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Visible Light Sensitization of TiO_2 Nanotubes by Bacteriochlorophyll-C Dyes for Photoelectrochemical Solar Cells

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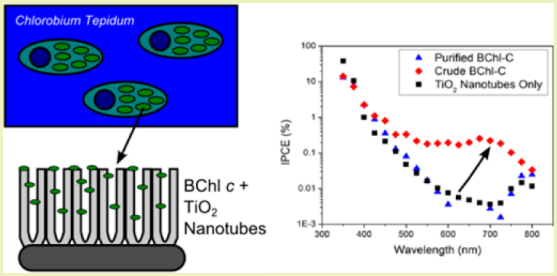
Supporting Information

ABSTRACT: Biomimetic sensitizers have evolved over millions of years to absorb and utilize sunlight and therefore are highly desirable to produce efficient, low cost, dye-sensitized photoelectrochemical solar cells. We report on the sensitization of TiO_2 nanotubes by bacteriochlorophyll-c (BChl *c*) extracted from photosynthetic bacteria. BChl *c* is notable for its high conversion efficiency inside the bacteria, which makes it a promising candidate for a naturally derived sensitizer for TiO_2. A photocurrent conversion efficiency of 0.1% was observed at 600−800 nm, corresponding to the absorption peak in BChl *c*; a photoanode efficiency of 0.23% was measured at around −0.1 V_{SCE}. Stability tests under simulated sunlight showed stable photocurrents over the course of 14 min. Mechanisms that currently limit the efficiency include the formation of BChl *c* aggregates on TiO_2, which may increase recombination, and possibly interface defects, which decrease charge injection to the nanotubes and trapping of photogenerated charges.



KEYWORDS: *Biomimetic materials, TiO_2 nanotubes, Bacteriochlorophyll-c, Photoelectrochemistry, Dye-sensitized solar cells*

INTRODUCTION

The TiO_2 nanotube array system has been widely investigated as a photoanode material for photoelectrochemical cells (PECs) as well as dye-sensitized solar cells (DSSCs).[1−7] These nanotubes are formed from the anodization of Ti in electrolytes containing fluoride ions and exhibit 1-D charge transport along the length of the nanotube,[8] making them a more attractive and potentially more efficient system compared to nanoparticle TiO_2 where charges must hop randomly from particle to particle with reduced mobility.[9,10] The increased light scattering of TiO_2 nanotubes and the lower recombination rates have both been noted as advantages of TiO_2 NTs over nanoparticle TiO_2.[11] Additionally, the long-term stability of TiO_2 nanotubes makes them technologically attractive for any photoelectrochemical application. However, the major drawback of TiO_2 is the large bandgap of anatase, 3.2 eV,[12] limiting the absorption to wavelengths below 378 nm and less than 10% of the solar radiation received.[13] As a consequence, the addition of dyes has been widely experimented with to extend the absorption of TiO_2 into the visible range. To date, the highest performing TiO_2-based DSSC modified by metallorganic dyes is a Zn porphyrin-sensitized device coupled with a Co(II/III) redox shuttle that produced cell efficiencies of 12.3% under sunlight.[14] Recent developments of free-standing TiO_2 nanotubes transferred to transparent substrates have overcome challenges of a highly resistive barrier layer and restriction of illumination direction, which has brought efficiencies up to 7.8% and made the nanotube system competitive with nanoparticle-based solar cells.[15,16]

There is a strong desire to develop inexpensive dyes for sensitization, and the natural chlorophyll structures found in biology are promising candidates for this application.[17] Chlorophylls extracted from spinach were used to sensitize TiO_2 and ZnO,[18] and a mixture of chlorophyll-a and chlorophyll-b extracted from spinach could be chemically processed to produce a Cu chlorophyll molecule that yielded up to 83% photon-to-current conversion efficiency at 400 nm, corresponding to an overall cell efficiency of 2.6%.[19] Exploiting the proton pumping mechanism of the photosensitive bacteriorhodopsin protein extracted from *Halobacterium salinarum*, Allam et al. achieved a current density of 0.65 mA/cm^2 photocurrent density for water splitting under AM 1.5 sunlight paired with 7 μm TiO_2 nanotubes.[20]

For photoelectrochemical applications, bacteriochlorophylls found in photosynthetic bacteria hold greater promise than their plant-derived counterparts.[21] Variants of these chlorophylls are differentiated by the chemical groups at the edges.[22] The

