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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

### G R A P H I C A L A B S T R A C T

Photon energy/ bandgap (eV)

- 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.

### ABSTRACT

500

1000

1500

Wavelength (nm)

2000

2500

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<sub>x</sub> 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<sub>2</sub>. 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

ARTICLE INFO

Broadband light absorption

Photoelectrochemcial cell

Keywords:

TiO<sub>x</sub> thin layer

Anodic oxidation

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  $\times$  10<sup>20</sup> 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 hydrogeneration method to synthesize disordered shell-crystal core structure realized the so-called black TiO<sub>2</sub> 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<sub>2</sub>) 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<sub>2</sub> film (thickness, 20–500 nm) on light absorption and conversion, and PECWS performance, demonstrating that Cu and Ag NPs giving a 3-fold higher enhancement than that of Au NPs [12].

Nitridation of TiO<sub>2</sub> can achieve broadband absorption in the wavelength of 250-2500 nm [16]. Without nitridation, TiO<sub>2</sub> is only a UV-driven semiconductor with an absorption edge at *ca.* 420 nm [17]. However, TiO<sub>2</sub> 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<sub>2</sub> or titanium oxide, note as TiO<sub>x</sub>, 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/TiOx interface, for efficient hot electron transfer [25–28]. Fabrication of  $TiO_x$  on Ti metal is a direct way to form Ti/TiO<sub>x</sub> interface. The anodic growth of TiO<sub>x</sub> 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 an underlying reflective substrate and a good conductor of electrons. When the thickness of the TiO<sub>x</sub> thin layer is tens to hundred nm, it can work as electron collector in a PEC WS cell [31]. However, investigations on Ti/TiOx 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<sub>x</sub> 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 Zhongnuo 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<sub>4</sub>F), ACS reagent with purity  $\geq$  98% and anhydrous 99.8% ethanol glycol (EG, HOCH<sub>2</sub>CH<sub>2</sub>OH) 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 anodic growth technique using a DC supply (E3647A, Keysight) of 60 V at ambient condition in a mixed organic electrolyte of 0.3 wt% NH<sub>4</sub>F and 6.0 vol% deionized H<sub>2</sub>O 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 Ti0.

### 2.3. Characterization

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 absorptance (Abs) of the samples was derived from Abs =  $\log_{10} (\frac{1}{R})$ , 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]:

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + 0.196 \tag{1}$$

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

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

where *J* is the photocurrent density (mA/cm<sup>2</sup>) at the potential and *P* is the incident light intensity of 100 mW/cm<sup>2</sup>.



Fig. 1. (a) Illustration of the electrochemical growth cell. (b) Photos of Ti10 and Ti60 sample [30]. (c) UV–Vis–NIR diffuse reflectance (DR) spectra of three samples Ti0 (commercial Ti), Ti10 (Ti0 was treated for 10 s), Ti60 (Ti0 was treated for 60 s) and AM 1.5 G (d–f) details of the DRS of Ti10 and Ti60 in (d) UV range, (e) Vis range, and (f) NIR range.

### 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 foil), 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, and 1303 nm, respectively. On the other hand, the Ti60 sample has 4 interference fringes at  $\lambda = 336$ , 441, 605, and 2017 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. 2.** SEM micrographs of the top view of the samples (a) Ti10 and (b) Ti60. (c) Scheme of the formation of Ti10 and Ti60 with different particle sizes and distribution. AFM characterization of surface morphologies of samples (d) Ti10 and (e) Ti60; (f) cross-sectional profiles of the two samples, at positions indicated by white lines in (d) and (e). Scale bars for (d) and (e) are 2 μm.



Fig. 3. EIS presented as Nyquist plots (a) Ti10 and Ti60 under simulated light condition (AM 1.5G, 100  $W/cm^2$ ) in 1 M NaOH aqueous solution, (a1) zoom-in of marked area in Fig. 3 (a); (b) Ti10 and Ti60 under dark condition in 1 M NaOH aqueous solution, and (b1) zoom-in of marked area of in Fig. 3 (b).

