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Rutile TiO₂ film with 100% exposed pyramid-shaped (111) surface: photoelectron transport properties under UV and visible light irradiation

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In this work, a facile hydrothermal method was employed to directly grow the rutile TiO₂ film with 100% exposed pyramid-shaped (111) surface onto a FTO conducting substrate, and the resulting rutile TiO₂ film was used as the photoanode after annealing at 450 °C for 2 h in argon (Ar) to investigate photoelectrocatalytic properties under UV and visible light irradiation. The photoelectrocatalytic activities of the resultant photoanode under UV (main wavelength of 365 nm) and visible light ($\lambda > 400$ nm) irradiation were evaluated using water as the probe compound. The photoelectrocatalytic activity of the UV light illuminated photoanode was found to be 0.144 mA mW⁻¹, significantly higher than that obtained from the visible light illuminated photoanode (0.102 μ A mW⁻¹). Despite this, the determined value of 0.102 μ A mW⁻¹ represents an excellent visible light photoelectrocatalytic activity of the photoanode. The origin of visible light activity could be attributed to the doped Ti³⁺ in the bulk TiO₂. The superior photoelectrocatalytic activity could be due to the high reactivity of the exposed high-energy (111) surface and the superior photoelectron transport property. A photoelectrocatalytic method was used to manifest the photoelectron transport properties inside the rutile TiO₂ film and concurrently quantify the inherent resistances (R_0) of UV and visible light illuminated photoanodes. The determined R_0 values were 93.5 and 91.3 Ω for UV and visible light illuminated photoanodes, respectively. The similar R_0 values imply a similar the photoelectron transport resistance inside the rutile TiO₂ film under UV and visible light irradiation, confirming that the measured R_0 is of an inherent property of the photocatalyst film. This also implies that the rate of charge recombination is similar under UV and visible light irradiation. To our knowledge, this is the first time the electron transport properties of a rutile TiO₂ photoanode have been concurrently investigated under UV and visible light irradiation.

1. Introduction

As a dominant semiconductor photocatalyst, titanium dioxide (TiO₂) has been extensively investigated for applications in environmental remediation, water disinfection, solar-driven hydrogen production and dye-sensitised solar cells, due to its excellent photocatalytic activity, outstanding photochemical stability and non-toxic nature.¹⁻⁶ For photocatalysis, the anatase TiO₂ has been widely accepted to be a more effective photocatalyst than that of rutile TiO₂. This is mainly because of its more negatively positioned conduction band edge potential favorable for the reduction half-reaction, which is often the rate limiting step of a photocatalysis process.⁷ Another issue is that the rutile TiO₂ are normally prepared by transformation of anatase TiO₂ under high temperature, resulting in large particle size and low surface area hence the poor photocatalytic efficiency.⁸ However, it has been demonstrated that these disadvantages faced by the rutile TiO₂ could be overcome by

immobilising the photocatalyst onto a conducting substrate and used as photoanode in photoelectrocatalytic applications.⁹⁻¹² For a particulate suspension photocatalysis system, it has been a common view that photocatalytic oxidation and reduction reactions occur at the different locations on the same photocatalyst particle, leading to a high rate of charge recombination.^{1, 10} The immobilisation of photocatalyst onto a conducting substrate allows the combination of electrochemical techniques with photocatalysis, namely, photoelectrocatalysis. The application of a suitable potential bias in photoelectrocatalysis minimises the charge recombination to significantly increase the photocatalytic efficiency.⁹⁻¹² Importantly, with a photoelectrocatalysis approach, the oxidation half-reaction (at the working electrode) is physically separated from the reduction half-reaction (at the auxiliary electrode), which allows the reaction of interest (*i.e.*, the photocatalytic oxidation of water and photoelectron transport at photocatalyst

film) to be studied in isolation.⁹⁻¹² This approach has been successfully employed to quantify the extent of photocatalytic degradation for sensing applications.^{9, 13}

It is well known that the performance of a semiconductor photoanode is highly dependent on its photoelectron transport properties inside the photocatalyst film.^{10, 12, 14-16} Such properties can be measured by the intensity-modulated photocurrent spectroscopy (IMPS) or intensity-modulated photovoltage spectroscopy (IMVS) techniques.^{14, 15} In this regard, our group has proposed and experimentally demonstrated a simple, rapid yet effective photoelectrochemical method, capable of manifesting the photoelectron transport process inside a semiconductor photocatalyst film (e.g., determining the inherent resistance of the photocatalyst layer, R_0),¹⁰⁻¹² which is a more convenient and direct approach when compared to the IMPS and IMVS techniques.

