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Fast formation of thin TiO$_x$ layer on titanium surface enabling a broadband light capture and fast charge carrier transfer

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HIGHLIGHTS

• Fast-formed thin film on Ti metals in 10 s (Ti10) and 60 s (Ti60).
• Ti10 and Ti60 showed broadband absorption in wavelengths of 250–2500 nm.
• The broadband absorption peaks can be tuned between 250 and 2500 nm.
• The charge carrier transfer rate showed a 10-time difference in maximum.

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- Broadband light absorption
- TiO$_x$ thin layer
- Anodic oxidation
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ABSTRACT

Improving light absorption and conversion ability is essential to improving the performance of photoelectrochemical (PEC) cells in converting and storing solar radiation into chemical energy. As part of this, realizing broadband light absorption in the wavelength of 250–2500 nm is promising to improve solar energy utilization. Previous studies have typically relied on noble metal functional materials to realize visible light harvesting over broadband light capture in PEC water splitting (WS) cells. Here, we report an electrochemical oxidation method to prepare thin TiO$_x$ layer on a Ti-foil surface. A nanostructured film is formed within 10–60 s with a tunable absorption range between 250 and 2500 nm, going beyond the 420 nm absorption edge of TiO$_2$. In addition to superior light capture ability, the film shows a 10-fold enhancement in the charge carrier transfer rate under AM 1.5 G light compared to that measured under dark conditions. The method proposed is simple, fast, and low-cost, and it has potential for large-area PEC cells with promoted charge carriers’ transfer.

1. Introduction

Solar energy is one of the most abundant sources of clean energy with major importance to mitigate climate change. The total solar energy incident on the Earth is around $3.0 \times 10^{24}$ J (J) per year, which is 5000 times higher than the global primary energy consumption in 2021,

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around 5.95 × 10^20 J [1,2]. It is obvious that solar energy is one of the most attractive renewable energy sources to be used to address the energy crisis and achieve net zero emissions. However, the major concerns hindering solar energy usage are the light-capture ability of materials and the conversion efficiency of devices.

Possible strategies to overcome the major challenges in effectively using solar energy is to improve the materials’ light-capture ability including: Constructing hetero/homo/tandem junctions and core-shell structures, doping levels with metal/non-metal elements, incorporating single atoms, realizing of localized surface plasmonic resonance (LSPR) [3–5]. For instance, using a hydrogenation method to synthesize disordered shell-crystal core structure realized the so-called black TiO_2 giving a major improvement in broadening the light absorption range from ca. 400–1300 nm together with enhanced intensity, meanwhile, yielding an excellent hydrogen (H_2) production rate in the photocatalytic water splitting (WS) test under simulated solar light [6].

More specifically, in the photoelectrochemical (PEC) WS cells, numerous attempts have been devoted to improving the absorption ability of materials in the visible light (Vis, 400–780 nm) range to a broader wavelength range from ultraviolet (UV) to near-infrared light (NIR), i.e. 250–2500 nm [7]. That can be explained by the theoretical conversion efficiency at the absorption edge of 800 nm, ca. 32% at maximum. While, the spectrum of natural solar light (air mass 1.5 G) consists of ~5% UV (250–400 nm), ~43% Vis (400–780 nm) and ~52% NIR (780–2500 nm) [8,9]. If the NIR light absorption is neglected, half incident solar energy will be lost in other types (e.g., heat energy). Therefore, materials and technologies to realize broadband absorption in the range of 250–2500 nm is of high importance in efficient capture and usage of photons, in particular to improve the conversion efficiency of solar radiation to chemicals [10–12].

To realize broadband absorption, both periodic structures, such as nm-sized nanocavities and nanotubes and non-periodic structures have been investigated [10]. Apart from structures, modifying the samples’ surface with metallic elements (Au, Ag and Cu) also can achieve broadband absorption via LSPR [13–15]. For example, Tesler et al. reported on the impact of Au, Ag and Cu nanoparticles (NPs)/Ti metal/-TiO_2 film (thickness, 20–500 nm) on light absorption and conversion, and PECWPS performance, demonstrating that Cu and Ag NPs giving a 3-fold higher enhancement than that of Au NPs [12].

