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COMMUNICATION

A visible light water-splitting cell with a photoanode formed by codeposition of a high-potential porphyrin and an iridium water-oxidation catalyst†

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A high-potential porphyrin is codeposited on TiO₂ nanoparticles together with our Cp*–iridium water-oxidation catalyst to give a photoanode for a water-splitting cell. The photoanode optically resembles the porphyrin yet electrochemically responds like the Ir catalyst when it is immersed in aqueous solutions. Photoelectrochemical data show that illumination of the codeposited anode in water results in a marked enhancement and stability of the photocurrent, providing evidence for light-induced activation of the catalyst.

1. Introduction

Geopolitical issues and environmental concerns emphasize the need for clean, secure, non-fossil energy sources.^{1–7} Solar energy collection and storage is one of the most promising lines for development. In this context, a biomimetic approach offers hope.^{8–11} Many advances in the field of ‘artificial photosynthesis’, including mimicry of energy transfer and charge separation^{12–18} and development of energy-storage catalysis,^{19–32} have been reported. In addition, sensitization of metal-oxide wide band-gap semiconductor surfaces with inorganic transition-metal complexes or organic dyes has been actively pursued in developing methods for converting solar energy to electricity by dye-sensitized solar cells.^{33,34} A promising direction

in this field is the use of semiconductors and dye-sensitized semiconductors as a platform for coupling photochemical charge separation with catalysis.^{35–39} Photoexcitation of a selected sensitizer on n- or p-type semiconductor electrodes will generate an initial charge-separated state that can be used to study subsequent hole or electron transfer to anodic or cathodic catalysts. Practical application of this integrated approach will ultimately require effective coupling of light capture, photochemical charge separation and efficient catalysis.

Herein, we report the optical and electronic properties of a high-potential porphyrin photoanode codeposited with a structural analog of our water-oxidation catalyst (Chart 1).^{30,32} The zinc porphyrin (**1**) and iridium catalyst (**2**) each contains a carboxylic acid group for attachment to TiO₂ nanoparticles (see the ESI†, Experimental procedures). In the catalytic complex, strongly donating ligand sets stabilize the needed high oxidation states of iridium. For the porphyrin dye, bis-pentafluorophenyl electron-withdrawing groups induce an electron deficiency that leads to a positive shift of the porphyrin radical cation/porphyrin redox couple to values that

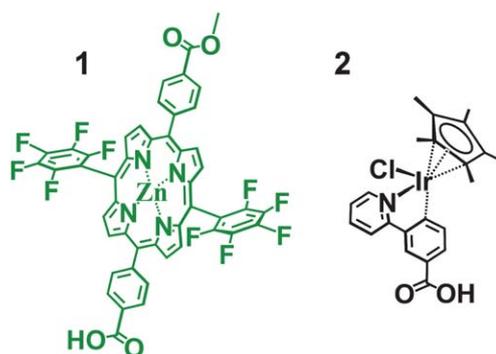


Chart 1 Compounds 1 and 2.

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Broader context

Artificial photosynthesis is a long-sought goal in solar energy research. By splitting water into O₂ and a fuel such as H₂, two problems are addressed: energy storage and the production of a potential transport fuel. This communication describes a water splitting photocell that uses a specially designed photoanode to which are attached both a high potential porphyrin dye for light absorption and a Cp*–iridium catalyst for water oxidation. The cell is completed by a standard Pt cathode.

permit water oxidation. Illumination of these photoanodes in complete cells results in a marked enhancement and stability of the photocurrent for electrodes in water, consistent with light-induced activation of the catalyst.

2. Results and analysis

2.1 Electrochemical characterization

The 10,20-bis(pentafluorophenyl) groups of **1** have a strong influence on the electrochemical properties of the porphyrin ring system as the electron-withdrawing nature of these functional groups destabilizes the formation of the radical-cation species.^{40,41} For dichloromethane solutions of the methyl ester of porphyrin (**1**), the first and second oxidations of the porphyrin are chemically reversible and occur with an $E_{1/2}$ of 1.35 and 1.59 V vs. NHE, respectively (see the ESI†, Fig. S7). Thus, the oxidized porphyrin species (**1**⁺) is thermodynamically capable of water oxidation (yet kinetically ineffective on its own).