Although TiO_2 photocatalysts have displayed excellent ultraviolet light (UV) activity but their visible light activity is poor due to its wide bandgap (e.g., 3.2 eV for anatase TiO_2).¹⁷⁻²² To date, the fabrication of pure TiO_2 with visible light activity without the need for doping is still an challenging issue for the research field. Recently, a powder form of pure rutile TiO_2 obtained by a hydrothermal method has demonstrated a noticeable visible light photocatalytic activity.^{21, 22} These studies confirmed that the doped Ti^{3+} in the bulk TiO_2 during hydrothermal reaction is responsible for the visible light activity.^{21, 22} Moreover, the formed Ti^{3+} sites in the bulk are demonstrated to be highly stable in air and water for repetitive use.^{21, 22} However, such a powder form of visible light active rutile TiO_2 is unsuitable for photoelectrocatalysis-based applications and its photoelectron transport property is difficult to be quantitatively characterised. It has been well-demonstrated that the photocatalytic activity of anatase TiO_2 depends not only on the size, shape and crystal phase but also crystal facets.^{6, 11, 23, 24} Apparently, this has been proven to be true for rutile TiO_2 . In our previous work, we have demonstrated that a photoanode made of rutile TiO_2 with {111} faceted surface exhibits high visible light photoelectrocatalytic activity toward oxidation of water and organics.²⁵

In this work, a facile and one-pot hydrothermal method was employed to directly grow the UV and visible light active pure rutile TiO_2 film with 100% exposed pyramid-shaped (111) surface onto the FTO conducting substrate and used as the photoanode after calcination at 450 °C in argon (Ar).²⁵ The structural, morphological, crystal phase and facet were characterised. A photoelectrocatalytic method previously developed by us was used to quantify the photoelectron transfer property inside the photocatalyst film.¹¹⁻¹³ The results confirmed that the resultant pure rutile TiO_2 photoanode with 100% exposed pyramid-shaped (111) surface possesses an excellent photoelectrocatalytic activities toward water oxidation under UV (main wavelength of 365 nm) and visible light ($\lambda > 400$ nm) illumination. To our knowledge, this is the first time the electron transport properties of a rutile TiO_2 photoanode was investigated.

2. Experimental section

Synthesis

The UV and visible light active pure rutile TiO_2 films with 100%

exposed pyramid-shaped (111) surface on FTO conducting substrates were fabricated by a facile and one-pot hydrothermal method.²⁵ In a typical synthesis process, titanium nitride (TiN, >95%, Aldrich) was used as reaction precursor to add into a mixture reaction solution (30 mL) containing 0.88 M hydrogen peroxide (H_2O_2 , 30%, Aldrich) and 1.5-9.2 M hydrochloric acid (HCl, 32%, Sigma-Aldrich). The investigated TiN concentration in reaction solution is 0.011-0.033 M. After magnetically stirring for 1 minute, the reaction solution was transferred into a Teflon-lined stainless steel autoclave (80 mL of volume). Before hydrothermal reaction, a piece of cleaned FTO conducting substrate (30 mm × 15 mm × 2 mm) was immersed into the above reaction solution with the conductive side facing up. The subsequent hydrothermal reaction was carried out at 200 °C for 24 h. After hydrothermal reaction, the autoclave was naturally cooled down to room temperature. The FTO conducting substrate was taken out, rinsed adequately with deionized water and allowed to dry in nitrogen stream. The obtained samples were then calcined in a tube furnace at 450 °C for 2 h in argon (Ar) circumstance with a heating rate of 5 °C/min.