Nitridation of TiO_2 can achieve broadband absorption in the wavelength of 250–2500 nm [16]. Without nitridation, TiO_2 is only a UV-driven semiconductor with an absorption edge at ca. 420 nm [17]. However, TiO_2 has been widely applied in solar energy conversion and storage systems due to its advantageous properties such as high refractive index, non-toxicity, chemical stability and low cost [18–20]. To realize the broadband absorption of TiO_2 or titanium oxide, note as TiO_x, both structure and LSPR can be considered as effective strategies. Using metallic NPs such as Au, Pt and Ag has been investigated [12,21–23]. Considering the high cost of noble Au and Pt, transition metals such as Ti are promising to realize LSPR for a high absorbance [24]. In addition, the work function of Ti (4.33 eV) is lower than both Au (5.1 eV) and Pt (5.6 eV), which enables a lower Schottky barrier of metal/-semiconductor interface, Ti/TiO_x interface, for efficient hot electron transfer [25–28]. Fabrication of TiO_x on Ti metal is a direct way to form Ti/TiO_x interface. The anodic growth of TiO_x on a Ti metal substrate has advantages of flexibility, high electrical conductivity, high-specific strength and easy-tailoring [29,30]. Meanwhile, the Ti-metal functions as a good conducting interfacial substrate and a good conductor of electrons. When the thickness of the TiO_x thin layer is tens to hundred nm, it can work as electron collector in a PEC WS cell [31]. However, investigations on Ti/TiO_x for broadband absorption in the wavelength of 250–2500 nm are handful in PEC cells.

In this work, an electrochemical oxidation method is used to demonstrate the fast formation of Ti/TiO_x producing a broadband light absorption in the wavelength range of 250–2500 nm. The improved solar light absorption, tuned absorption peaks, enhanced the mobility of charge carrier transfer and PEC WS performance are demonstrated. The role of surface roughness on light absorption and carrier transfer on Ti/TiO_x interface is discussed.

2. Experimental methods

2.1. Chemicals

Ti foils with 99.5% purity and thickness of 0.2 mm, were acquired from Beijing ZhongGuo Advanced Material Technology Co., Ltd. Pt foil electrode with purity >99.99% was purchased from Tianjin Aida Hengsheng Technology Development Co., Ltd. Ammonium fluoride (NH_4F), ACS reagent with purity ≥ 98% and anhydrous 99.8% ethanol glycol (EG, HOCH_2CH_2OH) were purchased from Sigma Aldrich. Sodium hydroxide (NaOH) was purchased from Merck KGaA. All the chemicals were used without further treatment.

2.2. Preparation of samples

The preparation process has been reported in detail in our previous work [30]. Two samples, noted as Ti10 and Ti60, were prepared with anodict growth technique using a DC supply (E3647A, Keysight) of 60 V at ambient condition in a mixed organic electrolyte of 0.3 wt% NH_4F and 6.0 vol% deionized H_2O in EG for 10 s and 60 s followed with a post-annealing step at 450 °C for 30 min with a heating rate of 3 °C/min in a muffle oven in air. When Ti10 and Ti60 were tested under light (L) illumination, they were noted as Ti10-L and Ti60-L. While Ti10 and Ti60 were tested under dark (D) condition, they were noted as Ti10-D and Ti60-D. Here, the commercial Ti foil is noted as Ti0.

2.3. Characterisation

Due to the optically opaque nature of the samples, the optical properties of the nanostructured surface were characterized with a reflectance (R) measurement using a Cary 5000 (Agilent, USA) UV–Vis–NIR spectrophotometer equipped with a DRA-2500 integrating sphere. The absorbance (Abs) of the samples was derived from Abs = log10 (J*), assuming T (transmittance) = 0. The morphology was observed with a Dual Beam focused ion beam-scanning electron microscope (FIB-SEM, Jeol 4700F). The Atomic Force Microscopy (AFM) topographic images were measured with a Bruker Dimension Icon AFM in peak-force tapping mode. Electrochemical Impedance Spectroscopy (EIS) was acquired in the frequency range of 100 kHz to 10 mHz using an AC amplitude of 20 mV signal at open circuit potential (OCP) under both light and dark conditions.

