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A NOVEL CHLOROPLASTMIMIC PHOTOVOLTAICS WITH FULL VISIBLE SPECTRUM OPERATION

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ABSTRACT

A novel and very simple chloroplastmimic photovoltaic scheme, in which water is photolyzed by a new photocatalyst fabricated by depositing a thin film of TiO_2 on an array of carbon nanotubes (CNT), has been made. Multiple reflections within the photocatalyst extend the optical response from the ultraviolet range to the full visible range. Hydrogen ions with various concentrations are separated by an artificial thylakoid membrane, resulting in a transmembrane chemiosmotic potential, generating ion-diffusion-induced electricity. Experimental results demonstrate that the proposed simple chloroplastmimic photovoltaics can produce a photocurrent directly from visible light.

1   INTRODUCTION

Chloroplasts are regarded as the most effective energy conversion plants of sunlight. Chloroplasts seize the energy of sunlight to produce the free energy stored in adenosine 5'-triphosphate (ATP) and nicotinamide adenine dinucleotide phosphate (NADP) via photosynthesis. Photosynthesis is an important biochemical process in which plants transform light energy from the sun into chemical energy. During photosynthesis, the ATP is synthesized by an ATP synthase enzyme by using the chemiosmotic potential across the thylakoid membranes of the chloroplasts. The hydrogen ions that are formed by the products of the photolysis of water by chlorophyll contribute to the transmembrane chemiosmotic potential.

The rate at which solar radiation reaches the earth's surface is 1,020 W/m². For centuries, human beings have attempted to mimic the conversion mechanisms of chloroplasts by harnessing the energy of sunlight. The conversion mechanism of the chloroplast represents a promising new energy resource. Conventional solar cells exploit the photovoltaic effect of semiconductors to produce electricity directly from sunlight. Despite the great major progress made over the last decade, the use of silicon-based solar cells remains more expensive than traditional electricity generation.

One promising approach for reducing costs even further involves dye-sensitized solar cells (DSSC) [1-4] that photo-sensitize wide-band-gap mesoporous oxide semiconductors. Michael Graetzel et al.[1] developed DSSC in 1991. The structure of a DSSC comprises of two electrodes and an electrolyte that contains iodide. One electrode is dye-absorbed nanoporous titanium dioxide (TiO_2) that is deposited on a transparent electrically conducting substrate – usually made of indium tin oxide (ITO). The other is only a transparent electrically conducting substrate. When sunlight passes through ITO, any dyes adsorbed on it are photo-excited. One of the electrons in the dye jumps from the valence band to the conduction band in TiO_2. The electron then diffuses across the porous film of TiO_2, arriving at ITO, and through the iodide-containing electrolyte, returning the oxidized dye molecules to their initial state. Since the DSSC uses the redox reaction of the electrolyte, it has been compared to the photosynthesis of chloroplasts. The performance of DSSC can be further improved using TiO_2 nanotube arrays, as demonstrated by recent works that water can be split using carbon-doped TiO_2 nanotube arrays [5-6].

This work presents a novel and very simple chloroplastmimic photovoltaic scheme. The novel photovoltaics generates electricity by ion diffusion. Like photosynthesis, artificial chlorophyll is adopted to photolyze water and thus generate hydrogen ions. Additionally an artificial thylakoid membrane is employed to separate hydrogen ions of various concentrations to establish a cross-membrane charismatic potential, generating ion-diffusion-induced electricity. An anodic aluminum oxide (AAO) membrane imitates the ion diffusion characteristic of a real cell membrane [7-9]. The water that is photolyzed by chlorophyll in chloroplasts is

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photolyzed by a combined TiO$_2$ and carbon nanotubes (CNT) [10-12] photocatalysis, shifting the absorption band of TiO$_2$ from the UV range (378 nm) to the visible spectrum, yielding a much broader absorption band. An electrochemical bath that employs an AAO membrane as the artificial thylakoid membrane to separate two vessels with a concentration gradient is constructed to measure the photocurrent of the proposed chloroplastmimic photovoltaics.