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mechanism that enables these bacteria to more efficiently use light is the self-assembly of bacteriochlorophyll molecules into structures that boost the absorption of photons, enabling the bacteria to run photosynthesis with a photon flux as low as one photon per 8 h.[23,24] Upon illumination, the bacteriochlorophyll is placed in an excited state, which is followed by transfer of charge to neighboring molecules for photosynthesis.[25,26] If the photogenerated electrons were injected into TiO_2 instead, this could potentially result in a highly efficient solar cell that would use these bacteriochlorophylls as sensitizers. The LUMO (−3.2 eV) and HOMO (−5.2 eV) levels of an aggregated mixture of BChl types including *c* indicate that these energy levels bracket the conduction band edge of TiO_2 (−4.2 eV),[21,27] which provides a driving force for electron injection into TiO_2 in a similar manner as the Ru-based N-719 dye used in DSSCs with a HOMO of −5.45 eV and a LUMO of −3.85 eV.[28] Frigaard measured the absorption spectra in solution of various chloro- and bacteriochloropylls and detected strong peaks at 364−469 and 654−795 nm.[29] Miyatake and Tamiaki characterized the absorption spectra of the bacteriochlorphyll-c (BChl *c*) and found a sharp absorption peak located at 740 nm for aggregates and 667 nm for the monomeric form, along with a broad absorption peak at 440 nm contributed by carotenoids.[22] Lu et al. have demonstrated a photoelectric response on mesoporous WO_3/TiO_2 films using a mixture of purple nonsulfur bacteria photosynthetic reaction centers.[26]

While bacteriochlorophyll-based photoelectrochemical systems have been proposed, they have not been used as dyes on TiO_2 nanotubes before. We report on the synthesis of BChl *c*-modified TiO_2 nanotubes, demonstrating the generation of photocurrent under visible light illumination and stable operation over 14 min under simulated sunlight. Slow photocurrent transients are observed under visible light, indicating losses due to trapping of photogenerated electrons within the BChl *c*. We find crude BChl *c* to be more effective than purified BChl *c*, suggesting that the purification process may denature the product or that it could somewhat hinder the attachment of these molecules to the TiO_2 nanotubes.

EXPERIMENTAL SECTION

TiO_2 nanotubes were synthesized by anodizing Ti foils (99%, annealed, metals basis, Alfa Aesar) that were cut into 2 cm × 0.7 cm × 0.127 cm sections. Prior to anodization they were degreased by sonication in acetone, isopropanol, and methanol. Anodization was carried out in a solution of 0.5 wt % NH_4F (99.99%, metals basis, Sigma-Aldrich) and 11 vol % H_2O (DI Millipore) in ethylene glycol (99.8% Sigma-Aldrich) at 20 V for 1 h.[30] In order to verify whether the TiO_2 nanotubes high surface area may effectively enhance the photocurrent, planar TiO_2 was used as a benchmark; the latter was synthesized by anodizing in 0.5 M H_2SO_4 at 20 V for 30 minutes, producing a flat oxide film. Anodization was controlled with a Kepco BOP-100 using LabVIEW connected to Ti foil as the anode and a Pt mesh as the cathode. Samples were annealed at 350 °C for 3 h in air in order to obtain the anatase TiO_2 phase.[31]

Adsorption of BChl *c* at the TiO_2 nanotube surface was carried by soaking TiO_2 nanotube samples for 1−7 days (see the Supporting Information for BChl *c* bacteria production, extraction, and absorption spectroscopy procedures). The morphology of the adsorbed aggregates was examined by using a field emission-scanning electron microscope (FE-SEM, JEOL 6700F). Photocurrent measurements were carried out in a solution of 0.2 M Na_2SO_4 and 0.1 M $NaCH_3COO$ (pH 7) in a three electrode configuration with a saturated calomel reference electrode (SCE) and a platinum mesh as the counter electrode. Monochromated light measurements between 350 and 800 nm were collected to identify the range of wavelengths where the addition of BChl *c* resulted in photocurrent generation. The illumination came from a Princeton TS428 tungsten/halogen lamp and SP1250 monochromator combinationwith a UV filter used at all wavelengths above 500 nm. The power density of the light as a function of wavelength was measured by a Newport Model 1931-C power meter with 0.35 cm radius detector, which was then used to calculate incident photocurrent efficiency (IPCE)[32] as a function of wavelength.

$$\mathrm{IPCE}\ (\lambda) = \text{electrons cm}^{-2}\ \text{s}^{-1}\ (\lambda)/\text{photons cm}^{-2}\ \text{s}^{-1}\ (\lambda)$$

The integrated incident intensity was 68 mW/cm^2. Monochromatic light measurements were controlled by a CHI-920C potentiostat at a fixed bias of 0.3 V_{SCE}. Photocurrent measurements were also taken under AM 1.5 simulated sunlight with an Oriel Sol 1A light source.

