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Unique catalytic properties of a butoxy chain-containing ruthenated porphyrin towards oxidation of uric acid and reduction of dioxygen for visible light-enhanced fuel cells

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ABSTRACT

This paper reports the photoelectrocatalytic activities of a ruthenated porphyrin $[Ru(phen)_2(IP\text{-}C_4O\text{-}TPP)]^{2+}$ (denoted as Ru(II)PTPP, phen = 1,10-phenanthroline, IP = imidazo[4,5-*f*][1,10]phenanthroline and TPP = 5,10,15,20-tetraphenylporphyrin) containing a covalently-linked butoxy chain (-C_4O-) between IP and TPP moieties by means of various electrochemical techniques in combination with absorption spectroscopy and scanning electronic microscopy. Ru(II)PTPP is assembled on the surface of CdS nanoparticles, showing two Ru(II)-based peaks at 0.296 V and 0.830 V, where uric acid (UA) can be photoelectrocatalytically oxidized in a linear range of 0.01-10.0 mmol L^{-1}. The $-C_4O$- chain endows the Ru(II)PTPP/carbon felt (CF) electrode with favorable dioxygen (O_2) binding sites to achieve a couple of new redox peaks at −0.213 V, where O_2 involves electrocatalytic reduction reactions. While employing 5.0 mmol L^{-1} UA as fuel, and 60 mL min^{-1} O_2 as oxidant, the proposed photoelectrochemical fuel cell shows open-circuit photovoltage of 0.656 V, short-circuit photocurrent density of 0.136 mA cm^{-2}, and maximum power density of 31.50 $\mu W\,cm^{-2}$ at 0.497 V under visible-light illumination of 0.18 mW cm^{-2}. The present study provides an interesting platform for the utilization of renewable energy sources.

1. Introduction

The conversion of solar energy and/or biomass energy to electricity is very important for the development and utilization of renewable energy [1,2]. Sunlight is converted either into chemical energy by photosynthesis pathways or into electricity by dye-sensitized solar cells and other types of photovoltaic systems [3]. The biological fuels can be oxidized to produce electricity by a microbial or enzymatic fuel cell [4–6]. Alternatively, a photoelectrochemical fuel cell is considered as a combination of dye-sensitized solar cell with enzymatic biofuel cell or non-enzymatic fuel cell, exhibiting crucial advantages for the renewable energy conversion [7–10]. The photosensitizers used in photoelectrochemical fuel cells are usually assembled on the surfaces of traditional semiconductors (e.g. TiO_2, SnO_2, ZnO, CdS), and play an important role in the photoelectrocatalytic oxidation process of added fuels [11,12]. In the past decades, much attention has been paid to the fabrication of photoelectrochemical fuel cells using various photosensitizers such as mono- and multi-nuclear ruthenium(II) polypyridyl complexes [13,14], different shaped porphyrin arrays [15,16], and ruthenated porphyrins [17]. Among these photosensitizers, a series of cationic ruthenated porphyrins has attracted considerable interest because they possess characteristic metal-to-ligand charge transfer (MLCT) transitions of Ru(II) polypyridyl complexes, and strong Soret and Q absorption bands of porphyrin moieties in visible light regions [18]. The majority of the ruthenated porphyrins are usually formed by the coordination or covalent linking of Ru(II) polypyridyl complexes with porphyrin moieties [19,20]. Some of them have been demonstrated to be appropriate photosensitizers with good photocatalytic and electrocatalytic activities [21,22]. The investigations into this kind of ruthenated porphyrins and their applications in photoelectrochemical fuel cells are still ongoing [23].

Uric acid (UA) is an enzymatic end product from purine derivatives in human metabolism [24]. The abnormal level of UA in serum and urinary excretion is known to reflect purine metabolism disorders, leading to an acute attack of gout disease along with increasing risk for the development of nephrolithiasis and

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hyperuricemia [25], therefore the assay and reuse of UA become very important [26]. So far, the electrochemical oxidation of UA has been widely investigated using various electrodes modified with uricase and peroxidase enzymes [27], conducting polymer [28], metal nanoparticles and nanoalloys [29], carbon nanomaterials [30], etc. However, the electrochemical oxidation of UA always undergoes pronounced fouling effects, exhibiting poor reproducibility [31], thereby there is an increasing attempt to promote the oxidation of UA [32].

In our previous studies, a $[Ru(tatp)_3]^{2+}$ (tatp = 1,4,8,9-tetra-aza-triphenylene) modified ZnO nanoparticle electrode has been used to improve the oxidation of UA, showing good reproducibility [33,34]. However, the need for ultraviolet (UV) light limits its practical applications in photoelectrochemical fuel cells. A great deal of attention is being paid to anionic and cationic ruthenated porphyrins because of their unique photophysical and electrochemical properties [35], DNA-photocleavage activities [36], and electrocatalysis towards the oxidation of organic molecules [37]. Simultaneously, some of ruthenated metal porphyrins have been found to have electrocatalytic activities towards the reduction of dioxygen (O_2) [38,39]. To date, despite the fact that spectral, structural and electrochemical properties of many ruthenated porphyrins and their applications have been documented [40,41], there are no reports on the photoelectrocatalytic oxidation of organic molecules and electrocatalytic reduction of dioxygen by ruthenated porphyrins with a flexible covalently- linked alkoxy chain, in particular, for visible light-enhanced fuel cells.

