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# Surface-Modified Titanium Dioxide Nanofibers with Gold Nanoparticles for Enhanced Photoelectrochemical Water Splitting

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**Abstract:** High-stability, high-efficiency, and low-cost solar photoelectrochemical (PEC) water splitting has great potential for hydrogen-energy applications. Here, we report on gold/titanium dioxide (Au/TiO<sub>2</sub>) nanofiber structures grown directly on a conductive indium tin oxide substrate, and used as photoelectrodes in PEC cells for hydrogen generation. The titanium dioxide nanofibers (TiO<sub>2</sub> NFs) are synthesized using electrospinning, and are surface-modified by the deposition of gold nanoparticles (Au NPs) using a simple photoreduction method. The structure and morphology of the materials were characterized by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The surface plasmon resonance (SPR) of the Au NPs was investigated by ultraviolet-visible (UV-Vis) diffuse reflectance spectroscopy. The PEC properties of the as-prepared photoelectrodes were measured. The obtained photoconversion efficiency of 0.52% under simulated-sunlight illumination by a 150 W xenon lamp of the Au/TiO<sub>2</sub> NFs structure with 15 min UV irradiation for Au NP deposition was the highest value from comparable structures. Working photoelectrode stability was tested, and the mechanism of the enhanced PEC performance is discussed.

**Keywords:** photoelectrochemical cell; electrospinning; hydrogen generation; water splitting; TiO<sub>2</sub> nanofibers

# 1. Introduction

Hydrogen is considered an important fuel for the future because of its high energy density, its abundance, and its environmental friendliness. Water splitting in a photoelectrochemical (PEC) cell is one of the most promising ways to produce hydrogen [1]. Since Fujishima and Honda reported water splitting using titanium dioxide (TiO<sub>2</sub>) as a photoelectrode in 1972 [2], various semiconducting metal oxides, such as zinc oxide (ZnO), ferric oxide (Fe<sub>2</sub>O<sub>3</sub>), tungsten oxide (WO<sub>3</sub>), and composite semiconductors have been investigated for this purpose [3–10]. Between them, TiO<sub>2</sub> is the most attractive material because of its low cost, high availability, low toxicity, and high stability against photocorrosion [11]. One-dimensional (1D) nanostructured forms of TiO<sub>2</sub>, such as nanowires, nanorods,



nanotubes, and nanofibers, receive significant attention for water-splitting applications, as they provide a direct conduction path for photogenerated electrons, which facilitates charge transport and reduces the recombination of electron-hole pairs [12]. Various morphologies of TiO<sub>2</sub> and their different synthesis routes have been studied [13–17]. Among them, the preparation of nanofibers by using the electrospinning technique has attracted much attention because it offers a high specific surface area and a mesoporous structure, which provides many reaction sites [18]. Moreover, electrospinning is a cost-effective, versatile, and simple technique. Therefore, titanium dioxide nanofibers (TiO<sub>2</sub> NFs) prepared by electrospinning are promising structures for hydrogen production through PEC water splitting.

Due to its large band gap (~3.0 eV for rutile and ~3.2 eV for anatase),  $TiO_2$  is only active in the ultraviolet (UV) spectral range, which contributes less than 5% of total energy of the solar spectrum. Realizing the broadband visible-light absorption of  $TiO_2$  is one of the prerequisites for enhancing the solar-energy conversion efficiency of  $TiO_2$ , since visible light amounts for about 45% of the solar spectrum [19]. Recently, many efforts have been made to extend the absorption of wide-band gap metal-oxide semiconductors to the visible range. Nonmetal and metal doping are the most common methods of achieving this [12,20], but the main drawback of these approaches is the reduction of electron-hole separation. Alternatively, the incorporation of noble metals, especially gold (Au), in metal-oxide semiconductors can increase visible-light absorption due to their surface-plasmon-resonance (SPR) effect [21–24]. In addition, the deposition of gold nanoparticles (Au NPs) on the TiO<sub>2</sub> surface can significantly reduce the recombination of electron-hole pairs in the UV region, as the Fermi level of Au is lower than that of TiO<sub>2</sub> [25]. Nevertheless, the design of plasmonic metal nanoparticle-decorated nanostructures with low cost, high stability, and high efficiency for PEC water splitting is still a challenge.