2 STRUCTURE OF THE CHLOROPLASTMIMIC PHOTOVOLTAICS

Figure 1 schematically depicts the structure of the proposed chloroplastmimic photovoltaics, including a water-containing electrochemical bath. Combined TiO$_2$ and CNT photocatalysis functions as artificial chlorophyll, and an AAO membrane serves as the artificial thylakoid membrane to separate the two vessels with a chemiosmotic potential. When visible light irradiates the artificial chlorophyll in one of the two vessels, the photolysis of water yields hydrogen ions and other free radicals. The hydrogen ions induce a cross-membrane chemiosmotic potential, which causes hydrogen ions to penetrate the artificial thylakoid membrane, generating diffusion current.
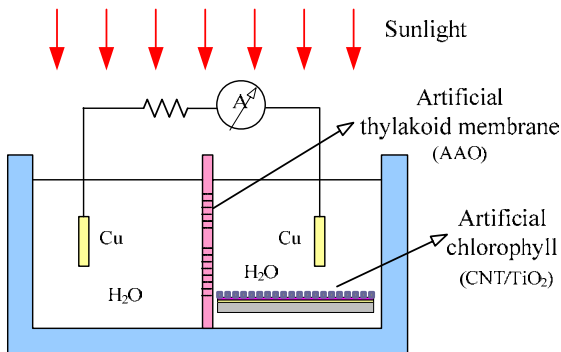
Figure 1. Proposed chloroplastmimic photovoltaics.

2.1 CNT/TiO$_2$ Nanostructure Assembly as the Artificial Chlorophyll

TiO$_2$ is a good photocatalyst under ultraviolet light. The strong oxidative potential of the positive holes oxidizes water to produce hydroxyl radicals. TiO$_2$ is an appropriate candidate for artificial chlorophyll. However, since only 4% of solar light falls in to the ultraviolet range, TiO$_2$ can only generate a small quantity of hydrogen ions, generating a transmembrane chemiosmotic potential, making water photolysis impractical. This work proposes a new artificial chlorophyll by depositing a thin film of TiO$_2$ on an array of CNTs. Multiple reflections occur between the surfaces of the TiO$_2$ film and the substrate, forming something of a light cavity. The new design effectively extends the optical response from the ultraviolet range to the full visible range.

The fabrication process of the combined TiO$_2$/CNT artificial chlorophyll is, (1) successively to deposit a 40 nm-thick titanium buffer layer and a 6 nm-thick nickel catalyst on the silicon substrate; (2) to grow a CNT array by microwave plasma-assisted chemical vapor deposition (CVD); (3) to deposit a 10 nm-thick layer of titanium, and (4) to dry-oxidize the top titanium layer to form titanium dioxide at 300 °C.

Figure 2 presents SEM image of the resulting CNT array. Figure 3 displays SEM images of the titanium thin film-covered CNT array.
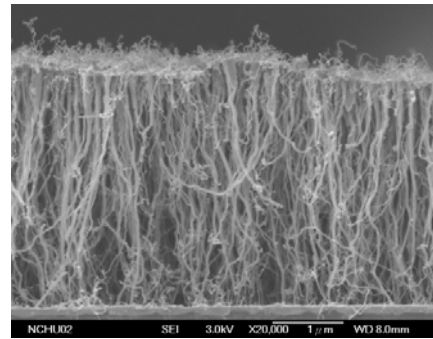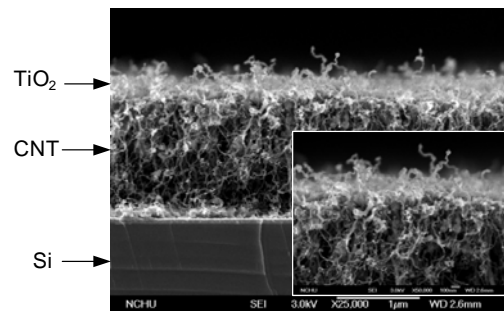
Figure 2. SEM image of CNT array

Figure 3. SEM image of CNT array covered with a TiO$_2$ film

2.2 The Artificial Thylakoid Membrane

The nanoporous AAO membrane is implemented to imitate the artificial thylakoid membrane. The pore diameter of the AAO membrane is about 50 nm. An electrochemical bath made of acryl with dimensions of 3.5 mm×2.5 mm×2.4 mm is made to examine the photocurrent. The AAO membrane is glued to the center of the bath to separate it into two smaller vessels across which is a chemiosmotic potential.

