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Nanostructure-induced colored TiO₂ array photoelectrodes with full solar spectrum harvesting†

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Different from regular bandgap narrowing for better sunlight absorption, a series of nanostructure-induced wedge-shaped colored TiO₂ array photoelectrodes exhibited full solar spectrum light harvesting and enhanced performances exemplified by photoelectrochemical (PEC) degradation of Ni(II)-EDTA. Finite element method (FEM) simulation confirmed the influence of the nanostructure towards light absorption in UV, visible, and near-infrared (NIR) regions.

Nowadays, the accelerated fossil energy consumption and the growing environmental pollution urge the rapid development of renewable, clean, and alternative energy sources.^{1–3} As a free, clean and abundant source of energy, sunlight can be captured and converted into chemical energy, electrical energy and thermal energy by different technologies.^{4–6} Since the creative water splitting and dye-sensitized solar cells (DSSCs) using sunlight were reported several decades ago,^{7,8} TiO₂ has attracted much more attention as a photocatalyst and photoelectrode due to its good corrosion resistance in aqueous solution, environmentally benign nature, and photochemical stability.^{9–13} However, pristine TiO₂ can only use UV light with a wide band gap (3.2 eV for anatase and 3.0 eV for rutile), while sunlight consists of ~5% UV light, ~40% visible light, and ~55% near-infrared (NIR) light, thus researchers have tried many clever methods to extend the usable solar spectrum to the visible and even the NIR region. Typical methods have made

a breakthrough to narrow down the band gap by doping,^{14,15} forming defects,¹⁶ or hydrogenation.¹⁷ Triggered by black TiO₂ with enhanced solar light absorption and a narrow band gap of ~1.5 eV induced by hydrogen insertion,¹⁷ a series of dark TiO₂ nanomaterials have been successfully prepared.^{18–21} Even NIR light can be up-converted into visible or UV light by doping rare-earth elements or introducing carbon quantum dots (CQDs) to TiO₂ samples.^{22–25} Besides, surface plasmon resonance (SPR) or localized surface plasmon resonance (LSPR) can offer TiO₂ a new opportunity to achieve full spectrum light absorption by introducing extra noble metal nanoparticles (NPs) to increase light scattering and excite electron-hole pairs.^{26–28} It is noticeable the extra component makes contribution to the absorption spectrum extending to the visible or NIR band region for TiO₂-based photocatalysts. Without doping, hydrogenation or SPR (LSPR), the TiO₂-based photocatalysts or photoelectrodes can hardly have full solar spectrum absorption. It is noteworthy that the UV absorption edge of most doped TiO₂ nanomaterials had a red shift at the cost of markedly decreased absorption intensity in the UV region.^{29,30}

It remains a big challenge to develop TiO₂ nanomaterials with full solar spectrum harvesting and with 100% UV absorption simultaneously. Many researchers have synthesized various nanostructured TiO₂ to obtain enhanced photochemical properties, such as nanosheets, nanowires, hierarchical nanostructures and other typical structures.^{31–33} However, structural control was thought to be an invalid way to change the band gap of TiO₂, as it could mainly accelerate electron transportation and the separation of photogenerated electrons and holes.^{34,35} Interestingly, ordered micro/nano-structures with a periodic refractive index could produce TiO₂ photonic crystals (PCs) to modulate light propagation in the visible or NIR region.^{36,37} An ordered quasi-PC structure might be a good option to provide full solar spectrum absorption, improved UV absorption, and thus a higher photocurrent density. Till now, pure TiO₂ nanomaterials with full solar spectrum absorption have not been reported by structural control.

As one kind of harmful chemical that causes water pollution, a metal complex is extremely difficult to be removed by

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conventional chemical or biological treatment due to its high solubility over a wide pH range and high resistance to biodegradation.³⁸ The electrochemical (EC) process is a typical method for the degradation of the refractory metallic complexes.^{39–41} To further save electric energy and improve the degradation efficiency, the EC method could be updated to a photoelectrochemical (PEC) process with a highly efficient photoelectrode under the irradiation of sunlight. In this communication, a series of colored TiO₂ samples (red, purple, blue, and green) grown on Ti foam were synthesized and used as photoelectrodes in the degradation of Ni(II)–EDTA with the aid of simulated solar irradiation. The one-dimensional (1D) quasi-PC structures combined with microstructures of Ti foam have enhanced UV absorption to nearly 100% and even can confine visible and NIR light, achieving full solar spectrum absorption. The red electrode showed a 100% removal efficiency of Ni(II)–EDTA and 94% recovery efficiency of Ni by the PEC method, much higher than the values (25% and 20%) obtained by bare Ti foam with the EC method. The relationship between nanostructure and enhanced light absorption of the red TiO₂ was also simulated and studied by the finite element method (FEM).