In the current work, we fabricated Au NPs surface-modified  $TiO_2$  NFs photoelectrodes and used them for PEC water splitting. The materials had several strengths. First,  $TiO_2$  NFs offer a large surface area and high porosity. Furthermore,  $TiO_2$  NFs can play a role as support for the deposition of Au NPs by simple photoreduction with uniform NP distribution and low NP aggregation [26]. Second, an Au NP-decorated  $TiO_2$  surface enhances photoabsorption in the visible spectral range, and prevents the electron-hole pair recombination process. All the above features improved PEC water-splitting efficiency.

#### 2. Results and Discussion

The crystalline nature of the prepared samples with UV irradiation times of 0, 5, 10, and 15 min, hereafter referred to as pure TiO<sub>2</sub>, 5-Au/TiO<sub>2</sub>, 10-Au/TiO<sub>2</sub>, and 15-Au/TiO<sub>2</sub>, respectively, was investigated via X-ray diffraction (XRD; shown in Figure 1). XRD patterns demonstrated the presence of anatase TiO<sub>2</sub>. Peaks at  $2\theta = 25.3^{\circ}$ , 33.45°, and 48.51° corresponded to diffractions on the (101), (004), and (200) planes of the TiO<sub>2</sub> anatase phase, respectively (JCPDS file no. 84 1286), and other peaks, labelled with asterisks, were attributed to indium tin oxide (ITO). The 10-Au/TiO<sub>2</sub> and 15-Au/TiO<sub>2</sub> also showed a peak at 38.1°, which corresponded to diffraction on the (111) plane of Au particles with a face-centered cubic structure (JCPDS file no. 65 8601). The peak intensity at 38.1° of the 15-Au/TiO<sub>2</sub> sample was higher than that of the 10-Au/TiO<sub>2</sub> sample, implying that the loading of Au NPs on the surface of the TiO<sub>2</sub> fibers increased with UV irradiation time.

The morphology of the pure and the Au-modified  $TiO_2$  NFs was characterized by field emission scanning electron microscopy (FE-SEM; Figure 2). As shown in Figure 2a and its inset, the pure structure of  $TiO_2$  NFs had high porosity created by two types of pores: nanopores on the surface of each individual nanofiber due to the burn-out of poly(vinylpyrrolidone) (PVP), and macropores formed by the random stacking of the fibers. The high porosity of  $TiO_2$  NFs is very convenient for Au deposition since it increases material permeability. Figure 2c and its inset show the morphology of the 15-Au/TiO<sub>2</sub> NFs sample. Au NPs were apparent as white dots, decorating the surface of the  $TiO_2$  NFs. Cross-section FE-SEM images of pure  $TiO_2$  NFs in Figure 2b and 15-Au/TiO<sub>2</sub> NFs in Figure 2d revealed that film thickness was about 3  $\mu$ m. Figure 2d also shows that Au NPs uniformly covered the entire TiO<sub>2</sub> NFs, which could be explained by the highly porous structure of the film of TiO<sub>2</sub> NFs.



**Figure 1.** X-ray diffraction (XRD) patterns using Cu–K $\alpha$  as radiation source of pure titanium dioxide-(TiO<sub>2</sub>) and gold (Au)-modified titanium dioxide nanofibers (TiO<sub>2</sub> NFs) samples with ultraviolet (UV) illumination times of 5 min (5-Au/TiO<sub>2</sub>), 10 min (10-Au/TiO<sub>2</sub>), and 15 min (15-Au/TiO<sub>2</sub>).



**Figure 2.** Top-view and cross-section field emission scanning electron microscopy (FE-SEM) images of (a,b) pure TiO<sub>2</sub> and (c,d) 15-Au/TiO<sub>2</sub> NFs on indium tin oxide (ITO) substrates. Insets of (a,c) are enlarged FE-SEM images.