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<sub>x</sub> 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<sub>x</sub> [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 [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 [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 [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 [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 [38]. Smooth surface reflects heavily than rough surface, which is the base of antireflection [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) [34] can mostly explain the relationship between the morphologies 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 µm.

$$2\left(\frac{1}{\lambda 1} - \frac{1}{\lambda 2}\right)n(\cos\phi')d = 1$$
(3)

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.



Fig. 4. (a) LSV curves of the Ti10 and Ti60 samples at a scan rate of 10 mV/s in 1 M NaOH under dark and AM 1.5 G simulated light (100 mW/cm<sup>2</sup>) conditions. (b) Pure light output deduced from (a). (c) ABPE% curves derived from (b).

## 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  $\ll$  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<sub>RHE</sub>. 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 Fe<sub>2</sub>O<sub>3</sub> semiconductor and its composites (0.40–0.80 V<sub>RHE</sub>) [42,43], but similar to anodic TiO<sub>2</sub> nanotube samples and remains comparable with the most promising semiconductor BiVO<sub>4</sub> (0.20-0.40 V<sub>RHE</sub>) [44-46]. At 1.23 V<sub>RHE</sub>, i.e., zero overpotential for oxygen evolution reaction, the photocurrent densities of Ti10 and Ti60 are 0.55 and 0.65 mA/cm<sup>2</sup>, respectively. Ti60 has a much higher photoconversion 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  $V_{\text{RHE}}$  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,



Fig. 5. Scheme of incident light reflection: Mirror surface and rough surface.

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,



Fig. 6. Light absorption on the  $Ti/TiO_x$  surface and the electrons transport.

and other defensive machines [24,48,49]. Enhancing light absorption through reducing reflection can be achieved by techniques such as surface texturing, creating micro-nano structures and thin film coatings. For example, using micro-nano composite structures have been observed to have extended absorption range over bulk material with enhanced photon coupling efficiency [35,47]. As shown in Fig. 5, the displayed roughness surface is contributed to the NPs or cavities with different sizes. The different particle sizes and those random distributions on the surface can further absorb reflected light and improve solar light capture. Furthermore, the different NPs sizes are consistent with the absorption range [47,48]. It is also widely acceptable that surface roughness can also affect surface temperature through light absorption. However,the effects from structure (roughness) on the charge carrier transport in an electrochemical device has received less attention.

### 4.2. Ti/TiO<sub>x</sub>

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 (*Pi*) of the of Ti10 sample is *Pi* (1303 nm, NIR) > *Pi* (331 nm, UV)> *Pi* (489 nm, Vis), whereas the sequence of *Pi* of the Ti60 is *Pi* (2017 nm, NIR) > *Pi* (605 nm, Vis)> *Pi* (441 nm, Vis) > *Pi* (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 highimaginary-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

 $Ti/TiO_x$  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  $V_{RHE}$  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 radiatoion 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.

### Data availability

The data that has been used is confidential.

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### Appendix A. Supplementary data