Experimental details about the preparations and photoelectrochemical tests are shown in the ESI.† Ti foam composed of microparticles with sizes of 200–500 μm (Fig. S1†) was used as the substrate to grow TiO₂ nanoarrays. By adjusting the reaction time, the red, purple, blue, green, and white TiO₂ nanoarrays on Ti foam (TF) were obtained, named R-TiO₂/TF, P-TiO₂/TF, B-TiO₂/TF, G-TiO₂/TF, and W-TiO₂/TF, respectively. The SEM image of the red sample in Fig. 1a with a magnified image inserted showed that the 1D array was composed of thin

wedge-shaped sheets with small top ends. According to the SEM images in Fig. S2,† the width of the wedge-shaped nanosheets from the red sample was measured to be about 140–170 nm at the bottom and 25–35 nm at the top, the thickness was 60–90 nm at the bottom and 10–20 nm at the top, and the length was about 2.4 μm. The TEM image of several 1D sheets from R-TiO₂ in Fig. 1b also confirmed the thin wedge-shaped structure. From the HRTEM image in Fig. 1c, a clear phase boundary (marked with a yellow dashed line) between anatase and TiO₂(B) could be seen. The XRD and Raman results confirmed that the color samples (R-TiO₂/TF, P-TiO₂/TF, B-TiO₂/TF, and G-TiO₂/TF) were the mixed phases of anatase and TiO₂(B) while the white one (W-TiO₂/TF) was pure anatase (Fig. S3 and S4†). Fig. 1d shows the macroscopic colors of the red, purple, blue, green, and white samples grown on Ti foam. Fig. 1e showed the UV-vis-NIR spectra of R-TiO₂/TF and the commercial P25. The P25 particles were used for comparison with an average diameter of 30–40 nm according to the SEM image in Fig. S5.† R-TiO₂/TF showed a full solar spectrum light absorption from 200 to 2500 nm with 95–98% absorption in the UV region (less than 90% for P25), an absorption peak at 490 nm in the visible region corresponding to the red color, and an absorption peak at 1240 nm in the NIR region. The other color samples also have absorption peaks at 521, 606, and 670 nm in the visible region, as well as at 1264, 1579, and 1852 nm in the NIR region for P-TiO₂, B-TiO₂, and G-TiO₂, respectively (Table S1, Fig. S6†).

We could also confirm the influence of nanostructure on the visible absorption by observing the color change along with the structural change through the precursors of Na₂Ti₃O₇ with metallic color and H₂Ti₃O₇ with red color (Experimental Section, and Fig. S7†). Besides, the sample turned white (W-TiO₂) as longer reaction time destroyed its structure (Fig. S8†). Meanwhile, X-ray photoelectron spectroscopy (XPS) detected no N-doping and Ti³⁺ ions in these samples (Fig. S9†), revealing that N-doping, Ti³⁺ defect states or oxygen vacancies could not be the reason that caused a color change.^{42–44} The effect came from mixed phases on color was also excluded by comparing with a white TiO₂ made of a mixed-phase of anatase and TiO₂(B) (Fig. S10†). Three typical electrodes, namely, R-TiO₂/TF, G-TiO₂/TF and W-TiO₂/TF were chosen and tested as photoanodes in a three-electrode system in a single-compartment quartz cell with colored TiO₂ on one side of Ti foam facing the light source (Fig. S11†). The colored TiO₂ sample was used as the photoanode for the degradation of Ni(II)–EDTA using the PEC process under the illumination of simulated sunlight. The tests are shown in detail in the ESI.† Moreover, our low-cost anodes have stable structures (note that the arrays were grown directly on the Ti foam, instead by traditional coating on the electrode). At the concentration of 0.1 mmol L^{−1}, the Ni(II)–EDTA removal efficiency approached 100% (red solid line), 90% (green solid line), 62% (black solid line), and 57% (orange solid line) for the R-TiO₂/TF, the G-TiO₂/TF, the W-TiO₂/TF, and the P25/TF anodes, respectively, with related Ni²⁺ recovery efficiency of 94% (red dotted line), 85% (green dotted line), 58% (black dotted line), and 54% (orange dotted line), respectively (Fig. 2a). The results revealed that the red electrode exhibited the best PEC activity in the decomposition of the Ni(II)–EDTA complex among all three

