

ENHANCED PHOTOELECTROCATALYTIC ACTIVITY OF A Pt-MODIFIED Ti/TiO₂/BiVO₄ PHOTOELECTRODE FOR WATER OXIDATION

IZBOLJŠANJE FOTOKATALITIČNE AKTIVNOSTI S PLATINO MODIFICIRANE Ti/TiO₂/BiVO₄ FOTOELEKTRODE ZA OKSIDACIJO VODE

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Pt was successfully deposited on the Ti/TiO₂/BiVO₄ photoelectrode surface using pulsed potential electrodeposition from an H₂PtCl₆ aqueous solution. The photoelectrodes were characterized with the XRD, SEM, EDS and XPS techniques. The prepared Pt-modified Ti/TiO₂/BiVO₄ electrode exhibited both an enhanced visible-light absorption and higher photoconversion efficiency for water oxidation under light irradiation. The photocurrent density on the Pt-modified Ti/TiO₂/BiVO₄ photoanode was about 0.3845 mA/cm² at 0.6 V (vs SCE), and the photoconversion efficiency was 8.4 times higher than that of Ti/TiO₂ and 2.1 times higher than that of the Ti/TiO₂/BiVO₄ photoanode. Electrochemical impedance spectroscopy was performed to confirm the charge transfer at the photoelectrode surface. It provided a strategy for the design of composite films for more efficient photoelectrochemical water-splitting applications.

Keywords: water oxidation, Ti/TiO₂/BiVO₄ photoanode, photoelectrochemical, nanotube

Avtorja članka sta uspešno, s postopkom pulzno-potencialnega električnega nanosa iz vodne raztopine H₂PtCl₆, nanesla platino (Pt) na površino Ti/TiO₂/BiVO₄ fotoelektrode. Izdelane fotoelektrode sta okarakterizirala z rentgensko difrakcijo (XRD), vrstično elektronsko mikroskopijo (SEM), energijsko disperzijsko spektroskopijo (EDS) in rentgensko fotoelektronsko spektroskopijo (XPS). Pripravljene s Pt modificirane Ti/TiO₂/BiVO₄ elektrode imajo izboljšano absorpcijo vidne svetlobe in so tudi fotokonverzijsko učinkovitejše pri obsevanju s svetlobo za vodno oksidacijo. Fototokovna gostota s Pt modificirane Ti/TiO₂/BiVO₄ fotoanode je okoli 0,3845 mA/cm² pri 0,6 V (v primerjavi z SCE), in fotokonverzijska učinkovitost je bila 8,4-krat višja kot pri Ti/TiO₂ in 2,1-krat višja kot pri Ti/TiO₂/BiVO₄ fotoanodah. Elektrokemijska impedančna spektroskopija je potrdila proces prenosa naboja na površini fotoelektrode, kar omogoča novo strategijo oblikovanja kompozitnih tankih plasti (filmov) za učinkovitejšo fotoelektrokemično cepitev vode (na vodik in kisik).

Gljučne besede: oksidacija vode, Ti/TiO₂/BiVO₄ fotoanoda, fotoelektrokemija, nanocevke

1 INTRODUCTION

Photocatalytic water splitting under visible light, namely the solar water splitting, has attracted great attention.¹ Many kinds of semiconductors such as TiO₂,^{2,3} WO₃⁴ and so on are considered to be the most promising materials with light-absorption ability. Various TiO₂ nanostructures including nanowires, nanofilms and nanofibers have been used as the photoanodes for solar water splitting.⁵⁻⁷ However, the bandgap of TiO₂ shows that TiO₂ has almost no visible-light-absorption ability.⁸

There are two main ways to solve this problem. One is to dope TiO₂ with other atoms to expand the light-absorption edge of TiO₂.^{9,10} The other is to combine TiO₂ with other narrow-bandgap materials to enhance the light-absorption ability.¹¹ BiVO₄ has been identified as a typical material that can enhance the visible-light response for solar water oxidation.^{12,13} Moreover, TiO₂/BiVO₄ can enhance the photocatalytic activity be-

cause of the suitable energy-level alignment between BiVO₄ and TiO₂.^{14,15}

Our work was designed to develop the photocatalytic performance of TiO₂ nanotubes by coupling them with BiVO₄.¹⁶ The photocurrent of the TiO₂ nanotube electrode was increased when coupled with BiVO₄. It was revealed that the method of the photoanode-film fabrication is an important factor for the photocatalytic activity. However, the photocatalytic activity of these photoanode films also needs to be improved for practical solar water splitting. Noble metals, especially Pt nanoparticles, have attracted attention because they can be used as the catalysts in the interfacial charge-transfer process.^{17,18} Therefore, the combination of Pt and Ti/TiO₂/BiVO₄ photoanodes was expected to enhance the photocatalytic performance of Ti/TiO₂/BiVO₄ electrodes. Pt nanostructures were deposited on Ti/TiO₂/BiVO₄ photoanodes using pulsed potential electrodeposition in an H₂PtCl₆ aqueous solution and the enhanced photocatalytic ability for solar water oxidation was confirmed.

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2 EXPERIMENTAL PART

2.1 Preparation of the Ti/TiO₂/BiVO₄ film photoelectrode

TiO₂ nanotubes were prepared with anodization in accordance with the previous findings¹⁶ and then annealed in a furnace at 450 °C for 2 h to obtain a Ti/TiO₂ film.