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### References

- Z. Chen, X. Yiliang, Z. Hongxia, G. Yujie, Z. Xiongwen, Optimal design and performance assessment for a solar powered electricity, heating and hydrogen integrated energy system, Energy 262 (2023), 125453.
- [2] BP's Statistical Review of World Energy 2022, 2022.
- [3] R. Asahi, T. Morikawa, H. Irie, T. Ohwaki, Nitrogen-doped titanium dioxide as visible-light-sensitive photocatalyst: designs, developments, and prospects, Chem. Rev. 114 (2014) 9824–9852.
- [4] W. Li, A. Elzatahry, D. Aldhayan, D. Zhao, Core-shell structured titanium dioxide nanomaterials for solar energy utilization, Chem. Soc. Rev. 47 (2018) 8203–8237.
- [5] Y. Chen, W. Zheng, S. Murcia-López, F. Lv, J.R. Morante, L. Vayssieres, C. Burda, Light management in photoelectrochemical water splitting – from materials to device engineering, J. Mater. Chem. C 9 (2021) 3726–3748.
- [6] X.B. Chen, L. Liu, P.Y. Yu, S.S. Mao, Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals, Science 331 (2011) 746–750.
- [7] M. Jia, Q. Liu, W. Xiong, Z. Yang, C. Zhang, D. Wang, Y. Xiang, H. Peng, J. Tong, J. Cao, H. Xu, Ti<sup>3+</sup> self-doped TiO<sub>2</sub> nanotubes photoelectrode decorated with Ar-Fe<sub>2</sub>O<sub>3</sub> derived from MIL-100(Fe): enhanced photo-electrocatalytic performance for antibiotic degradation, Appl. Catal. B Environ. 310 (2022), 121344.
- [8] S.M. Schieke, Peter Schroeder, Krutmann Jean, Cutaneous effects of infrared radiation: from clinical observations to molecular response mechanisms, Photodermatol. Photoimmunol. Photomed. 19 (2003) 228–234.
- [9] D. Barolet, F. Christiaens, M.R. Hamblin, Infrared and skin: friend or foe, J. Photochem. Photobiol., B 155 (2016) 78–85.
- [10] L. Mascaretti, A. Schirato, R. Zbořil, Š. Kment, P. Schmuki, A. Alabastri, A. Naldoni, Solar steam generation on scalable ultrathin thermoplasmonic TiN nanocavity arrays, Nano Energy 83 (2021), 105828.
- [11] A.S. Rana, M. Zubair, Y. Chen, Z. Wang, J. Deng, M.T.S. Chani, A. Danner, J. Teng, M.Q. Mehmood, Broadband solar absorption by chromium metasurface for highly efficient solar thermophotovoltaic systems, Renew. Sustain. Energy Rev. 171 (2023), 113005.
- [12] A.B. Tesler, T. Sannomiya, S. Hejazi, R. Mohammadi, N. Vogel, M. Altomare, P. Schmuki, Metallic nanoparticle-on-mirror: multiple-band light harvesting and efficient photocurrent generation under visible light irradiation, Nano Energy 90 (2021), 106609.
- [13] M. Torras, P. Molet, L. Soler, J. Llorca, A. Roig, A. Mihi, Au/TiO<sub>2</sub> 2D-photonic crystals as UV–Visible photocatalysts for H<sub>2</sub> Production, Adv. Energy Mater. 12 (2021), 2103733.
- [14] L. Mascaretti, A. Dutta, S. Kment, V.M. Shalaev, A. Boltasseva, R. Zboril, A. Naldoni, Plasmon-enhanced photoelectrochemical watersplitting for efficient renewable energy storage, Adv. Mater. 31 (2019), e1805513.
- [15] Z.J. Zhao, S.H. Hwang, S. Jeon, B. Hwang, J.Y. Jung, J. Lee, S.H. Park, J.H. Jeong, Three-dimensional plasmonic Ag/TiO<sub>2</sub> nanocomposite architectures on flexible substrates for visible-light photocatalytic activity, Sci. Rep. 7 (2017) 8915.
- [16] B.R. Bricchi, L. Mascaretti, S. Garattoni, M. Mazza, M. Ghidelli, A. Naldoni, A. Li Bassi, Nanoporous titanium (oxy)nitride films as broadband solar absorbers, ACS Appl. Mater. Interfaces 14 (2022) 18453–18463.
- [17] M.M. Rashid, B. Simončič, B. Tomšič, Recent advances in TiO<sub>2</sub>-functionalized textile surfaces, Surface. Interfac. 22 (2021), 100890.
- [18] J. Cai, J. Ye, S. Chen, X. Zhao, D. Zhang, S. Chen, Y. Ma, S. Jin, L. Qi, Self-cleaning, broadband and quasi-omnidirectional antireflective structures based on mesocrystalline rutile TiO<sub>2</sub> nanorod arrays, Energy Environ. Sci. 5 (2012) 7575.
- [19] L. Yao, J. He, Recent progress in antireflection and self-cleaning technology from surface engineering to functional surfaces, Prog. Mater. Sci. 61 (2014) 94–143.
- [20] C. Moon, B. Seger, P.C.K. Vesborg, O. Hansen, I. Chorkendorff, Wireless photoelectrochemical water splitting using triple-junction solar cell protected by TiO<sub>2</sub>, Cell Rep. Phys. Sci. 1 (2020), 100261.
- [21] X. Hou, K. Aitola, H. Jiang, P.D. Lund, Y. Li, Reduced TiO<sub>2</sub> nanotube array as an excellent cathode for hydrogen evolution reaction in alkaline solution, Catal. Today 402 (2022) 3–9.
- [22] X.D. Gao, G.T. Fei, S.H. Xu, B.N. Zhong, H.M. Ouyang, X.H. Li, L.D. Zhang, Porous Ag/TiO<sub>2</sub>-Schottky-diode based plasmonic hot-electron photodetector with high detectivity and fast response, Nanophotonics 8 (2019) 1247–1254.