We have previously reported the catalytic performance of a homogeneous Cp*Ir water oxidation catalyst in a mixed-solvent solution (acetonitrile–water mixture) with Ce(IV) as the primary oxidant.^{30,32} Now, we report a close analogue (**2**) bearing a carboxylic acid group for surface attachment to TiO₂. Cyclic voltammograms of **2** deposited on a TiO₂-sintered FTO working electrode (**2-TiO₂**) in 0.1 M Na₂SO₄ exhibit an increase of anodic currents at potentials positive of 1 V vs. NHE (Fig. 1, left). These results indicate that immobilization of the catalyst onto the electrode surface allows operation under aqueous conditions when the required potentials are applied. Rotating electrode (RRDE) measurements (see the ESI†, Fig. S10) confirm that oxygen can be formed at the surface of a sintered TiO₂ Pt-disc electrode functionalized with **2**. Further, electrodes codeposited with **1** and **2** (**1 + 2-TiO₂**) maintain the catalytic feature observed in cyclic voltammograms of TiO₂ on FTO electrodes treated solely with **2**, a crucial feature for deployment in photocatalytic-electrochemical cells. The overall current density is,

however, significantly lower in the codeposited material; some diminution may be expected, as the presence of porphyrin sensitizers limits the surface area available for catalyst deposition. Cyclic voltammograms of the unfunctionalized TiO₂-sintered FTO working electrode, as well as electrodes treated only with **1**, are included in Fig. 1; neither gives rise to the increased anodic currents observed for electrodes treated with **2**. The surface loadings for **1-TiO₂** and **2-TiO₂** as determined by quantitative mass spectrometry (see the ESI†, Experimental procedures) are 3.4×10^{-8} and 7.6×10^{-8} mol cm⁻², respectively.

2.2 Optical characterization

The spectral features of the codeposited material (**1 + 2-TiO₂**) (Fig. 1, right) are dominated by the porphyrin due to its relatively high molar extinction coefficient (see the ESI†, Fig. S7). Likewise, the porphyrin dye extends the absorption of the anode well into the visible region. Thus, the codeposited anode is optically more similar to **1-TiO₂** yet electrochemically responds like **2-TiO₂** in aqueous solutions. The intersection of the normalized absorption and emission spectra of compound **1** in dichloromethane yields an estimated $E^{0,0}$ transition energy of ~ 2.12 eV (see the ESI†, Fig. S8). The estimated potential for the excited-state couple (E^0 (**1**⁺/**1**^{*}) ≈ -0.77 V vs. NHE) is negative of the TiO₂ conduction band (TiO₂ CB ≈ -0.57 V vs. NHE).⁴² Thus, **1**^{*} should be energetically capable of injecting electrons into the conduction band of TiO₂ and photochemically generating the **1**⁺ radical-cation species at the surface.

2.3 Time-resolved terahertz measurements

Interfacial electron-transfer dynamics of functionalized metal-oxide nanoparticle thin films were studied with subpicosecond temporal resolution by time-resolved terahertz spectroscopy (see the ESI†, Experimental procedures). Results obtained for a 400 nm optical pump/THz probe of TiO₂ colloidal nanoparticle thin films, including unfunctionalized as well as **1-TiO₂**, **2-TiO₂**, and **1 + 2-TiO₂**, are