Characterisation

The structural characteristics of the samples were investigated by scanning electron microscope (SEM, JSM-6300F), transmission electron microscope (TEM, Philips F20), and X-ray diffraction (XRD, Shimadzu XRD-6000, equipped with a graphite monochromatic $\text{Cu K}\alpha$). The chemical compositions of the samples were analysed by X-ray photoelectron spectroscopy (XPS, Kratos Axis ULTRA incorporating a 165 mm hemispherical electron energy analyzer), and the UV-vis diffuse reflectance spectra of the samples were recorded on a Varian Cary 5E UV-vis-NIR spectrophotometer.

Theoretical calculations

All computations are performed using the Vienna ab initio simulation package (VASP) based on the all-electron projected augmented wave (PAW) method.^{26, 27} A plane-wave basis set is employed to expand the smooth part of wave functions with a kinetic energy cut-off of 400 eV. For the electron-electron exchange and correlation interactions, the functional of PBE,²⁸ a form of the general gradient approximation (GGA), is used throughout. The Brillouin-zone integrations were performed using Monkhorst-Pack grids of special points, with gamma-point centered ($2 \times 4 \times 1$) k-points meshes used for the surface. When the geometry is optimized, all atoms are allowed to relax. A variable cell technique is employed to simultaneously optimize the lattice constant and the atomic structure to encounter the complexity and low-symmetry of the rutile TiO_2 crystals. And the lattice constants and geometric structure are optimized until the residual forces were below 0.001 eV/Å.

Photoelectrochemical measurements

The photoelectrochemical measurements were performed through a photoelectrochemical cell with a quartz window for illumination.^{11, 12} A three-electrode mode, consisting of a TiO_2 nanostructured photoanode, a saturated Ag/AgCl reference electrode and a platinum mesh counter electrode, was applied in the experiments. 0.10 M NaNO_3 solution was used as supporting electrolyte. A voltammograph (CV-27, BAS) was used for the

application of potential bias. Potential and current signals were recorded using a Macintosh (AD Instruments). The illuminated area of the photoanode was 0.785 cm^2 . UV illumination was carried out using a 150 W xenon arc lamp light source with focusing lenses (HF-200W-95, Beijing Optical Instruments). To avoid the electrolyte being heated-up by the infrared light, a UV-band-pass filter (UG 5, Avotronics Pty. Ltd.) was used. The UV light intensity was regulated and carefully measured at 365 nm. For visible light experiments, the wavelengths of the incident light lower than 400 nm was cut off by a UV-400 filter. The light intensity of visible light was carefully measured with a visible-irradiance meter (Nova-Oriel, OPHIR).

3. Results and discussion

Fig. 1A shows XRD patterns of the as-synthesised product (curve a) and the calcined sample at 450°C in Ar (curve b). The measured diffraction peaks for the samples before and after calcination can be indexed to a rutile phase TiO_2 with lattice parameters of $a = 4.584 \text{ \AA}$ and $c = 2.953 \text{ \AA}$ (JCPDS, Card No. 89-4920).^{22, 25} The high intensity for the (002) peak are observed from both samples, indicates the synthesised structure is well crystallised and grows perpendicular to the substrate.²⁹ Fig. 1B shows the SEM image of the rutile TiO_2 sample after calcination at 450°C . It reveals an evenly distributed surface structure with well-defined pyramid-shaped crystal facets (Fig. 1B and top inset). The cross-sectional SEM image (bottom inset in Fig. 1B) indicates that a rod-like array film with exposed pyramid-shaped crystal facets is directly grown on the FTO substrate, having a film thickness of *ca.* $5 \mu\text{m}$. To obtain more detailed structural information, the calcined products were further examined by TEM technique, as shown in Fig. 1C. It can be seen that the whole rutile crystal is a combination of cuboid and pyramid-shaped structures, as schematically shown in Fig. 1D. The SAED and HRTEM image (insets in Fig. 1C) demonstrate a good single-crystal nature of the rutile TiO_2 structure. SAED pattern further indicates that the cuboid crystal facets are parallel to [110], the pyramid-shaped crystal facets are parallel to [111], and a preferred growth along [001] direction.^{22, 25} The HRTEM image confirms the fringe spacings of $3.23 \text{ \AA}$ and $2.95 \text{ \AA}$, which are consistent with the *d* values of (110) and (001) planes of the tetragonal rutile TiO_2 , respectively. Based on the above investigations, it can be confirmed that the top exposed pyramid-shaped crystal facets are {111} facets as illustrated in Fig. 1D.^{22, 25}