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- [23] C. Lee, Y. Park, J.Y. Park, Hot electrons generated by intraband and interband transition detected using a plasmonic Cu/TiO<sub>2</sub> nanodiode, RSC Adv. 9 (2019) 18371–18376.
- [24] F. Ding, J. Dai, Y. Chen, J. Zhu, Y. Jin, S.I. Bozhevolnyi, Broadband near-infrared metamaterial absorbers utilizing highly lossy metals, Sci. Rep. 6 (2016), 39445.
- [25] F. Li, L. Zhang, S. Wu, Z. Li, Y. Wang, X. Liu, Au nanoparticles decorated ZnO nanoarrays with enhanced electron field emission and optical absorption properties, Mater. Lett. 145 (2015) 209–211.
- [26] Y. Magari, H. Makino, S. Hashimoto, M. Furuta, Origin of work function engineering of silver oxide for an In–Ga–Zn–O Schottky diode, Appl. Surf. Sci. 512 (2020), 144519.
- [27] S. Yang, P. Zhou, L. Chen, Q. Sun, P. Wang, S. Ding, A. Jiang, D.W. Zhang, Direct observation of the work function evolution of graphene-two-dimensional metal contacts, J. Mater. Chem. C 2 (2014) 8042–8046.
- [28] J. Xue, O. Elbanna, S. Kim, M. Fujitsuka, T. Majima, Defect state-induced efficient hot electron transfer in Au nanoparticles/reduced TiO<sub>2</sub> mesocrystal photocatalysts, Chem. Commun. 54 (2018) 6052–6055.
- [29] X. Hou, Z. Li, L. Fan, J. Yuan, P.D. Lund, Y. Li, Effect of Ti foil size on the micro sizes of anodic TiO<sub>2</sub> nanotube array and photoelectrochemical water splitting performance, Chem. Eng. J. (2021), 131415.
- [30] X. Hou, P.D. Lund, Y. Li, Controlling anodization time to monitor film thickness, phase composition and crystal orientation during anodic growth of TiO<sub>2</sub> nanotubes, Electrochem. Commun. 134 (2022), 107168.
- [31] A. Afzal, A. Habib, I. Ulhasan, M. Shahid, A. Rehman, Antireflective self-cleaning TiO<sub>2</sub> coatings for solar energy harvesting applications, Front. Mater. 8 (2021), 687059.
- [32] D.K. Zhong, M. Cornuz, K. Sivula, M. Grätzel, D.R. Gamelin, Photo-assisted electrodeposition of cobalt–phosphate (Co–Pi) catalyst on hematite photoanodes for solar water oxidation, Energy Environ. Sci. 4 (2011) 1759.
- [33] Z. Ni, H. Wang, Q. Zhao, J. Zhang, Z. Wei, H. Dong, W. Hu, Ambipolar conjugated polymers with ultrahigh balanced hole and electron mobility for printed organic complementary logic via a two-step CH activation strategy, Adv. Mater. 31 (2019), e1806010.
- [34] G.L. Chiarello, A. Zuliani, D. Ceresoli, R. Martinazzo, E. Selli, Exploiting the photonic crystal properties of TiO<sub>2</sub> nanotube arrays to enhance photocatalytic hydrogen production, ACS Catal. 6 (2016) 1345–1353.
- [35] W. Wang, L. Qi, Light management with patterned micro- and nanostructure arrays for photocatalysis, photovoltaics, and optoelectronic and optical devices, Adv. Funct. Mater. 29 (2019), 1807275.
- [36] N. Masahashi, Y. Mizukoshi, S. Semboshi, K. Ohmura, S. Hanada, Photo-induced properties of anodic oxide films on Ti<sub>6</sub>Al<sub>4</sub>V, Thin Solid Films 520 (2012) 4956–4964.