Fig. 1 (a) Overview of the SEM image of R-TiO₂/TF with a partially enlarged SEM image inserted. (b) TEM image of several wedge-shaped sheets from the red sample. Scale bar: 250 nm. (c) HRTEM image taken from (b), showing the phase boundary between the anatase phase and TiO₂(B). (d) The macroscopic colors of the red, purple, blue, green, and white samples grown on Ti foam in sequence. (e) UV-vis-NIR spectra of R-TiO₂/TF and the commercial P25. The inset simply illustrated the structural influence of R-TiO₂/TF and P25 on incident light.

Fig. 2 (a) Degradation (solid lines) and recovery efficiency (dotted lines) of $0.1 \text{ mmol L}^{-1} \text{ Ni(II)-EDTA}$ with the PEC method using photoanodes of R-TiO₂/TF (red), G-TiO₂/TF (green), W-TiO₂/TF (black) and P25/TF (orange). The separate photocatalysis (pink) with R-TiO₂ and the electrochemical degradation (blue) with Ti foam as the anode were also carried out. (b) Degradation of MO at 15 mg L^{-1} with R-TiO₂/TF under photocatalysis in multiple cycles. (c) Transient photocurrent response (1.0 V vs. SCE) for the R-TiO₂/TF (red), the G-TiO₂/TF (green), the W-TiO₂/TF (black) electrode without Ni(II)-EDTA, and the R-TiO₂/TF electrode (blue line, with 0.1 mmol L^{-1} of Ni(II)-EDTA in the solution). (d) Nyquist plots for the three electrodes.

color anodes and P25/TF with the highest Ni^{2+} recovery efficiency on the cathode. It was interesting to note that the red anode with only photocatalysis showed a Ni(II)-EDTA removal efficiency of about 50% (pink solid line), obviously including contribution from the adsorption of Ni(II)-EDTA on the anode to some extent. With only an electrochemical process, the bare Ti foam as the anode provided a degradation efficiency of about 25% (blue solid line) and a metal recovery efficiency of about 20% (blue dotted line). As shown in Fig. S12,[†] the observed current in the cyclic voltammetry curve confirmed that Ni(II)-EDTA was readily oxidized with the potential beyond 0.56 V SCE . Under neutral conditions, the valence band potential of TiO₂ is around 2.0 V (vs. SCE) , with the photo-excited holes which have the ability to directly degrade the Ni(II)-EDTA contaminant or induce some reactive oxygen species (ROS) for further mineralization.³⁴ Obviously, the synergetic photocatalysis and electrochemical reaction efficiently enhanced the degradation of Ni(II)-EDTA and Ni collection. In addition, the width of space charge layer at the photoanode interface was probably enhanced in the presence of an applied bias, resulting in a band bending in the TiO₂ semiconductor. This was also attributed to the high photo-excited electron-hole separation efficiency in the PEC system.^{45–47} Moreover, it was confirmed that the

decomposition product of Ni(II)-EDTA contained small organic acids, NO_3^- , and other small molecules through decomplexation and further oxidation by the PEC treatment (Fig. S13 and S14, and Table S2[†]). Deposition of a small quantity of nickel on TiO₂ can modify the optoelectronic properties of TiO₂ and thereby can influence the photocatalytic activity.^{48,49} Therefore, XPS was performed to analyze the surface composition of the R-TiO₂ photoanode and Ti foil cathode after the degradation of Ni(II)-EDTA. The results showed that metallic Ni was not detected at the surface of R-TiO₂/TF but deposited on the surface of the Ti foil under a powerful electric field in the PEC process (Fig. S15 and S16[†]).