To optimize the PEC performance, various Au-modified TiO<sub>2</sub> NFs samples with different UV irradiation times were fabricated. Figure 3a shows that the 5-Au/TiO<sub>2</sub> sample had few Au NPs. This is consistent with the XRD pattern in Figure 1, in which no Au(111) peak was observed for this sample. The samples that were exposed to UV irradiation for longer, namely, 10-Au/TiO<sub>2</sub> NFs, 15-Au/TiO<sub>2</sub> NFs, and 20-Au/TiO<sub>2</sub> NFs in Figure 3b–d, respectively, showed an increased amount of NPs and NPs with a large size. We measured the diameter distribution for approximately 50 Au NPs on each

sample. The data are plotted in Figure 3e–g and were fitted with a Gaussian function. The average particle diameters were  $16.1 \pm 2.6$  nm for 10-Au/TiO<sub>2</sub> NFs (Figure 3e),  $20.8 \pm 1.9$  nm for 15-Au/TiO<sub>2</sub> NFs (Figure 3f), and  $28.5 \pm 2.9$  nm for 20-Au/TiO<sub>2</sub> NFs (Figure 3g).



**Figure 3.** (**a**–**d**) FE-SEM images of Au/TiO<sub>2</sub> NFs with UV irradiation times of 5, 10, 15, and 20 min, respectively. (**e**–**g**) Diameter distribution of Au NPs measured for (**e**) 10-Au/TiO<sub>2</sub> NFs, (**f**) 15-Au/TiO<sub>2</sub> NFs, and (**g**) 20-Au/TiO<sub>2</sub> NFs, from corresponding SEM images (**b**–**d**).

Transmission-electron-microscopy (TEM) measurements were performed to further investigate the grown Au/TiO<sub>2</sub> crystals. Figure 4a depicts a low-magnified TEM image of the 15-Au/TiO<sub>2</sub> NF sample. It shows that Au NPs were homogeneously deposited on the TiO<sub>2</sub> NFs with an average diameter of around 20 nm. The high-resolution TEM (HR-TEM) image in Figure 4b indicates the contact region between the crystal structure of the TiO<sub>2</sub> NFs and Au NPs. Additionally, the image demonstrates the single crystalline atomic arrangements of TiO<sub>2</sub> and Au in which the lattice fringes are clearly visible. Accordingly, the distance between neighboring fringes was approximately 3.2 Å, which corresponded to the (110) lattice plane of the anatase TiO<sub>2</sub>. On the other hand, the fringe spacing of 2.3 Å corresponded to the (111) lattice plane, and could thus be related with the face-centered cubic phase of the crystalline Au structure. These TEM results are consistent with the XRD data shown in Figure 1.

The chemical states of the pure  $TiO_2$  and 15-Au/ $TiO_2$  NFs samples were measured by X-ray photoelectron spectroscopy (XPS). The wide scan of the two samples is shown in Figure 5a, and it confirmed the presence of titanium (Ti) and oxygen (O) (in both samples), and of Au (in the 15-Au/ $TiO_2$  sample). For elemental analysis, all binding energies were calibrated by referencing the C–C peak of C 1s at 284.8 eV. In Figure 5b, the O 1s core-level peak is shown, and the peak could be deconvoluted into two peaks at 530.2 and 532.2 eV for the pure  $TiO_2$  NF sample. For the 15-Au/ $TiO_2$  NFs sample,