RESULTS AND DISCUSSION

Figure 1 compares the morphology of bare TiO_2 nanotubes (a) with those modified by adsorption of crude bacteriochlorophyll

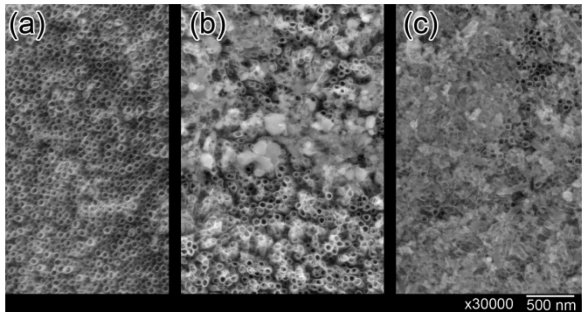

Figure 1. Surface morphology of BChl *c* modified TiO_2 nanotubes (a) no deposited material, (b) 1 day of soaking, and (c) 4 days of soaking.

for 1 day (b) or 4 days (c). Only the samples modified with crude BChl *c* were analyzed because no change in color was observed when the purified material was added on the TiO_2 nanotubes. BChl *c* aggregates are seen to form at random sites, eventually covering the entire surface. The precise character of these aggregates is difficult to evaluate due to the pronounced topography of the TiO_2 nanotube surface; others however have observed on flat surfaces the formation of self-assembled cyclic structures.[33] The increase in aggregate size with longer adsorption time would eventually lead to thickening of the BChl *c* layer as well as to the photogeneration of charge carriers at locations farther from the TiO_2/BChl *c* interface, possibly hindering charge collection and causing recombination. We have observed similar effects with TiO_2 nanotubes modified by Cu_2O and Fe_2O_3 inorganic sensitizers.[34]

The incident photon-to-current conversion efficiency (IPCE) is reported as a function of wavelength in Figure 2(a). For unmodified TiO_2 nanotubes, the photocurrent efficiency drops to below 10^{-3} % beyond 500 nm. Little change is observed in the UV portion of the spectrum after BChl *c* modification; however, efficiency on the order of 0.1% is observed in the wavelength range centered between 600 and 800 nm. This absorption peak coincides with the absorption peak for BChl *c* (Figure S1, Supporting Information) as reported both by Frigaard[29] and Miyatake and Tamiaki.[22] As more BChl *c* is being adsorbed with increased deposition time, the photocurrent efficiencies at all wavelengths are indeed observed to decrease. Next, the behavior of purified BChl *c* is compared with the crude material in Figure 2(b). We find that purified BChl *c* provides no enhancement in the photocurrent as a function of wavelength, and the IPCE spectrum in Figure 2(b) is indistinguishable from that of the unmodified TiO_2 nanotubes. In Figure 2(c), the photocurrent

