 0.5-cm diameter) was defined by adhesive tape. Electrodes were dried in a climatic chamber (55% humidity, 22 °C) for 17 h. The resulting PTSA-SWCNT/BOD/MTMOS electrodes consisted of a catalytic layer containing 19.8 μg of BOD on one side that could be exposed to the air from the other side. The electrodes were stored in a fridge at 4 °C until used. PECBFC performance was measured during the first day of using a new biocathode since its output can be significantly reduced after several hours of operation [20].

For the photoelectrochemical cell we used a standard PMMA UV–visible spectroscopy cuvette. The electrodes were positioned as shown in the schematic in Fig. 1. A hole drilled in one of the transparent walls was aligned with the active surface area, limited to 0.2 cm^2, of the photoanode the cuvette was resealed with glue. Electrical contact was provided from the back of the photoanode by a piece of copper tape. The cuvette was filled with electrolyte solution and the photoanode was illuminated by light from the lamp transmitted through the transparent wall opposite the photoanode and the electrolyte. The reference and counter electrodes are placed in the electrolyte solution above the beam of light. In all experiments 0.1 M phosphate buffer (pH 8) was used as electrolyte.

For photoelectrochemical biofuel cell experiments a second hole (positioned in the frosted side-wall) was drilled in the photoanode half-cell (cuvette). The second half-cell was constructed in a similar manner – a hole was drilled in a cuvette and the biocathode was aligned with the hole and resealed with glue. Electrical contact was provided from the back side by a piece of copper tape. A second hole was drilled in the frosted side-wall of the cuvette. Both half-cells were joined by the side wall holes with a Nafion membrane placed between them (Fig. 1 – right).

3. Results and discussion

3.1. TRIS photooxidation on TNTs

We carried out experiments to investigate the photooxidation of TRIS on titania nanotubes under illumination (100 mW/cm^2 with an AM1.5 filter), curves I, and in the dark, curves II. The concentration of TRIS solution was 0.25 M (curves a), which is the typical concentration used in buffer solutions. The TRIS data was compared with blank experiments in clean 0.1 M phosphate buffer (pH 8) (curves b) (Fig. 2).

One can clearly see that the presence of TRIS in the solution