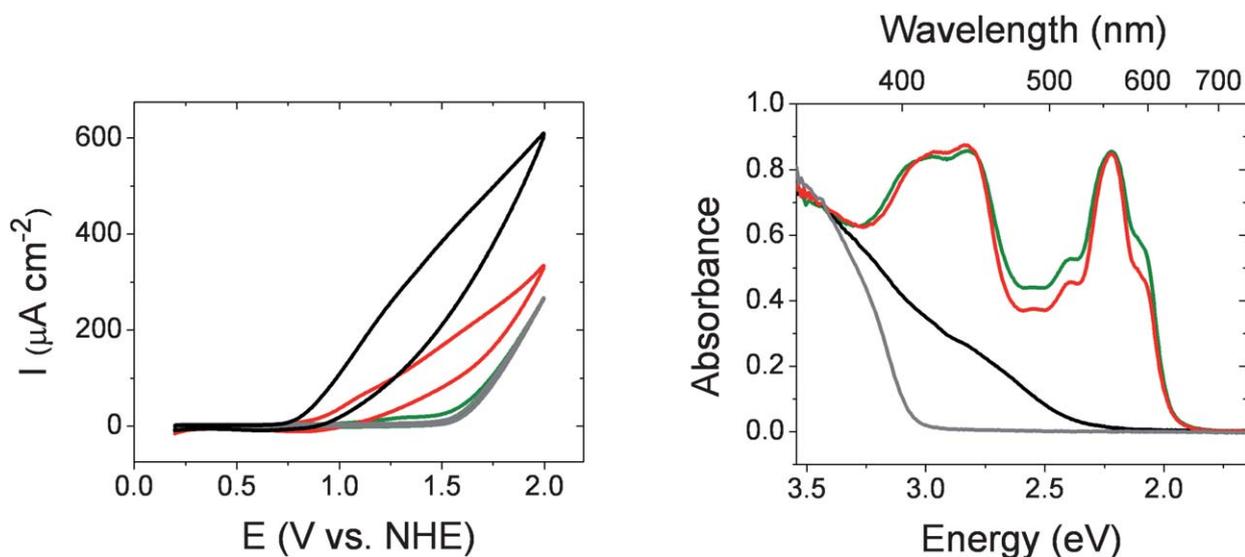


Fig. 1 Cyclic voltammograms (left) of TiO₂ (grey), **1-TiO₂** (green), **2-TiO₂** (black), and **1 + 2-TiO₂** (red) deposited on a conductive FTO-coated glass working electrode in water (0.1 M Na₂SO₄) as well as diffuse reflectance spectra (right) of a thin film of TiO₂ (grey), **1-TiO₂** (green), **2-TiO₂** (black), and **1 + 2-TiO₂** (red).

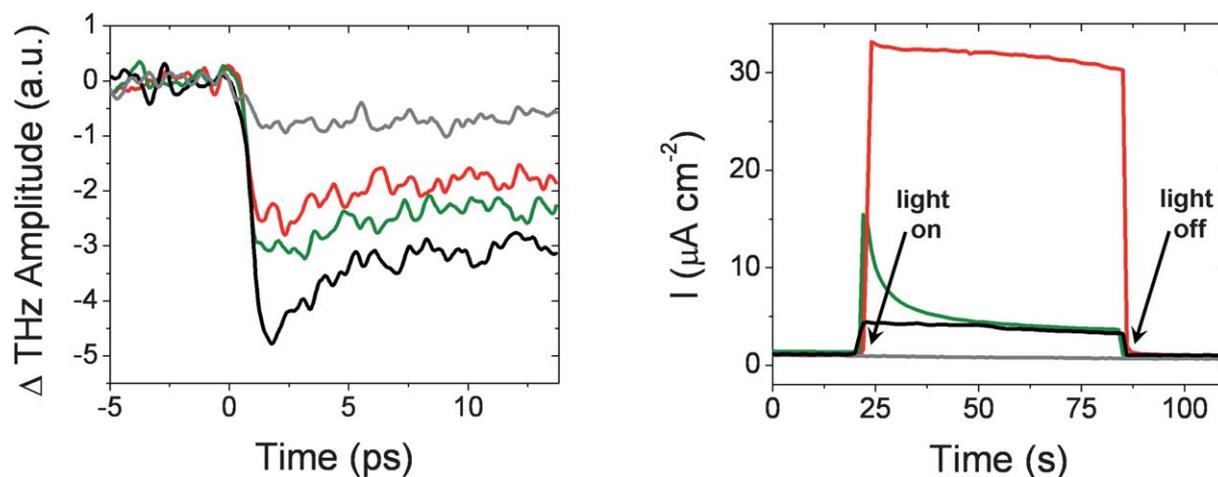


Fig. 2 (left) Time-resolved terahertz probe spectra obtained with a 400 nm optical pump of a thin film of TiO_2 (grey), 1-TiO_2 (green), 2-TiO_2 (black), and $1 + 2\text{-TiO}_2$ (red), and (right) three-electrode photocurrent measurements using a H-cell configuration (see the ESI†, Experimental procedures) with a 0.3 V external bias for TiO_2 (grey), 1-TiO_2 (green), 2-TiO_2 (black), and $1 + 2\text{-TiO}_2$ (red) deposited on conductive FTO-coated glass working electrodes in water (0.1 M Na_2SO_4) upon illumination with a $\sim 200 \text{ mW cm}^{-2}$ white-light source coupled to a 400 nm long-pass filter.