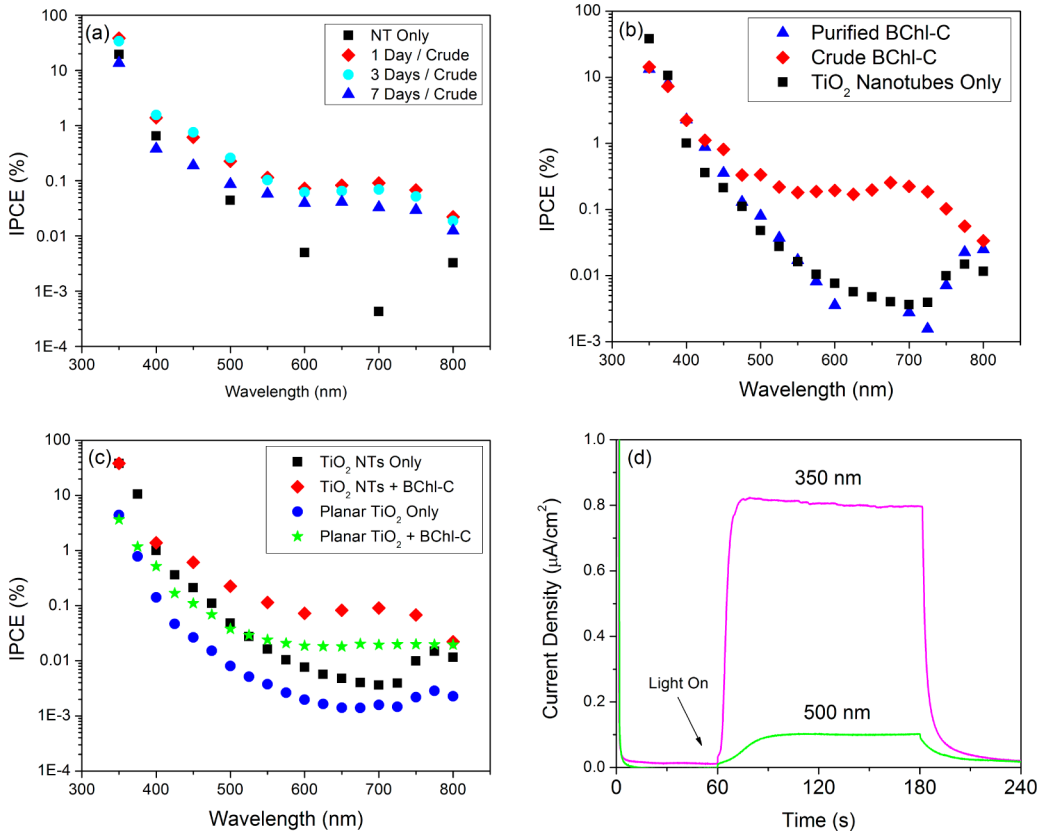

Figure 2. Photocurrent measurements on TiO_2 nanotubes and TiO_2 nanotubes modified by BChl *c*. (a) Effect of adsorption time shows that an optimal soaking time is 1 day, and further coverage decreases photocurrent efficiency. (b) IPCE from crude BChl *c* is compared with that of purified BChl *c*; visible light absorption is only seen in the crude material. (c) Performance of TiO_2 nanotubes is compared with that of planar TiO_2, showing an enhancement likely due to the high surface area. (d) Photocurrent transients for 350 and 500 nm illumination are compared. The slow onset under 500 nm illumination is associated with trap-filling behavior when visible light is absorbed by BChl *c* aggregates.

efficiency of the planar TiO_2 films is compared with that of TiO_2 nanotubes to verify that the higher surface area morphology of the nanotubes indeed contributes to enhance efficiency; the enhancement observed is on the order of 5−10 times. Finally, the photocurrent transients in the UV at 350 nm and in the visible at 500 nm are shown in Figure 2(d). While a sharp onset is observed for the response under UV light, corresponding primarily to photocurrent generation from TiO_2 nanotubes, the response in the visible range at 500 nm has a slow onset transient. A slow onset response is characteristic of the accumulation of photogenerated charges in trap states,[35,36] which suggests the presence of defects in the BChl *c* aggregates associated with disorganized molecular assemblies. The addition of the linker 3-mercaptopropionic acid has been shown to improve adhesion of bacteriorhodopsin to TiO_2 nanotubes and suggests that the attachment of BChl *c* may be similarly enhanced.[20]

The performance and stability of the TiO_2 nanotubes modified by 2 days of soaking in BChl *c* were tested under simulated sunlight. A linear sweep voltammetry LSV (Figure 3(a)) was collected under simulated sunlight from about −0.5 to +0.6 V_{SCE}. The photoanode efficiency under applied bias (Figure 3(b)) was calculated using the expression

$$\eta = J_{pc}(E_{OER} - E_{applied})/P$$

where J_{pc} is the photocurrent density, E_{OER} is the potential of the oxygen evolution reaction at pH 7 ($E_{OER} = 1.23\ V_{SHE} - 0.059$ pH $= 0.576\ V_{SCE}$), and P is the power density of simulated sunlight (100 mW/cm^2). Photoanode efficiencies reach a maximum of 0.05% for the unmodified TiO_2 nanotubes and 0.23% for the BChl *c* modified TiO_2 nanotubes. A major challenge of narrow bandgap inorganic semiconductors, such as Cu_2O, for TiO_2 sensitization is their tendency to rapidly degrade under illumination, on the order of only minutes.[37,38] While in the bacteria, the BChl are contained in chlorosomes that protect against degradation;[39] studies involving the use of BChl *a* as sensitizers for medical phototreatment or fluorescence imaging raise concerns about potential instabilities due to oxidation during illumination. This limitation may necessitate the development of more stable derivatives by substituting the central metal atom with Pd.[40,41] Therefore, it is important to establish if similar instabilities may occur for photoelectrochemical applications. Figure 3(c) shows the photocurrent transients for both TiO_2 nanotubes, which are known to be stable, and TiO_2 nanotubes modified with BChl *c*. A 60 s delay in the dark is permitted in order to allow the dark current to establish a steady state value. As TiO_2 itself is stable, the measurement for the nanotubes was only held for 120 s to establish a baseline photocurrent as a comparison before turning the light off. For the BChl *c* modified TiO_2 nanotubes, after an initial spike associated with equilibration to surface recombination,[42] the photocurrent transients reach a steady state with no sign of decay over the course of 14 min. This indicates that under these operating conditions, the BChl *c* modification is stable. Longer tests are needed to establish the stability of BChl *c* on time scales on the