When we decreased the concentration of Ni(II)-EDTA from 0.1 to 0.05 mmol L^{-1} , the removal efficiency could be increased to 100%, 100%, 94%, and 74% for R-TiO₂/TF, G-TiO₂/TF, W-TiO₂/TF and P25/TF electrodes, respectively, with corresponding Ni^{2+} recovery efficiencies of 86%, 86%, 78%, and 65% (Fig. S17[†]). The synergetic effect of photocatalysis and the applied electric field brought about the highly efficient degradation of Ni(II)-EDTA *via* decomplexation followed by anodic oxidation. To check the effect of the absorbed visible light, control experiments were carried out with a filter ($\lambda > 400 \text{ nm}$). The corresponding removal efficiencies of $0.05 \text{ mmol L}^{-1} \text{ Ni(II)-}$

EDTA were 62% (PEC) and 21% (PC) for R-TiO₂/TF (red lines), and 38% and 12% for P25/TF (black lines), respectively, suggesting that the visible light might influence the Ni(II)-EDTA degradation when using the R-TiO₂/TF photoanode (Fig. S18†). It is to be mentioned that the energy consumption (E_c) by PEC degradation with the aid of simulated solar light in our experiment was calculated by eqn (1). The E_c was only 0.08 kW h m⁻³ using the R-TiO₂/TF photoanode, much lower than that of the pure electrochemical process by Ti foam (3.15 kW h m⁻³) and other reported results (Table S3†).

$$E_c = \frac{1000Pt}{60V \times \log(C_t/C_0)} \quad (1)$$

where P is the electric power of the electrochemical system ($P = UI$, kW), V is the volume (L) of the solution in the reactor, t is the degradation time (min), C_0 is the initial concentration of the metal-complex, and C_t is the concentration of the metal complex over a period of time.

Compared with the photocatalytic process as summarized in Table S4,† our PEC process with the R-TiO₂/TF photoanode had higher Ni(II)-EDTA removal (100%), considerable Ni²⁺ recovery (94%), lower catalyst content (0.4 g L⁻¹), and easier to operate with multiple cycles than conventional photocatalysis using powder TiO₂. Although the PEC method has been widely used in the degradation of organic dyes, antibiotics, and other hazardous organic molecules,^{50–52} it is relatively rare in the degradation of the metal-EDTA complex. We reported a total (100%) degradation of EDTA and 94% metal recovery, indicating much enhanced Ni(II)-EDTA degradation and Ni recovery efficiency using R-TiO₂/TF as the photoelectrode with the PEC method. In contrast to the other studies for the degradation of metal-EDTA (Table S5†), a relatively highly efficient PEC activity, with a 100% degradation of EDTA and 94% metal recovery, can be achieved here, exhibiting the practical application potential. Further investigation on the degradation of methylene orange (MO) using R-TiO₂/TF was conducted to assess the durability of the electrode (Fig. 2b). The results showed that the R-TiO₂/TF electrode displayed a highly stable photocatalytic activity with 90% MO color removal after 30 h and 72% mineralization efficiency (Fig. S19†). The different color electrodes showed different photocatalytic activities (Fig. S20†), giving an anodic degradation of 95%, 75%, and 61% by the R-TiO₂/TF G-TiO₂/TF and W-TiO₂/TF electrodes at their first cycle, respectively. The result also confirmed the excellent photocatalytic activity of the R-TiO₂/TF sample.

To further investigate the photocatalytic activity of the color electrodes, the transient responses of the photocurrent of the R-TiO₂/TF, G-TiO₂/TF and W-TiO₂/TF electrodes under simulated sunlight by an applied bias of 1.0 V vs. SCE were measured. It is known that the e⁻-h⁺ separation efficiency plays an important role in the photocatalytic reaction. A higher photocurrent means a higher e⁻-h⁺ separation efficiency.⁵³ As shown in Fig. 2c, the R-TiO₂/TF electrode exhibited the highest value of 2.0 mA cm⁻² (1.0 V vs. SCE), which was almost twice as that of the G-TiO₂/TF electrode and 2.5 times that of the W-TiO₂/TF electrode. It was interesting to see that the photocurrent increased to 2.1 mA cm⁻² when adding 0.1 mmol L⁻¹ Ni(II)-