Fig. 1 (A) XRD patterns of the as-synthesised and calcined product in Ar. (B) SEM image of the calcined TiO_2 sample in Ar; insets of high magnification SEM image (top) and cross-sectional SEM image (bottom). (C) TEM image of an individual rod-like structure; insets of SAED pattern (top) and HRTEM image (bottom). (D) Schematic diagram of an individual rod-like structure.

Fig. 2 (A) Optical photos of the FTO substrate and the as-synthesised samples with and without H_2O_2 . (B) SEM image of the as-synthesised sample without H_2O_2 . (C) and (D) SEM images of the as-synthesised samples with different HCl concentrations. (E) and (F) SEM images of the as-synthesised samples with different TiN concentrations. (G) SEM image of the as-synthesised sample at 180°C for 24 h; 30 mL of reaction solution containing 0.88 M H_2O_2 , 4.6 M HCl and 0.022 M TiN. (H) SEM image of the as-synthesised sample at 200°C for 18 h. 30 mL of reaction solution containing 0.88 M H_2O_2 , 4.6 M HCl and 0.022 M TiN.

To optimise the formation of the rutile TiO_2 film with 100% exposed pyramid-shaped (111) surface onto FTO substrate, the effect of hydrothermal reaction conditions on the resultant rutile TiO_2 morphology was investigated. It was found that the presence of H_2O_2 in the reaction solution is critically important to the direct formation of high quality rutile TiO_2 film with exposed (111) surface onto FTO substrate. In absence of H_2O_2 , the formed film was found to possess very poor mechanical properties that easily break into pieces and peel off the substrate (Fig. 2A). Moreover, the formed film displays irregular surface morphologies with imperfect pyramid-shaped crystal facets (Fig. 2B). This could be ascribed to the formation of peroxotitanium complex by Ti^{4+} reacting with H_2O_2 during hydrothermal reaction to slow the hydrolysis of titanium precursor to favor the formation of {111} facets.^{12, 30-32} The effect of HCl and TiN precursor's concentration in the reaction solution was

investigated by maintaining the H_2O_2 concentration at 0.88 M and the reaction temperature at 200 °C for 24 h. Our experiments demonstrate that high quality rutile TiO_2 films with exposed pyramid-shaped (111) surface can be formed onto FTO substrate with HCl concentrations between 3.1-6.8 M when the concentration of TiN precursor is kept at 0.022 M. The particulate film (Fig. 2C) or irregular aggregate film (Fig. 2D) are obtained when low (1.5 M) or high (9.2 M) concentrations of HCl were used. Figs. 2E and F show the SEM images of the samples fabricated in a reaction solution (with a total volume of 30 mL) containing 0.88 M H_2O_2 , 4.6 M HCl and different concentrations of TiN at 200 °C for 24 h. When 0.011 M TiN was used, a usual morphology of rutile TiO_2 having sub-micrometer-sized rectangular parallelepiped structures without exposed pyramid-shaped {111} crystal facets become the dominant structures formed onto the FTO substrate.³³ Uniform rutile TiO_2 films with exposed pyramid-shaped (111) surface can be formed on the FTO substrate with the concentration of TiN ranged from 0.017 to 0.033 M (Fig. 2F, TiN concentration of 0.028 M). Moreover, the sizes of the exposed pyramid-shaped structures was found to decrease with increasing TiN concentration in reaction solution (Fig. 1B and Fig. 2F). The experimental results indicate that the rutile TiO_2 film with exposed high-quality (111) surface cannot be obtained when the reaction temperature was below 200 °C (e.g., 180 °C shown in Fig. 2G). It was also found that a reaction time of 24 h is necessary to obtain high-quality rutile TiO_2 film with exposed pyramid-shaped (111) surface. A shorter reaction time results in the formation of rutile TiO_2 film with exposed imperfect pyramid-shaped structures as shown in Fig. 2H. The above investigations suggest that to directly grow high-quality rutile TiO_2 film with exposed pyramid-shaped (111) surface onto the FTO substrate, the optimal reaction solution (30 mL) composition should be 0.88 M H_2O_2 , 4.6 M HCl and 0.022 M TiN, and the optimal reaction temperature and time should be 200 °C and 24 h, respectively. Such optimal experimental conditions were subsequently adopted.