3 PHOTORESPONSE OF THE CHLOROPLASTMIMIC PHOTOVOLTAIC CELL

3.1 Optical absorption spectra of the CNT/TiO2 Artificial Chlorophyll

The first new development described herein is that of the CNT/TiO$_2$ nanostructure assembly, as artificial chlorophyll. The optical absorption spectra were obtained using a UV/Vis spectrophotometer in reflection mode to elucidate the light-harvesting characteristics of the CNT/TiO$_2$ assembly. For comparison, the absorption of a pure TiO$_2$ film deposited on an Si substrate was also measured. Figure 4 shows the absorption spectra of the pure TiO$_2$ film and the CNT/TiO$_2$ assembly. The TiO$_2$ film yields a strong UV absorption peak at λ = 335 nm, associated with the fundamental transition (valence band to conduction band) of TiO$_2$ with an energy gap of E_g= 3.2 eV. In contrast, the absorption of the CNT/TiO$_2$ assembly reveals two notable features. First, light absorption extends over the UV and visible ranges (250 - 850 nm); second, multiple absorption peaks are presented.
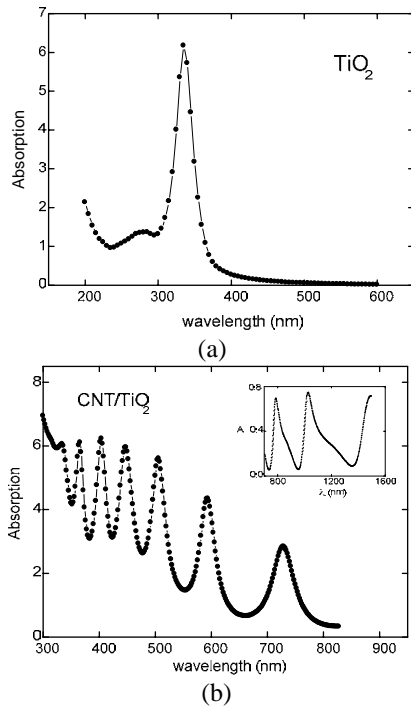
Figure 4. Optical absorption as a function of wavelength for (a) a pure TiO_2 film (b) the CNT/TiO_2 nanostructure assembly. (Inset) Absorption in the near-infrared region 0.75-1.6 μm .

Figure 5 plots the absorption of the CNT/TiO_2 assembly as a function of photon energy. The spectrum exhibits a periodic oscillation with a period of $\Delta E \approx 0.4$ eV. The oscillatory absorption can be interpreted as follows.
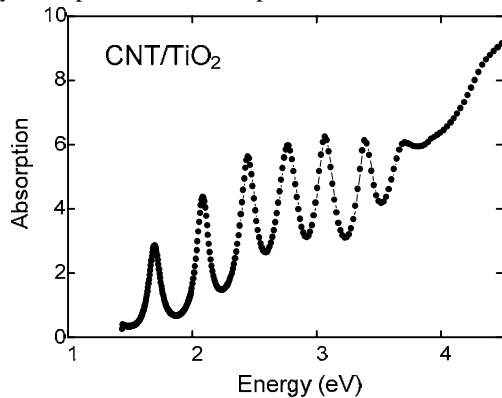

Figure 5. Optical absorption as a function of photon energy for CNT/TiO_2 assembly. The absorption is calculated from the equation $(1-R)^2/2R$, where R is the ratio of the reflected intensity of the sample to that of a reflectance standard.

Figure 6 schematically depicts the solar light that is incident on the assembly, which traverses first through the TiO_2 film; then through the CNT layer and finally through the Si substrate. The refractive indices of TiO_2 and Si in the visible range are $n_1(TiO_2) \approx 3$ and $n_2(Si) \approx 4$, respectively [13]. The packing density of the CNT layer is low. Therefore, the refractive index is assumed to equal that of air $n_0 = 1$. The reflectivity at the interface of two media is $R = ((n-n')/(n+n'))^2$, where n and n' are the refractive indices of the two media. The large mismatch between the refractive indices of the CNT and the TiO_2 film results in substantial reflection; the same phenomenon occurs at the Si/CNT interface. Consequently, multiple reflections occur between the surfaces of the Si and TiO_2 film. The superposition of the multiply-reflection beams yields an oscillatory absorption spectrum. The principle is similar to that of a Fabry-Perot interferometer. The oscillatory period between two parallel planes can be calculated by the equation $\Delta \nu = 1/2n_0 d$ where d is the thickness of the CNT layer and ν is the frequency in cm^{-1}. According to the SEM image in Fig. 3, $d \approx 1.5 \mu m = 1.5 \times 10^{-4}$ cm. Accordingly, $\Delta \nu = 3300$ cm^{-1} or, equivalently, $\Delta E \approx 0.41$ eV, which value agrees closely with that in Fig. 3. The inset in Figure 4(b) plots the absorption in the near-infrared region (0.7-1.5 μm). Oscillatory behavior is also observed, supporting further the claim that multiple reflections occur [14].
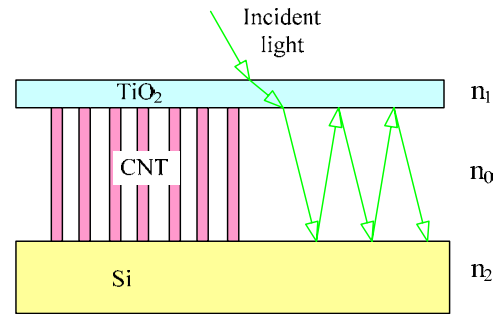