EDTA to the electrolyte. This was mainly due to the fact that more photogenerated holes or ·OH had opportunities to oxidize Ni(II)-EDTA molecules under a higher applied bias voltage.^{54,55} Moreover, the similar trend can be observed when 0.8 V bias voltage was applied (Fig. S21†). In addition, no obvious photocurrent change under the applied bias voltage of 0.5 V could be observed which was probably due to the fact that the quantity of separated hole-electron pairs under a low voltage did not have sufficient potential to oxidize Ni(II)-EDTA with a low concentration (0.1 mmol L⁻¹) and as a result most of the photocurrent was generated from photoelectrochemical water oxidation (Fig. S21†). Additionally, the R-TiO₂/TF photoanode also gave an apparent response to light on/off under visible light (Fig. S22†), which explained the much enhanced removal efficiency of 62% by the PEC method under visible irradiation. Fig. 2d revealed the results of the interfacial properties between the electrode and the electrolyte in terms of electrochemical impedance spectroscopy (EIS) measurements. The semicircle in the Nyquist plot at high frequency represents the charge-transfer process, with its diameter reflecting the charge-transfer resistance.⁵⁶ The R-TiO₂/TF electrode had a diameter smaller than the other two electrodes, implying faster electron mobility over this electrode, due in part to its smaller length (2.4 μm) versus the green (3.0 μm) and the white (4.0 μm) electrodes. The results clearly demonstrated the photocatalytic superiority of the R-TiO₂/TF electrode over the other two electrodes.

The results showed that the enhanced PEC activity was due to its nearly 100% UV light absorption and part transformation of visible light by the wedge-shaped nanostructure. In order to better understand the relationship between the wedge-shaped nanostructure and light absorption over the full solar spectrum, numerical FEM simulation was carried out. Details of FEM simulation are illustrated in the ESI.†

In Fig. 3a, a simplified periodical wedge-shaped array model was used in the FEM model and a single sheet from it was illustrated with 5 parameters of T_1 and W_1 (thickness × width) at the top, T_2 and W_2 at the bottom, and the length (L). According to the SEM images (Fig. S2 and S23†), the size ratios of $W_1 : W_2$ and $T_1 : T_2$ were set as 1 : 5. Two sets of parameter ranges in Table S6† for R-TiO₂ were also chosen from the analysis of SEM images. Obviously, the synthesized nanoarray was not uniform and even some sheets could aggregate and form a bigger structure, which might influence the NIR absorption, simplified to another bigger set of parameters for the model.

As shown in Fig. 3b, the influence of the wedge-shaped nanostructure on the UV, visible, and NIR absorption was disclosed by FET simulation. The UV absorption peak from 330 to 400 nm was controlled by the parameter of T_2 (an absorption at ~355 nm corresponding to $T_2 = 60$ –90 nm for the R-TiO₂ array), implying the sheet thickness of R-TiO₂ had the main role in UV wave bands. The visible light absorption from 410 to 800 nm could be adjusted by another parameter of width (W_2) along the direction of E_x . When W_2 changed from 140 to 350 nm, their macroscopic colors changed from red to green with the absorption peak position red shifted simultaneously. Simulated results showed visible-light absorption peaks at 485 nm for R-

Fig. 3 (a) A simplified wedge-shaped array model. A single wedge-shaped sheet used in the FEM simulation could be marked by five parameters of tip width (W_1), end width (W_2), tip thickness (T_1), end thickness (T_2), and length (L). Both ratios of $W_1 : W_2$ and $T_1 : T_2$ were set as 1 : 5. (b) FEM simulated absorption spectra in UV, visible, and NIR regions towards the R-TiO₂ sample (red lines in the three parts). The different wave band was mainly influenced by different sizes of the thickness and width of the sample. By changing the parameter of W_2 from 140 to 350 nm, various visible absorptions in accord with red, purple, blue, and green samples were obtained in the visible region of (b). (c) Simulated electric field ($|E|$) distributions of the wedge-shaped sheet from the red TiO₂ at different wavelengths (Part I, $\lambda = 355$ nm; Part II, $\lambda = 490$ nm; Part III, $\lambda = 1240$ nm).