Fig. 3 (A) UV/Vis absorption spectra of the calcined sample in Ar. (B) Plot of transformed Kubelka-Munk function versus the energy of light.

Fig. 3A shows the UV-visible diffuse reflectance spectra of the rutile TiO_2 film with 100% exposed pyramid-shaped (111) surface on FTO substrate after calcination at 450 °C for 2 h in Ar. Fig. 3B shows the derived plot of the Kubelka-Munk function versus the energy of the absorbed light.¹ Assuming the synthesised rutile TiO_2 is an indirect semiconductor, the bandgap of the obtained rutile TiO_2 with exposed pyramid-shaped {111} facets is extrapolated to be 2.96 eV, which is narrower than the bandgap for normal form of rutile TiO_2 (i.e., 3.10 eV), giving a

raise to the visible light activity.^{34, 35} A similar phenomenon was recently reported by Feng *et al.*²² Their studies confirmed that the presence of Ti^{3+} in the bulk TiO_2 creates a vacancy band of electronic states below the conduction band (CB), leading to a narrowed bandgap capable of absorbing visible light.²² This has also been demonstrated by our recent study.²⁵

Fig. 4 Atomic structures of rutile TiO_2 (110) and (111) surfaces.

For rutile TiO_2 , theoretical and experimental studies have demonstrated that {111} crystal facets are high energy facets, possessing superior activity toward photocatalytic oxidation.³⁶⁻³⁸ In this work, the first-principle DFT calculations was employed to study the surface energy of the {110} and {111} faceted rutile TiO_2 . The atomic structure of (111) surface used for the calculation was established according to the rutile TiO_2 crystal structure. The calculated surface energies are 0.35 J/m² and 1.46 J/m² for (110) and (111) surfaces, respectively (Fig. 4). Our calculation results suggest that the surface energy for {111} faceted rutile TiO_2 is 4 times greater than that of a commonly obtained {110} faceted rutile TiO_2 , which could be an important attribute for the high photocatalytic activity.

Fig. 5 (A) and (B) Voltammograms obtained from the rutile TiO_2 film photoanode in 0.10 M NaNO_3 supporting electrolyte, under different UV and visible light intensities, respectively. (C) and (D) Relationships of saturation photocurrent with UV and visible light intensity. The saturation photocurrent data were derived from voltammograms shown in Figs. 5A and B at +0.40 V of applied potential, respectively.

The as-synthesised rutile TiO_2 with 100% exposed pyramid-shaped (111) surface on FTO substrate was thermally treated at 450 °C for 2 h in Ar and used as photoanodes for evaluation of UV and visible light photoelectrocatalytic activities using water