these two peaks shifted slightly to higher binding energy due to the presence of Au. The peak at lower binding energy (530.2 eV) was associated with Ti–O–Ti bonding, while the peak at higher binding energy (532.2 eV) was assigned to Ti–OH binding [27]. After Au decoration, the intensity of the Ti–O–Ti peak decreased relative to the Ti–OH peak. This result is consistent with the suppression of the peak intensity corresponding to Ti–O and Ti–OH bonding in the Ti 2p core-level spectrum (Figure 5c). The Ti 2p core-level peak consisted of Ti  $2p_{1/2}$  and Ti  $2p_{3/2}$  peaks at 465.2 and 458.7 eV, which corresponded to Ti<sup>4+</sup> in the anatase phase of TiO<sub>2</sub>. Moreover, as can be seen on the Ti  $2p_{3/2}$  peak of the 15-Au/TiO<sub>2</sub> NFs sample, there was a small shift to higher binding energy, which could be attributed to the electron transfer from Ti to Au and TiO<sub>2</sub> [28]. In the Au 4f spectrum (Figure 5d), peaks centered at 84.2 and 87.7 eV were associated with Au  $4f_{7/2}$  and Au  $4f_{5/2}$  states, respectively. The Au  $4f_{7/2}$  peak had a small positive shift (0.2 eV) in comparison to that of the bulk Au at 84.0 eV, supporting the strong interaction between Au and TiO<sub>2</sub>, leading to the higher binding energy of Au  $4f_{7/2}$  in Au/TiO<sub>2</sub> NFs. These results confirmed the existence of Au on the surface of the TiO<sub>2</sub> NFs.



**Figure 4.** (a) Transmission-electron-microscopy (TEM) and (b) high-resolution TEM (HR-TEM) images of 15-Au/TiO<sub>2</sub> NF sample.



**Figure 5.** (**a**) Wide-scan and high-resolution X-ray photoelectron spectroscopy (XPS) spectra of (**b**) O 1s, (**c**) Ti 2p, and (**d**) Au 4f states of pristine TiO<sub>2</sub> and 15-Au/TiO<sub>2</sub> NF samples.

The optical properties of the pure TiO<sub>2</sub> NFs and Au/TiO<sub>2</sub> NFs samples were analyzed by diffuse reflectance absorption spectroscopy. As shown in Figure 6, all samples had large absorbance in the UV region (wavelengths below 380 nm), which corresponded to the large band gap of anatase TiO<sub>2</sub> (~3.2 eV). Compared with pure TiO<sub>2</sub> NFs, Au/TiO<sub>2</sub> NFs samples showed strong absorption of visible light in the 490–650 nm range, which could be attributed to the SPR effect of Au NPs. Additionally, samples with more and larger Au NPs showed higher absorption intensity and a slight redshift of the SPR, which is consistent with common knowledge about the SPR of Au NPs [29].



**Figure 6.** Diffuse reflectance absorption spectra of pure TiO<sub>2</sub> NFs and Au/TiO<sub>2</sub> NFs with different UV illumination times.

The higher visible-light absorption of the Au/TiO<sub>2</sub> NF films was expected to produce more electron-hole pairs, resulting in better PEC performance. To investigate the PEC water-splitting properties of the prepared photoelectrodes, I-V and I-t curves were measured by using a 0.5 M sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) electrolyte under illumination by a 150 W xenon lamp. Figure 7a,b presents the photocurrent density and the corresponding photoconversion efficiency as functions of the applied potential for Au/TiO<sub>2</sub> NF photoelectrodes with different UV irradiation times. Au NPs deposited on the  $TiO_2$  NFs had strong impact on the photoconversion efficiency of the electrodes. In particular, the efficiency of the pure TiO<sub>2</sub> NFs photoelectrodes was 0.15% at a potential of 0.5 V versus silver/silver chloride (Ag/AgCl). For the Au NPs samples, photoconversion efficiency was larger. It reached a maximal value of about 0.52% for the 15-Au/TiO<sub>2</sub> NFs photoelectrodes. The higher PEC performance likely originated from the larger size and amount of the deposited Au NPs, which not only generated more electron-hole pairs, but also more effectively charged separately due to the formation of an interface electric field between TiO<sub>2</sub> and Au. In the 20-Au/TiO<sub>2</sub> NF photoelectrodes, there may have been too many Au NPs on the TiO<sub>2</sub> surface, which negatively affected PEC performance. The obtained efficiency of 0.52% for 15-Au/TiO<sub>2</sub> NFs photoelectrodes was comparable to or even better than those of previous reports for Au/TiO<sub>2</sub> nanostructures [27,28,30,31].