- [37] X. Liu, P. Chu, C. Ding, Surface modification of titanium, titanium alloys, and related materials for biomedical applications, Mater. Sci. Eng. R Rep. 47 (2004) 49–121.
- [38] Y. Zhang, M.K. Choi, G. Haugstad, E.B. Tadmor, D.J. Flannigan, Holey substratedirected strain patterning in bilayer MoS<sub>2</sub>, ACS Nano 15 (2021) 20253–20260.
- [39] S. Anantharaj, S. Noda, Appropriate Use of electrochemical impedance spectroscopy in water splitting electrocatalysis, Chemelectrochem 7 (2020) 2297–2308.
- [40] E.P. Randviir, C.E. Banks, Electrochemical impedance spectroscopy: an overview of bioanalytical applications, Anal. Methods 5 (2013) 1098.
- [41] A.R.C. Bredar, A.L. Chown, A.R. Burton, B.H. Farnum, Electrochemical impedance spectroscopy of metal oxide electrodes for energy Applications, ACS Appl. Energy Mater. 3 (2020) 66–98.
- [42] P.-F. Liu, C. Wang, Y. Wang, Y. Li, B. Zhang, L.-R. Zheng, Z. Jiang, H. Zhao, H.-G. Yang, Grey hematite photoanodes decrease the onset potential in photoelectrochemical water oxidation, Sci. Bull. 66 (10) (2021) 1013–1021.
- [43] Y. Fu, C.-L. Dong, W. Zhou, Y.-R. Lu, Y.-C. Huang, Y. Liu, P. Guo, L. Zhao, W.-C. Chou, S. Shen, A ternary nanostructured α-Fe<sub>2</sub>O<sub>3</sub>/Au/TiO<sub>2</sub> photoanode with reconstructed interfaces for efficient photoelectrocatalytic water splitting, Appl. Catal. B Environ. 260 (2020), 118206.
- [44] A. Qayum, M. Guo, J. Wei, S. Dong, X. Jiao, D. Chen, T. Wang, An in situ combustion method for scale-up fabrication of BiVO<sub>4</sub> photoanodes with enhanced long-term photostability for unassisted solar water splitting, J. Mater. Chem. 8 (2020) 10989–10997.
- [45] S. Wang, T. He, J.-H. Yun, Y. Hu, M. Xiao, A. Du, L. Wang, New iron-cobalt oxide catalysts promoting BiVO<sub>4</sub> films for photoelectrochemical water splitting, Adv. Funct. Mater. 28 (2018), 1802685.
- [46] S. Wang, T. He, P. Chen, A. Du, K. Ostrikov, W. Huang, L. Wang, In situ formation of oxygen vacancies achieving near-complete charge separation in planar BiVO<sub>4</sub> photoanodes, Adv. Mater. 32 (2020), 2001385.
- [47] X. Yao, X. Hu, W. Zhang, X. Gong, X. Wang, S.C. Pillai, D.D. Dionysiou, D. Wang, Mie resonance in hollow nanoshells of ternary TiO<sub>2</sub>-Au-CdS and enhanced photocatalytic hydrogen evolution, Appl. Catal. B Environ. 276 (2020), 119153.
- [48] J. Yan, P. Liu, C. Ma, Z. Lin, G. Yang, Plasmonic near-touching titanium oxide nanoparticles to realize solar energy harvesting and effective local heating, Nanoscale 8 (2016) 8826–8838.
- [49] M. Chen, Y. He, Plasmonic nanostructures for broadband solar absorption based on the intrinsic absorption of metals, Sol. Energy Mater. Sol. Cell. 188 (2018) 156–163.
- [50] Y. Oshida, E.B. Tuna, O. Aktoren, K. Gencay, Dental implant systems, Int. J. Mol. Sci. 11 (2010) 1580–1678.