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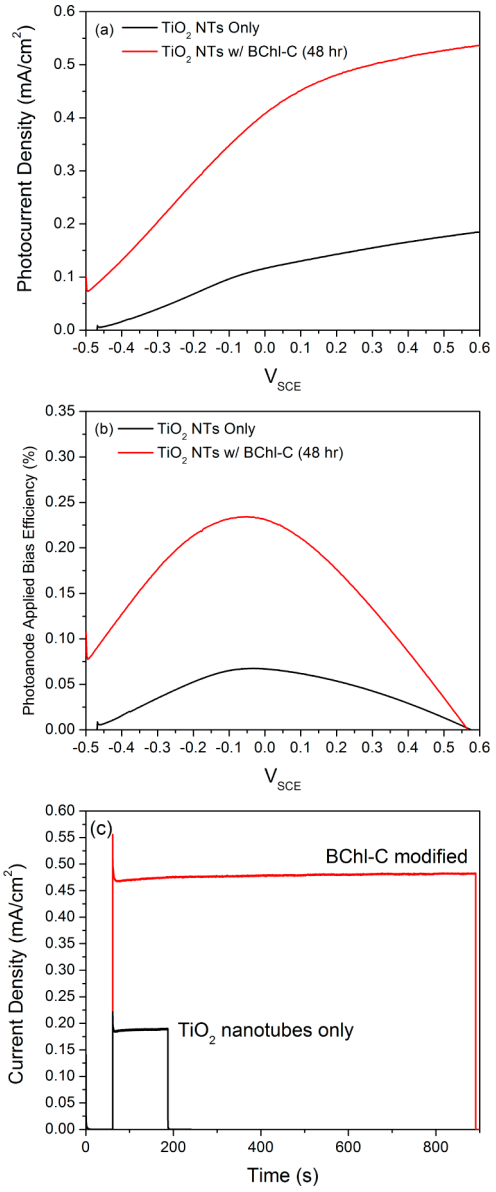

Figure 3. (a) LSV of TiO_2 nanotubes and BChl *c* modified TiO_2 nanotubes, (b) calculated photoanode efficiency of TiO_2 nanotubes as a function of potential, and (c) stability of TiO_2/BChl *c* photoanodes tested under simulated sunlight, showing no losses in photocurrent over the course of 14 min.

order of hours and days, which are more representative of the actual operating conditions of a photoelectrochemical solar cell.

These results serve as a first proof of concept that BChl *c* can be used as a visible light sensitizer when paired with TiO_2 nanotubes. Visible light photogenerated charge carriers in the BChl *c* aggregates can in fact be injected in TiO_2, and the stability of the configuration appears satisfactory. The main drawback is that the photocurrent efficiencies in the visible light range are below 1%. It is important to understand the origin of such low efficiency, specifically whether this may be due to the aggregation of BChl *c*, hindering charge collection, or low injection probability due to interface defects or perhaps electronic effects. The interface between the nanotubes and the BChl *c* is a likely source of charge trapping; the slow onset transients under visible light illumination in fact point to this as an area where the photocurrent conversion efficiencies may be improved. Both issues could be tackled by promoting the adsorption of mono- or multilayer adsorption of ordered BChl *c* assemblies, enabling control of the amount of BChl *c* deposited and fostering reproducible contacts at the interface. The molecular organization of the sensitizers has shown to be essential for exciton transport.[43] Functionalization of BChl *c* molecules to form mono- or multilayers on TiO_2 is therefore likely to strongly enhance their performance.

In summary, TiO_2 nanotubes have been successfully sensitized by BChl *c*. Photocurrent measurements under monochromatic light have demonstrated a photon-to-current conversion efficiency of 0.1% in the window of 600−800 nm, which coincides with the observed absorption peaks in the BChl *c* absorption spectra. BChl *c* aggregates were observed by SEM, their size increasing with longer adsorption time; this aggregation, coupled with strong trapping of photogenerated charges, resulted in a limited photocurrent efficiency. The better performance of the crude material indicates the lack of a need for purification, which potentially would reduce the complexity of fabrication of similar devices. The stability of BChl *c*/TiO_2 was tested under simulated sunlight, and the photocurrents were observed to be stable at least over the course of 14 min.

■ ASSOCIATED CONTENT

Supporting Information

Procedures for growing the bacteria precursors, extracting bacteriochlorophyll-c, and taking UV−vis spectra, along with the absorption spectrum obtained on BChl *c*. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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