2.4. Photoelectrochemical tests

Linear sweep voltammetry (LSV) curves were recorded with a scan rate of 10 mV/s in simulated sun light source from a Xenon lamp (94011A-ES, LCS-100, Newport). The measured potential versus (vs.) Ag/AgCl electrode was converted to that versus reversible hydrogen electrode (RHE) with the Nernst equation [32]:

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{pH} + 0.196 \] (1)

The applied bias photon-to-current efficiency (ABPE) was calculated with the following equation:

\[ \text{ABPE} (%) = J \times (1.23 - V_{\text{RHE}})/P \] (2)

where J is the photocurrent density (mA/cm^2) at the potential and P is the incident light intensity of 100 mW/cm^2.
3. Results

3.1. Optical properties

Fig. 1 (a) gives an illustration of the rapid (10 s and 60 s) electrochemical growth of a thin layer on Ti0 (commercial Ti), denoted as Ti10 and Ti60, respectively. When the electrochemical growth time is 10 s, the film of Ti10 shows a blue color appearance (Fig. 1 (b)), whereas the surface of Ti60 shows a yellow-grey color. The UV–Vis–NIR reflectance spectra of Ti0, Ti10, and Ti60 were recorded in the wavelength range of 250–2500 nm as shown in Fig. 1 (c) as a function of the photon energy following the relation $E_g = 1240/\lambda$, eV [33]. The solar spectrum is plotted in the same figure. Over the whole test range, the light absorption intensities of both Ti10 and Ti60 are much stronger than that of Ti0. A huge absorption difference is seen in the Vis-NIR range. Both Ti10 and Ti60 show multi-band absorption in Fig. 1 (c). The Ti10 has 3 interference fringes at $\lambda = 331, 489, \text{ and } 1303 \text{ nm}$, respectively. On the other hand, the Ti60 sample has 4 interference fringes at $\lambda = 336, 441, 605, \text{ and } 2017 \text{ nm}$, respectively. The observed optical phenomena that span from UV to NIR originate from both intraband and interband transitions, which provide an optical readout of the time-dependent optical properties [34]. The optical properties of the samples represent

![Fig. 1.](image1)

![Fig. 2.](image2)
a systematic variation of the chemical composition and atomic structure. The enhanced absorption intensities in the whole test range can be attributed to (i) different particle sizes and size distribution of TiO\textsubscript{x} on the surfaces of Ti10 and Ti60; (ii) LSPR effect from the Ti metal that favors the separation of photo-induced charge carrier and accelerates the electron transfer; and (iii) Mie scattering from complex structures originating from different diameters of NPs, film thickness, and refractive index of Ti and TiO\textsubscript{x} \cite{35}. Fig. 1 (d) shows the absorbance of both Ti10 and Ti60 in the UV range of 250–380 nm. The absorption peak of Ti10 locates at 331 nm, and the absorption peak of Ti60 has a 5 nm red shift. As mentioned above, the appearance of Ti10 and Ti60 are different, which is due to the difference in the visible range absorption as shown in Fig. 1 (e). Typically, the color of the anodic treated surface corresponds to the reflectance of the sample \cite{36}. In Fig. 1 (e), Ti10 shows one absorption peak at 489 nm corresponding to light blue color (#00fbff), which is also in agreement with the appearance of the Ti10 sample. The Ti60 sample has two absorption peaks locating at 441 and 605 nm, respectively, which corresponds to the deep blue (#000bff) and orange color (#ffad00). The intensity of the peak locating at 605 nm is stronger than that at 441 nm, meaning that the color of the sample shifts from blue to orange direction \cite{36}. Thus, the interference color is near the soil color, yellow to yellow-brown, which is also in agreement with the appearance of Ti60. In an overview, it is noted that Ti60 has a higher absorptance intensity than Ti10 in the Vis range. More specifically, the light absorption intensity of Ti60 in the wavelength of 410–700 nm is higher than the highest absorption peak of Ti10 at 441 nm in Fig. 1 (e). Fig. 1 (f) shows the broadband absorption of both Ti10 and Ti60 in the NIR range attributed to the micro-nano structure to capture photons and existing of the Ti, which will discussed later.