as the probe compound. The selection of water as the probe compound for the evaluation was because of the global interest in water splitting for hydrogen production using TiO_2 based photocatalysts.^{39, 40} All photoanodes were fixed into a special electrode holder with a 0.785 cm^2 exposed area for illumination and photocurrent measurement. Figs. 5A and B show the voltammograms of the photoanodes in 0.10 M NaNO_3 supporting electrolyte with or without light illumination. The results confirm the photoelectrocatalytic activities of the photoanode toward water oxidation under both UV and visible light irradiations. For all cases without illumination, only a negligible dark current was observed. For all cases under UV and visible light illumination, the measured photocurrents (I_{ph}) initially increased linearly with the applied potential bias due to the limitation of free photoelectron transport within the rutile TiO_2 photocatalyst films.¹⁰⁻¹² The photocurrents saturated at higher potentials (*ca.* 0.32 V and 0.33 V under UV and visible light illumination, respectively) owing to the limitation of the interfacial processes at the photocatalyst/electrolyte interface.¹⁰⁻¹² An increase in the light intensity leads to an increase in the saturated photocurrents (I_{sph}). For a given light intensity (ϕ), the magnitude of I_{sph} represents the maximum rate of water oxidation.¹⁰⁻¹² Figs. 5C and D show the plots of I_{sph} against ϕ for UV and visible photocatalysis, respectively. The I_{sph} values for UV and visible light photocatalysis were derived from the voltammograms shown in Figs. 5A and B at $+0.40 \text{ V}$, respectively. Linear relationships were obtained for both cases, having slope values of 0.144 mA mW^{-1} ($R^2 = 0.999$) and $0.102 \text{ } \mu\text{A mW}^{-1}$ ($R^2 = 0.998$) for UV and visible light photocatalysis, respectively. Under the employed experimental conditions, the slope of the $I_{\text{sph}}-\phi$ curve represents the photoelectrocatalytic activity of the photoanode.¹⁰⁻¹² The higher slope value obtained under UV illumination suggests a higher UV photoelectrocatalytic activity of the photoanode. In this work, the determined value of $0.102 \text{ } \mu\text{A mW}^{-1}$ from the visible light illuminated photoanode represents an excellent visible light photoelectrocatalytic activity, although this value is much lower than the determined photoelectrocatalytic activity for the UV light illuminated photoanode, which could be attributed to highly reactive $\{111\}$ faceted surface.^{22, 36, 37} A number of narrow bandgap (*e.g.*, CdS) semiconductor photocatalysts have been reported to have higher visible light photocatalytic activities.^{18, 41} However, they are often suffered from severe photocorrosion.⁴² In this work, the fabricated Ti^{3+} doped rutile TiO_2 film possesses concurrently UV and visible light activities. Importantly, such a self-doped semiconductor photocatalyst has high photocorrosion resistance and thermal stability,^{21, 22} promising for photocatalysis-based applications.

We have previously demonstrated that the photoelectron transport resistance can be used to manifest the charge transport process inside a photocatalyst and developed a simple, effective photoelectrocatalytic method capable of quantitatively characterise the intrinsic photoanode resistance (R_0) under UV illumination.¹⁰⁻¹² However, concurrently determining R_0 values of the same photoanode under UV and visible light has not been conducted. It is well known that UV light promoted photoelectrons will occupy higher energetic positions because such photoelectrons possess higher energies than those promoted by visible light. This may mean that the transport pathways inside

the photocatalyst for UV light promoted photoelectrons could differ from those of visible light promoted photoelectrons. This is an interesting scientific query for the field of semiconductor photocatalysis. Such a query could be answered by concurrently determining R_0 values of the same photoanode under UV and visible light illumination.

Fig. 6 (A) and (B) Relationships between the measured resistance and saturation photocurrent under UV and visible light illumination, respectively. (C) and (D) Relationships between the resistance and the inversed saturation photocurrent under UV and visible light illumination, respectively. Data were derived from Figs. 5A and B.

For each given light intensity (UV and visible light), the voltammograms shown in Figs. 5A and B revealed a linear photocurrent increase with applied potential bias, before being levelled off. The linear part of the voltammogram exhibits a pure resistor-type behaviour, meaning that the overall reaction is controlled by the photoelectron transport process inside the photocatalyst layer.¹⁰⁻¹² Under such conditions, the photocurrent (the rate of the overall reaction) is determined by the rapidity of the photoelectron transport across the photocatalyst layer.¹⁰⁻¹² The overall resistance (R) value of each voltammogram obtained from UV and visible light illuminated photoanode can be calculated based on the reported method.¹⁰⁻¹² Plotting R values against I_{sph} values derived from Figs. 5A and B give hyperbolic curves as shown in Figs. 6A and B for UV and visible light illuminated photoanode, respectively. The quantitative relationship between R and I_{sph} can be expressed as:

$$R = k/I_{\text{sph}} + R_0 = R_1 + R_0 \quad (1)$$

where k is a proportionality constant; I_{sph} is the saturation photocurrent; R_0 and R_1 are the constant and the variant components of the resistance, respectively.