illustrated in (Fig. 2, left). There is negligible change in the THz transmittance of the bare TiO_2 sample, consistent with the negligible absorbance at 400 nm. Results obtained for 1-TiO_2 indicate effective photoinduced charge injection. These results are consistent with the estimated excited-state potential of **1** versus the more positive potential of the TiO_2 conduction band. Also evident in Fig. 2 is the relatively large change in THz amplitude obtained for thin films of **2** on TiO_2 . Further, the signal obtained for the codeposited film is less intense in comparison with those obtained for films treated only with **1** or **2**, indicating a decrease in the number of electrons which have become mobilized in the TiO_2 conduction band in the first 10 ps after photoexcitation. This decrease in electron injection suggests that the electron injection for the codeposited films is not simply a result of independent electron injection from both **1** and **2** and that the mechanism of electron injection is altered when **1** and **2** are codeposited on the surface of TiO_2 .

2.4 Photocurrent measurements

Photocurrent measurements were conducted with TiO_2 sintered on conductive FTO-coated glass working electrodes in 0.1 M Na_2SO_4 using a three-electrode configuration with a Ag/AgCl reference electrode, a 0.3 V bias potential (see the ESI†, Experimental procedures) and a Pt counter electrode. The anode compartment was separated from the cathode with a coarse glass frit and illuminated with a $\sim 200 \text{ mW cm}^{-2}$ light source (Fig. 2, right). In all experiments, a 400 nm long-pass filter was used to avoid direct band gap excitation of TiO_2 (Fig. 1, right). Thus, illumination of untreated TiO_2 anodes results in negligible photocurrent under these conditions. For porphyrin-sensitized photoanodes lacking the catalyst (1-TiO_2), illumination results in a sharp transient current arising from the initial, yet unsustained, injection of electrons from the photoexcited porphyrin species (1^*). Photocurrent of a similar intensity is observed for catalyst-sensitized photoanodes lacking the porphyrin dye (2-TiO_2). In contrast to these results photoexcitation of codeposited anodes gives rise to a significantly increased and sustained photocurrent (on the seconds timescale) in complete cells,

consistent with the model of visible light-induced activation of the catalyst.

3. Conclusions

Our bioinspired photochemical cell consists of a high-potential porphyrin attached to a TiO_2 surface that is codeposited with an iridium-based water-oxidation catalyst. Our characterization indicates the catalyst remains active on the surface. Photoexcitation of the surface-attached porphyrin generates the porphyrin excited-state species (1^*), which is energetically poised to inject electrons into the conduction band of TiO_2 , forming the relatively high potential porphyrin radical cation (1^+), a species that is thermodynamically capable of acting as a primary oxidant of water.

Time-resolved optical pump/terahertz probe measurements are consistent with our energetic model based on electrochemical and optical data. These measurements allow for a direct non-contact probe of the timescale and efficiency of photoinduced charge injection and recombination or trapping. We have previously found a good correlation between this type of THz measurement and efficiencies of dye-sensitized solar cells.⁴³ However, the present lack of correlation between the THz measurements and photocurrent generation indicates that charge injection on a ps timescale is not the limiting factor in photocurrent generation in complete cells.

Photoexcitation of complete cells, under our conditions (see the ESI†, Experimental procedures), gives rise to a photocurrent that is significantly increased and sustained in comparison with results obtained in control experiments lacking any one component of the complete cell. These results are consistent with our working model of the sustained current arising from light activation of the catalyst resulting from the transport of holes from photooxidized porphyrin dyes and/or possible migration of holes from other oxidized iridium sites. Our photocurrents ($\sim 30 \mu\text{A cm}^{-2}$) compare favorably to those in prior work,^{36,38} but we do need a bias voltage, as in one prior case.³⁶ A bias voltage was avoided in the work of Brimblecombe *et al.*,³⁸ but UV irradiation was employed. In a future full paper, we aim to provide quantitative efficiency data on the basis of a better

understanding of the loading of the components and the oxygen output of the cell.

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