### 3.2. Surface

SEM top views of the Ti10 and Ti60 samples are shown in Fig. 2 (a) and (b). Both the film thickness and the top-surface layer morphology affect the optical properties, viz. reflectance or transmittance, which further influence their performance. The NPs are randomly distributed with sizes 30–150 nm. The NPs are more uniform with a smaller size in Ti60 than those in Ti10. The formation of samples with different particle sizes and size distribution are illustrated in Fig. 2 (c). Besides the morphology of the top surface, the film thickness of the samples is important to the electro-optical properties. Similar to the self-formed native passivation layer on aluminum metals, an oxide layer forms on the Ti surface when it is exposed to air, viz., a passivation layer. As for Ti0, the thickness of the passivation layer is around 1.2 nm, which may continuously grow to a thickness of ca. 25 nm in 4 years \cite{37}. Furthermore, as reported by Hou et al., the film thickness of the Ti10 was ca. 70 nm and that of the Ti60 was ca. 90 nm \cite{30}. The AFM images of both samples shown in Fig. 2(d–e) have been leveled by zero order polynomial vertical row alignment using Gwyddion \cite{38}. Smooth surface reflects heavily than rough surface, which is the base of antireflection \cite{19}. Fig. 2 (f) shows the surface roughness of Ti10 and Ti60, with an average of 66 and 37 nm, respectively. The film thickness of the samples and the interference fringes correlated in Equation (3) \cite{34} can mostly explain the relationship between themorphologies of the samples and the UV–Vis–NIR measurements, though the result in Fig. S1 does not support disappearance of the interference fringes at a thickness larger than 2 \textmu m.

\[
2\left(\frac{1}{\lambda_1} + \frac{1}{\lambda_2}\right)\frac{n}{\cos \phi} d = 1
\]

where \(n\) is the refractive index of the film, \(\phi\) the angle of refraction, \(d\) is the film thickness, \(\lambda_1\) and \(\lambda_2\) are two consecutive peaks or valley wavelengths.
3.3. Charge carrier transfer: Electrochemical impedance spectroscopy analysis

EIS results shown in Fig. 3 are obtained at OCP in 1 M NaOH solution to monitor the charge carrier barriers between interfaces and are further used to analyze the structural and electronic properties of Ti10 and Ti60 under both light (Ti10-L and Ti60-L) and dark (Ti10-D and Ti60-D) conditions [39]. The EIS curves are presented as Nyquist plots including the overview plots and the zoom-in parts recorded under light and dark conditions. The charge carrier barriers of the samples under dark and light conditions can be deduced from the radii of the arcs of the Nyquist plots [21]. The sequence of the radii of the four arcs is Ti60-L < Ti10-L < Ti60-D ≪ Ti10-D. The result indicates that both Ti10 and Ti60 are photon-sensitive materials to realize the photoinduced charge separation and transfer, even though the XRD patterns of both samples only have peaks of hexagonal closely packed Ti metal α-phase (JCPDS no. 44–1294) [30]. Monitoring the pure electrical properties in dark conditions, a 5-fold difference of charge carrier resistances were found in the kinetically controlled region between Ti10 (ca. 900 Ohm) and Ti60 (ca. 4400 Ohm). Furthermore, the Ti60-D sample exhibits two regions, the semicircle (circular arc) in the high frequency range relates to the kinetics and the arc in the low frequency range indicates diffusion controlled electron transfer [40, 41]. This work suggests the possibility to enhance the electrodes for a fast charge carrier transfer. Electrical conductivity has a direct effect on the performance of the material in electrical devices, e.g., a highly reactive electrode requires a high electrical conductivity.

3.4. Photoelectrochemical water splitting performance

In Fig. 4 (a), Ti10 and Ti60 are employed as the photoanode in a PEC WS cell to record the linear sweep voltammetry (LSV) curves in the range of 0–1.8 V_{RHE}. The photocurrent density values from the LSV curves offer evidence for both the electrical properties of the charge transfer and the solar energy capture capability. The onset potential of both samples is nearly at the same location at around 0.20 V_{RHE}, which is lower than that of the Fe₂O₃ semiconductor and its composites (0.40–0.80 V_{RHE}) [42,43], but similar to anodic TiO₂ nanotube samples and remains comparable with the most promising semiconductor BiVO₄ (0.20–0.40 V_{RHE}) [44–46]. At 1.23 V_{RHE}, i.e., zero overpotential for oxygen evolution reaction, the photocurrent densities of Ti10 and Ti60 are 0.55 and 0.65 mA/cm², respectively. Ti60 has a much higher photocurrent conversion ability due to its higher light absorption and lower charge carrier resistance under light illumination. The ratio of both the photocurrent density at 1.23 V_{RHE} and the radius of Nyquist plot between the Ti10 and Ti60 under light are almost equal to 0.84. This indicates that the charge carrier barrier directly affects the device’s performance. The solar conversion efficiency of the PEC WS was also evaluated by computing the ABPE% of samples under light conditions, as shown in Fig. 4 (c). The highest ABPE% values of Ti10 and Ti60 are 0.24% and 0.28%, respectively. In comparison to Ti10, Ti60 has a cathodic shift of around 0.04 V_{RHE} at the corresponding highest ABPE% value. These results suggest the possibility to develop a large-area, low-cost and broadband light absorption surface.