Based on Equation 1, the total reaction resistance (R) consists of a variant ($R_1 = k/I_{\text{sph}}$) and a constant (R_0) component. For a given photoanode, R_1 represents the interfacial reaction resistance, depending on experimental conditions (*i.e.*, light intensity and reactant concentration), while R_0 collectively represents the TiO_2 crystal boundary resistances and the resistances at TiO_2 /conducting substrate interface, which is an intrinsic property of the photocatalyst layer (hence the photoanode), independent of experimental conditions.¹⁰⁻¹² Figs. 6C and D show the plots of R

values against $1/I_{\text{sph}}$ values for UV and visible light illuminated photoanode. The obtained liner relationships indicate that the variant resistance component is inversely proportional to I_{sph} . R_0 values of 93.5 Ω and 91.3 Ω for UV and visible light illuminated photoanode can be respectively obtained from the intercepts of $R-1/I_{\text{sph}}$ curves shown in Figs. 6C and D. Interestingly, the determined R_0 value for the UV light illuminated photoanode is very close to that of the visible light illuminated photoanode. This demonstrates that under the experimental conditions, the rutile TiO_2 photoanode possesses similar intrinsic resistance for UV and visible light photocatalytic processes. This also implies that the rate of charge recombination is similar under UV and visible light irradiation. This also implies that although the UV and visible light promoted photoelectrons could percolate across the semiconductor photocatalyst layer via different energetic pathways, the electron transport resistances of all energetic pathways inside the semiconductor photocatalyst are similar.

Fig. 7 Relationships between onset potential and light intensity (UV and visible light); the onset potential data were derived from Figs. 5A and B.

It has been widely accepted that for n-type semiconductors (e.g., TiO_2), the flat band potential (no band bending) and the surface Fermi level coincide essentially with the conduction band edge potential.⁴³ Nelson and co-workers have demonstrated that onset potential measurement (onset for anodic photocurrent in $I-E$ curves) can be used to approximate the top conduction band edge potential of TiO_2 film.⁴⁴ Fig. 7 shows the relationships between the onset potential and light intensity for UV and visible light illuminated photoanode. The onset potential values used in Fig. 7 are derived from the voltammograms shown in Figs. 5A and B. For all light intensities investigated, the measured onset potentials from the UV light illuminated photoanode are more negative than that obtained from the visible light illuminated photoanode. The measured onset potentials for both UV and visible light illuminated photoanode are found to be cathodically shifted with increased light intensity. The light intensity shows a more significant effect on onset potentials of UV light illuminated photoanode. These suggest that the top edge of the conduction band changes with light intensity. The cathodically shifted onset potentials at higher light intensity also suggest that the photoelectrons tend to occupy lower energetic levels within the conduction band before higher energetic levels.

Conclusions

We have successfully applied a facile hydrothermal method to directly grow the rutile TiO_2 film with 100% exposed pyramid-shaped (111) surface onto a FTO conducting substrate and used as the photoanode after calcined at 450 $^{\circ}\text{C}$ for 2 h in argon (Ar). The resultant photoanode possesses excellent UV and visible light photoelectrocatalytic activities toward water oxidation. The determined value of 0.102 $\mu\text{A mW}^{-1}$ from the visible light illuminated photoanode represents an excellent visible light photoelectrocatalytic activity, although the value is much lower than the determined photoelectrocatalytic activity (0.144 mA mW^{-1}) under UV light illumination. The origin of visible light activity can be attributed to the doped Ti^{3+} in the bulk TiO_2 . The superior photoelectrocatalytic activity could be due to the high reactivity of the exposed high-energy (111) surface and the superior photoelectron transport property. A photoelectrocatalytic method has been successfully applied to manifest the photoelectron transport properties inside the rutile TiO_2 film and concurrently quantify the inherent resistances of UV and visible light illuminated photoanode. The determined R_0 values were 93.5 and 91.3 Ω for UV and visible light illuminated photoanode, respectively. The similar R_0 values imply a similar photoelectron transport resistance inside the rutile TiO_2 film under UV and visible light irradiation, confirming that the measured R_0 is an inherent property of the photocatalyst film. This also implies that the rate of charge recombination is similar under UV and visible light irradiation. To our knowledge, this is the first time the electron transport properties of a rutile TiO_2 photoanode have been concurrently investigated under UV and visible light irradiation.

Notes and references

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