TiO₂ ($W_2 = 140$ – 170 nm), 514 nm for P-TiO₂ ($W_2 = 180$ – 200 nm), 606 nm for B-TiO₂ ($W_2 = 220$ – 280 nm), and 668 nm for G-TiO₂ ($W_2 = 300$ – 350 nm), which were in good agreement with the UV-vis results (Fig. 1e and S6†). The simulation parameters for the P-TiO₂, B-TiO₂, and G-TiO₂ samples are shown in Table S8.† The simulation also checked and confirmed the parameter of L had very little influence on the visible adsorption (Fig. S24†). In the NIR region from 1000 to 2000 nm, the FEM simulation gave an absorption peak at the wavelength of ~ 1245 nm by increasing W_2 two or three times (up to 500–550 nm) as the 1D wedge sheets might easily aggregate and form bigger sizes (Fig. S25†), which was in agreement with the NIR absorption peak value from R-TiO₂ in Fig. 1e. The FEM simulation revealed that our wedge-shaped nanoarray had remarkable UV, visible-light, and NIR absorption through interaction between the comparable structural sizes (thickness and width) and the different wave bands, explaining the full solar spectrum harvesting from R-TiO₂. It is noteworthy that most modification on TiO₂ through doping or hydrogenation to red-shift the UV absorption edge was at the cost of decreased UV absorption. As summarized in Table S7,† the UV absorption ratio of TiO₂ at 300 nm after and before modification was about 0.65–1.00. But we could increase the UV absorption to 1.12 through structural control, which played an important role in the degradation of Ni(II)-EDTA.

Besides, the electric field ($|E|$) distribution of the wedge-shaped sheet is shown in Fig. 3c, irradiated at a wavelength of 355 (UV), 490 (visible), and 1240 nm (NIR) marked with I, II, and III, respectively. From the simulated $|E_y|$ in Part I, it could be

seen that the light was confined at the bottom space of the wedge-shaped sheets, which explained the absorption peak in the UV region (Fig. 3b). Moreover, the wedge-shaped sheet confined the light of 490 nm not only in the space but also within its structure at the bottom ($|E_x|$, Part II). And the wedge-shaped sheet with a bigger width could also confine the light at around 1240 nm in the space and within its structure at the bottom in the near-infrared region ($|E_x|$, Part III). The results of the electric field simulations confirmed the influence of the wedge-shaped nanostructure on light absorption in the full solar spectrum. To sum up, it was the wedge-shaped nanoarray that resulted in the enhanced PEC activity of R-TiO₂/TF in the degradation of Ni(II)-EDTA.

Conclusions

In summary, quasi-photonic crystal wedge-shaped colored TiO₂ nanoarrays grown on Ti foam have been synthesized by a simple hydrothermal method. By subtly adjusting the size of the arrays to change their visible light absorption, various colored TiO₂ samples including red, purple, blue, and green could be obtained. Within these color electrodes, the red one (R-TiO₂/TF anode) exhibited a photocurrent of 1.5 mA cm^{-2} (0.5 V vs. SCE), a 100% degradation of 0.1 mmol L^{-1} of Ni(II)-EDTA with a 94% recovery of Ni(II). The electric energy consumption under simulated sunlight was only 0.08 kW h m^{-3} , much lower than that of most reported electrochemical processes. By comparison, the white TiO₂ array showed a photocurrent of 0.6 mA cm^{-2} , a 62% degradation of Ni(II)-EDTA and a 58% recovery of Ni(II). The synergetic photocatalysis and electrochemical reaction efficiently enhanced the degradation of Ni(II)-EDTA and Ni collection. Additionally, the width of the space charge layer at the photoanode interface was probably enhanced in the presence of an applied bias, resulting in band bending in the TiO₂ semiconductor. This was also attributed to the high photo-excited electron-hole separation efficiency in the PEC system. We also confirmed the enhanced degradation of Ni(II)-EDTA driven by visible light ($\lambda > 400$ nm) with the PEC method. FEM simulation was taken to disclose the influence of the wedge-like nanostructure towards UV, visible-light, and NIR absorption. The results showed that the thickness of the wedge-shaped sheets was the key factor for enhanced UV absorption and visible-light absorption (causing various colors), while the width of aggregated bigger structures led to NIR absorption. Thus, the much enhanced PEC properties of R-TiO₂/TF could be attributed to its nearly 100% UV-light absorption and partial constraints of the visible band, which were influenced by the thickness and width of the wedge-shaped nanostructure. Besides, the 1D array structure and the mixed phase of TiO₂(B) also might improve e^- - h^+ separation and electron transfer.

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