4. Discussion

4.1. Surface roughness

In nature, it is obvious that the reflection of light from mirror surface (i.e. ice) is stronger than that from a sand area (rough surface) due to the difference of the surface roughness. That has already well imitated to make a rough surface to reduce the sunlight loss in the solar energy conversion and storage systems, such as solar cells, aerospace, aircraft,
4.2. Ti/TiO$_2$

The observed optical phenomena span from UV to NIR and include interband transitions, also representing a systematic variation of chemical composition and atomic structure, which provide an optical readout of the anodization time-dependent optical properties. As introduced in Fig. 1, both samples showed absorption peaks in UV, Vis and NIR. The sequence of the peak intensity ($P_i$) of the of Ti10 sample is $P_i$ (1303 nm, NIR) > $P_i$ (331 nm, UV) > $P_i$ (489 nm, Vis), whereas the sequence of $P_i$ of the Ti60 is $P_i$ (2017 nm, NIR) > $P_i$ (605 nm, Vis) > $P_i$ (441 nm, Vis) > $P_i$ (336 nm, UV).

In Fig. 6, the absorbed photons from UV, Vis and NIR excite electrons to the conduction band (CB) and transfer among surface and interface to finish the reduction and oxidation of water. The Ti metal with the high-imaginary-part-permittivity can reach a broadband absorption by the intrinsic absorption without enhanced magnetic resonance [49]. Besides, the intrinsic absorption properties of metal can also function as a simple-structure absorber with the broadband absorption ability. The fast formed layer in Fig. 6 is similar to the function of NPs on the mirror to contribute to multiple-band light harvesting and enhanced photocurrent density [12]. The harvested photons can assist in enriching the charge carrier density by continuously accelerating the electron transport speed between metal and semiconductor. The EIS of Ti60 gives a 10-time enhancement in the rate of the charge carrier transfer over Ti10 in aqueous solution under dark conditions. In addition, the Ti metal also has excellent corrosion resistance due to the spontaneous formation of a 2–7 nm thick oxide layer in air which is of importance in industry application [36,50]. Furthermore, the broadband absorption of the Ti/TiO$_2$ is willing to be carried out and reported in other environmentally benign electrolytes (such as NaCl solution or sea water) rather than the 1 M NaOH electrolyte utilized in this work.

5. Conclusion

In summary, an electrochemical oxidation method was used to form a thin layer on a flexible Ti metal substrate in very short time interval of 10 and 60 s. The enhanced UV–Vis–NIR absorption of Ti10 and Ti60 exceeds the absorption limit of the traditional bulk semiconductor material. The Ti10 has 3 interference fringes at $\lambda = 332, 493,$ and 1302 nm, whereas Ti60 has 4 interference fringes at $\lambda = 335, 440, 604,$ and 1992 nm, respectively. The surfaces of Ti10 and Ti60 are covered by randomly distributed Ti–O based particles with diameters from ca. 30–150 nm. The difference of the EIS results recorded under both dark and light conditions reveals that the electrochemical oxidation method creates photon sensitivity materials. The resistances of the samples under both light and dark conditions follows Ti60-$L$ < Ti10-$L$ < Ti60-$D$ < Ti10-$D$. The performance of the electrode at 1.23 V$_{\text{RHE}}$ under light is consistent with the ratio of the radius in Nyquist plots for Ti10 and Ti60. Our results demonstrate a new approach towards the development of fast and cost-efficient electrode for efficient solar radiation capture in the UV–Vis–NIR range.

Notes

The authors declare no competing financial interest.

CRediT authorship contribution statement

Xuelan Hou: Methodology, Investigation, Visualization, Data curation, Writing – original draft. Hang Zhang: Visualization, Writing – review & editing. Yongdan Li: Writing - review & editing. Peter D. Lund: Methodology, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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