In the current work, we expect to investigate the photoelectrocatalytic oxidation of UA and electrocatalytic reduction of O_2 by $[Ru(phen)_2(IP\text{-}C_4O\text{-}TPP)]^{2+}$ containing a covalently-linked butoxy chain ($-C_4O-$) between IP and TPP moieties (phen = 1,10-phenanthroline, IP = imidazo[4,5-*f*][1,10]phenanthroline and TPP = 5,10,15,20-tetraphenylporphyrin), denoted as Ru(II)PTPP. An important attempt is made to evaluate the photoelectrocatalytic oxidation of UA in the absence and presence of O_2 by Ru(II)PTPP assembled on a CdS nanoparticle modified indium-tin oxide (ITO) electrode, as well as the electrocatalytic reduction of O_2 by Ru(II) PTPP immobilized on a carbon felt (CF) electrode. It is interestingly found that the flexible butoxy chain endows Ru(II)PTPP with multifunctional catalytic properties, which can be applied to the fabrication of visible light-enhanced UA fuel cells.

2. Experimental section

2.1. Chemicals and materials

Tris(hydroxylmethyl)aminomethane (Tris) from Sigma was used to prepare a buffer solution with doubly distilled water, consisting of 0.01 mol L^{-1} Tris/0.05 mol L^{-1} NaCl (pH 7.2). Cadmium chloride ($CdCl_2$), sodium thiosulphate ($Na_2S_2O_3$) and uric acid (UA) were used as received. UA was dissolved with buffer solutions (pH 12.4), in which singly charged urate ions were formed [42]. Prior to each measurement, the test solution was adjusted to pH 7.2, at which the predominant tautomer of UA was a triketo form [43]. Ru(II)PTPP was synthesized following previously reported procedures [44], and its structure was shown in Fig. 1.

2.2. Instruments and methods

Voltammetric measurement was performed on a CHI660a electrochemical system (Shanghai, China). Unless otherwise noted, the modified electrode was employed as the working electrode, while using a titanium sheet counter electrode and an Ag/AgCl reference electrode with 0.05 mol L^{-1} NaCl salt bridge. Ultraviolet (UV)-visible absorption spectra were performed by a UV-1700 spectrophotometer (Shimadzu, Japan). A Zeiss Ultra55 field-emission scanning electron microscope (SEM, Germany) was employed to analyze the surface appearance of the modified electrode.

2.3. Preparation of Ru(II)PTPP/CdS/ITO and Ru(II)PTPP/CF electrodes

The CdS/ITO electrode was prepared following previously reported electrochemical deposition procedures [45]. Briefly, an indium-tin oxide (ITO) sheet (10 Ω sq^{-1}, Nanbo Co., Shenzhen, China) was employed as the working electrode to prepare a CdS

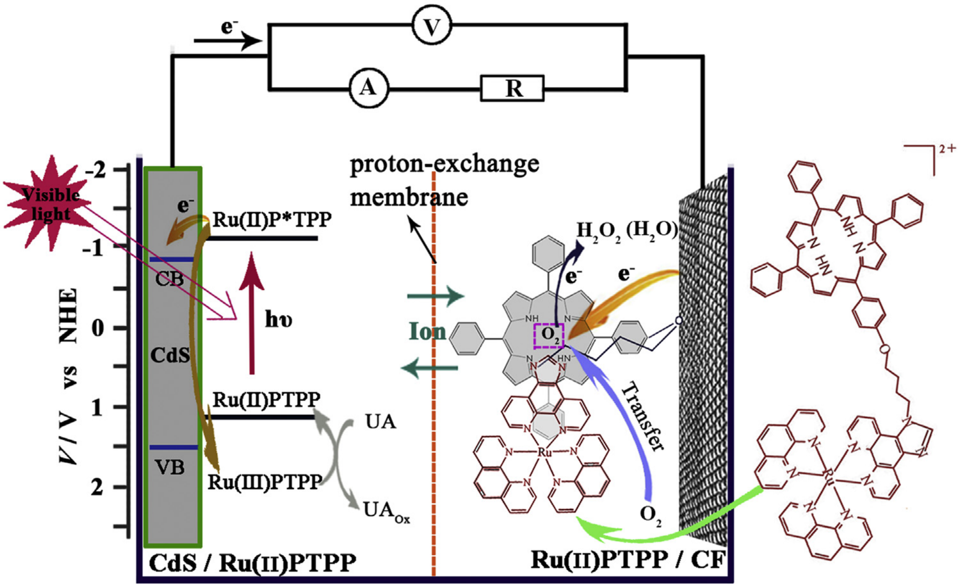

Fig. 1. Schematic illustration of visible light-enhanced UA/O_2 fuel cell employing Ru(II)PTPP/CdS/ITO photoanode and Ru(II)PTPP/CF cathode. Inset shows the structure of Ru (II)PTPP.