The current density–time curves of 15-Au/TiO<sub>2</sub> NFs photoelectrodes at a fixed bias of 0.5 V versus Ag/AgCl under on/off cycles and continuous light illumination are demonstrated in Figure 7c and its inset. The results revealed the fast photoresponse and excellent photostability of the prepared photoelectrodes, demonstrating that there was little electrochemical electrode corrosion during electrolysis.



**Figure 7.** (a) Current densities and (b) corresponding photoconversion efficiencies of Au/TiO<sub>2</sub> NFs with different UV irradiation times. (c) I-t curve and photocurrent (inset) of 15-Au/TiO<sub>2</sub> NFs sample at  $V_{\text{bias}} = 0.5 \text{ V vs.}$  (Ag/AgCl) with on/off cycles and continuous light illumination, and (d) I–V curves of pure TiO<sub>2</sub> NFs and 15-Au/TiO<sub>2</sub> NFs samples under green-light illumination ( $\lambda = 540 \text{ nm}$ ).

To evaluate the effect of Au NP SPR enhancement, the photocurrent densities of pure TiO<sub>2</sub> NFs and of 15-Au/TiO<sub>2</sub> NFs under green-light illumination from a light-emitting diode (LED;  $\lambda$  = 540 nm) are compared in Figure 7d. There was almost no photocurrent from pure TiO<sub>2</sub> photoelectrodes in this light region because the band gap of TiO<sub>2</sub> was larger than the excitation photon energy. In contrast, the photocurrent of the 15-Au/TiO<sub>2</sub> photoelectrode further increased with bias potential under green-light illumination. This photoelectrochemical behavior is most likely due to the SPR effect of Au NPs. Therefore, we can conclude that the introduction of Au NPs on TiO<sub>2</sub> NFs increases the light absorption and facilitates the charge transfer at the electrode/electrolyte interface, leading to a significant enhancement of PEC performance.

On the basis of the above results, we propose an electron-transfer mechanism in Au/TiO<sub>2</sub> NFs, as depicted in Figure 8. Under ultraviolet-light illumination, TiO<sub>2</sub> is activated/photoexcited to generate electrons and holes. Because the Fermi level of Au NPs is lower ( $E_F = +0.45$  V vs. NHE at pH = 7 for bulk Au) than the conduction-band energy level of TiO<sub>2</sub> ( $E_{CB} = -0.5$  V vs. NHE at pH = 7), excited electrons easily transfer to the surface of Au. As a result, this phenomenon reduces the electron-hole recombination rate. In the visible region, Au NPs act as sensitizers. They resonantly absorb photons and generate hot electrons via SPR excitation. These hot electrons are directly injected from the Au NPs to the conduction band of the TiO<sub>2</sub> and later move to the ITO substrate. Finally, electrons are transferred to the Pt electrode to reduce water and to generate hydrogen.



**Figure 8.** Excitation mechanism under UV light and charge-transfer mechanisms between Au NPs and TiO<sub>2</sub> NFs under visible-light excitation.

## 3. Materials and Methods

#### 3.1. Materials

All chemicals were purchased and utilized without further purification: poly(vinylpyrrolidone) (PVP) (wt 360000, Sigma-Aldrich Co., Ltd., St. Louis, MO, USA), ethanol ( $C_2H_5OH$ ,  $\geq$ 99.8%), acetic acid ( $CH_3CO_2H$ ,  $\geq$ 99%), titanium tetraisopropoxide ( $Ti(OiPr)_4$ ; 97%, Sigma-Aldrich Co., Ltd., St. Louis, MO, USA), chloroauric acid trihydrate (HAuCl<sub>4</sub>, Sigma-Aldrich Co., Ltd., St. Louis, MO, USA), sodium sulfate ( $Na_2SO_4$ ,  $\geq$ 98%, Sigma-Aldrich Co., Ltd., St. Louis, MO, USA), and distilled water (18.4 M $\Omega$  cm<sup>-1</sup>).