Figure 6. CNT/TiO_2 nanostructure assembly. Multiple reflections occur between surfaces of Si and TiO_2.

The benefit of the CNT/TiO_2 nanostructure assembly is that light that covers the full visible and some of the UV range can be produced without the use of dyes. The additional absorption in the near-infrared range also increases the absorption efficiency of solar cells, as reported in the literature[15].

3.2 Measurement of Photocurrent
An electrochemical system PARSTAT 2236 (Princeton Applied Research) is employed to examine the potency of the proposed chloroplastmimic photovoltaics. Visible light with a power of 500 W is used as the light source. The experiments are conducted in the dark, as the light source is alternately switched on and off. Figure 7 displays the experimentally measured photocurrent of the proposed chloroplastmimic photovoltaics. For comparison, the ion diffusion current of pure water and the photocurrent of photovoltaics using pure TiO_2 as the photocatalyst are also presented. The area of the pure TiO_2 film is 15mm×5mm and its thickness is 10nm. The thin film of the CNT/TiO_2 sample has the same dimensions as that of the pure TiO_2 sample and the height of the CNT array is 1.5 μm. The negative sign of the ion diffusion current of pure water is presumed to be associated with the conducting particles that are inherently present in the devices. The ion diffusion current of pure water can thus be regarded as the

reference point. Deviation from the reference point is associated with the effective photocurrent.
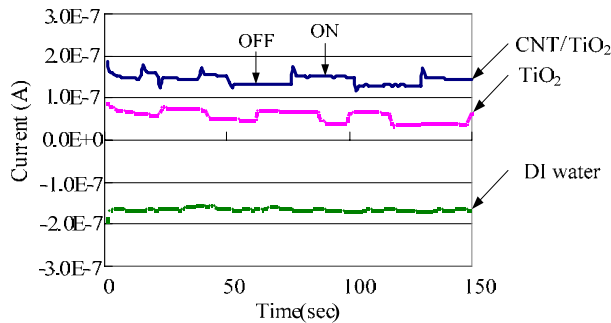

Figure 7. Photocurrent of chloroplastmimic photovoltaics with (a) TiO_2 (b) CNT/TiO_2 as artificial chlorophyll; the current of the DI water is the reference point. The current steps correspond to the light-on/light-off states.

Experimental results demonstrate that the proposed photovoltaics can effectively produce electricity when irradiated under visible light. The CNT/TiO_2 nanostructure assembly can generate almost 30% more of the amount of electricity generated by pure TiO_2. Since the ion diffusion-induced current is proportional to the concentration of the hydrolyzed hydrogen ions, the results also imply that the CNT/TiO_2 nanostructure assembly can harvest much more energy from sunlight than can be harvested by pure TiO_2 photocatalysis. The novel photocatalysis can be further implemented to generate hydrogen from sunlight efficiently.

4   CONCLUDING REMARKS

In summary, a new chloroplastmimic photovoltaic scheme based on nanotechnology was developed. The proposed chloroplastmimic photovoltaics utilize a combined TiO_2/CNT photocatalysis to mimic the function of the enzyme in a chloroplast, and an AAO membrane to imitate the ion diffusion characteristic of a real cell membrane. Experimental results reveal that the proposed simple chloroplastmimic photovoltaics can generate photocurrent directly from sunlight. The CNT/TiO_2 nanostructure assembly shifts the absorption spectrum of TiO_2 from the UV range to the visible light range, broadening the photoresponse. Therefore, it can harvest much more energy from sunlight than pure TiO_2 photocatalysis can. The novel photocatalysis is able to be implemented efficiently to generate hydrogen from sunlight.

Acknowledgment

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