## 3.2. Preparation of Au NPs modified TiO<sub>2</sub> NFs

The TiO<sub>2</sub> NFs on ITO substrates were fabricated by the electrospinning method using electrospinning equipment from Tong Li Tech and a spray time of 30 min, followed by calcination in air at 500 °C for 2 h, similar to our previous report [32]. A photoreduction process [28] was used to deposit Au NPs on the surface of TiO<sub>2</sub> NFs. Chloroauric acid trihydrate was briefly dissolved in a solvent mixture of water and ethanol (volume ratio 1:3) to form a 5 mM solution of chloroauric acid (HAuCl<sub>4</sub>). We dispersed 1 mL of the above solution and 0.02 g of (PVP) in 50 mL ethanol in a Pyrex Petri dish to form an Au<sup>3+</sup> solution. The TiO<sub>2</sub> NFs on the ITO substrate were then immersed in a prepared solution, followed by irradiation, for different irradiation times, with a 20 W UV lamp to reduce Au<sup>3+</sup> to Au<sup>0</sup>. PVP was used as a surfactant to prevent the size development of Au NPs on the nanofibers. Irradiation time was optimized to enhance photoconversion efficiency. After irradiation, samples were dried at 60 °C in the ambient. Finally, Au-modified TiO<sub>2</sub> NFs samples were calcinated for 1 h in air at 450 °C to remove the PVP.

## 3.3. Characterization

The morphology and structure of the fabricated photoelectrodes were examined by using field emission scanning electron microscopy (FE-SEM; Hitachi S4800, Ibaraki, Japan), high-resolution transmission electron microscopy (HR-TEM; JEOL JEM 2100F, Tokyo, Japan), and X-ray diffraction (XRD, D8 Bruker Advance, Bruker, Billerica, MA, USA) using Cu K<sub> $\alpha$ </sub> radiation with a step size of 0.02°. Optical-absorption spectra were obtained with a UV-vis spectrophotometer (Cary 300, Agilant, Santa Clara, CA, USA). The chemical composition and chemical bonds of the prepared materials were analyzed by X-ray photoelectron spectroscopy (XPS) (XR4, Thermo Scientific, Waltham, MA, USA).

The PEC properties of the as-prepared materials were investigated with a three-electrode electrochemical analyzer (Potentiostat/Galvanostat Model DY2300, Digi-Ivy, Inc., Shenzhen, China), using the fabricated nanostructure films formed on ITO as a working electrode, a platinum (Pt) wire as

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a counter electrode, and Ag/AgCl in saturated KCl as a reference electrode. The electrolyte was a 0.5 M aqueous solution of Na<sub>2</sub>SO<sub>4</sub>. A 150 W xenon lamp (Gloria X150A, Zolix Instruments C.o., Ltd., Beijing, China) with intensity of 100 mW/cm<sup>2</sup> was utilized as a simulated sunlight source to evaluate the photon-to-current conversion efficiency of the photoelectrodes. Green light from a LED (L128-GRN, RS Components Ltd., Riyadh, Saudi Arabia), with a wavelength of 540 nm and an intensity of 1.2 mW/cm<sup>2</sup> was used to determine the SPR properties of the Au NPs. All measurements were performed with front-side illumination of the photoelectrodes and linear sweep potential at a scan rate of 50 mV/s. The exposed area of the working electrode to the electrolyte was fixed at 1 cm<sup>2</sup> using nonconductive epoxy resin. The equations used to calculate the photoconversion efficiencies are provided in [11].

# 4. Conclusions

In this study, we report a facile method to fabricate Au NPs decorated  $TiO_2$  NFs by combining electrospinning and a photoreduction process. Owning to its high porosity, the  $TiO_2$  NF structure provided a high surface area that facilitated Au NP deposition. The 15-Au/TiO<sub>2</sub> NF sample with average Au NPs diameters of around 20 nm showed the highest PEC water-splitting efficiency of 0.52%, which was 3.5 times higher than that of the pristine  $TiO_2$  NF counterpart. The improved PEC efficiency of the Au/TiO<sub>2</sub> NFs photoelectrode was probably a result of synergistic effects between the structure of  $TiO_2$  NFs and the SPR of the Au nanoparticles. Au/TiO<sub>2</sub> NF photoelectrodes are promising for applications in solar-to-hydrogen energy-conversion devices.

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