BiOI was electrodeposited on a TiO₂ substrate.¹⁹ Bi(NO₃)₃·5H₂O was dissolved in a 0.4 M KI solution and the pH was adjusted to 1.7 by adding HNO₃, obtaining a 0.04 M Bi(NO₃)₃ solution. Then, the solution was mixed with absolute ethanol containing 0.23 M p-benzoquinone under vigorous magnetic stirring. A CHI660E electrochemical workstation (Shanghai Chenhua Device Company, China) was used for electrodeposition and the subsequent photocatalytic performance. Electrodeposition was performed potentiostatically at -0.15 V vs SCE at room temperature for 15 s.

Then the working electrode was put into a DMSO solution containing 0.2 M vanadyl acetylacetonate (VO(acac)₂) and was heated at 450 °C for 2 h in air. In order to remove the excess V₂O₅ from the Ti/TiO₂/BiVO₄ photoanode, the sample was soaked in 1 M NaOH solution for 2 h while being stirred. At last, the resulting Ti/TiO₂/BiVO₄ photoanode was rinsed with deionized water and dried in air.

2.2 Preparation of a Pt-modified Ti/TiO₂/BiVO₄ film electrode

Pt nanoparticles were loaded on Ti/TiO₂/BiVO₄ with pulsed electrodeposition in a 4 mmol/L H₂PtCl₆ solution. The deposition process was also conducted on the CHI660E workstation in a pulsed potentiostatic regime with negative pulse at -0.5 V vs SCE for 75 ms and -0.2 V vs SCE for 200 s. The electrodeposition time was about 500 s.

2.3 Characterization of Ti/TiO₂/BiVO₄ and Pt-modified Ti/TiO₂/BiVO₄ electrode

The surface morphology of the photoelectrodes was observed with a field-emission scanning electron microscope (FESEM, Hitachi S-4700). The composition was investigated with energy-dispersive X-ray spectroscopy (EDS). The microstructure of the Pt-modified Ti/TiO₂/BiVO₄ film was characterized with a transmission electron microscope (TEM, Tecnai G2 F30) combined with an energy-dispersive X-ray spectroscopy detector. The composition present in the film electrode was also characterized with a small-angle diffractometric study carried out on a Rigaku D/max 2550PC X-ray automatic diffractometer. The surface composition and chemical-valence status of the elements were characterized using a Kratos AXIS Ultra DLD (Japan) X-ray photoelectron spectroscopy (XPS). The optical performance of the as-prepared photoanodes was evaluated using a UV-vis Lambda 750S with a wavelength ranging from

300 nm to 600 nm. The band gap of the semiconductor was calculated employing the following equation:²⁰

$$(\alpha h\nu)^2 = h\nu - E_g \quad (1)$$

Where α is the absorption coefficient, ν is the light frequency and E_g is the band gap of the semiconductor.

Electrochemical measurements were recorded in 0.2 M Na₂SO₄ by CHI660E using a platinum sheet and a saturated SCE electrode as the counter electrode and reference electrode, respectively. Electrochemical impedance spectroscopy (EIS) was carried out under the open-circuit voltage with frequencies ranging from 10⁵ Hz to 10⁻² Hz with an AC voltage amplitude of 5 mV. The potentials of the I-V curves and the PEC performance experiments were also controlled with CHI660E. A 150-W Xe lamp (25 mW/cm², Beijing Trust Tech Co. Ltd) was used to provide visible light.

The photoconversion efficiency is a function of the photocurrent density and can be calculated using the following equation:^{21,22}

$$\eta = \frac{J(E_{RHE} - V_{app})}{P_{light}} \quad (2)$$

where J is the photocurrent density at the measured bias, E_{RHE} is the standard reversible potential of 1.23 V corresponding to the Gibbs free energy change per photon required for water splitting, V_{app} is the applied bias potential vs SCE and P_{light} is 25 mW/cm² in our work.

3 RESULTS AND DISCUSSION

3.1 XRD analysis

The crystalline structures of the annealed Ti/TiO₂ film and Ti/TiO₂/BiVO₄ photoanode were characterized with x-ray diffraction (XRD). The Ti/TiO₂ film showed that the peaks appear at around 20° corresponding to TiO₂ in the amorphous state due to the broad peak. From the XRD pattern, the diffraction peaks of Ti from the Ti

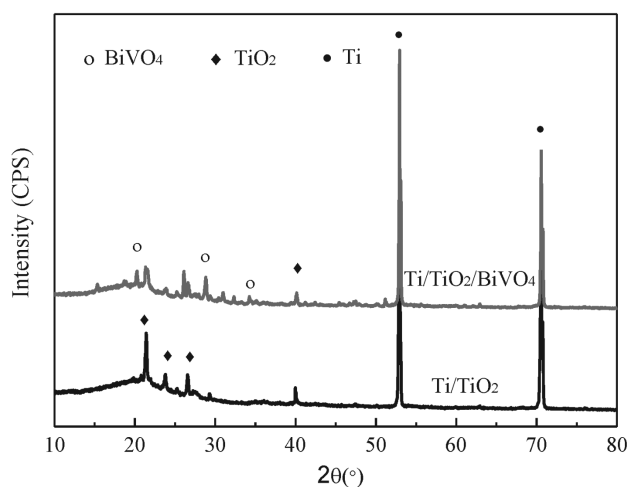


Figure 1: XRD patterns of the Ti/TiO₂ film and Ti/TiO₂/BiVO₄ photoanode

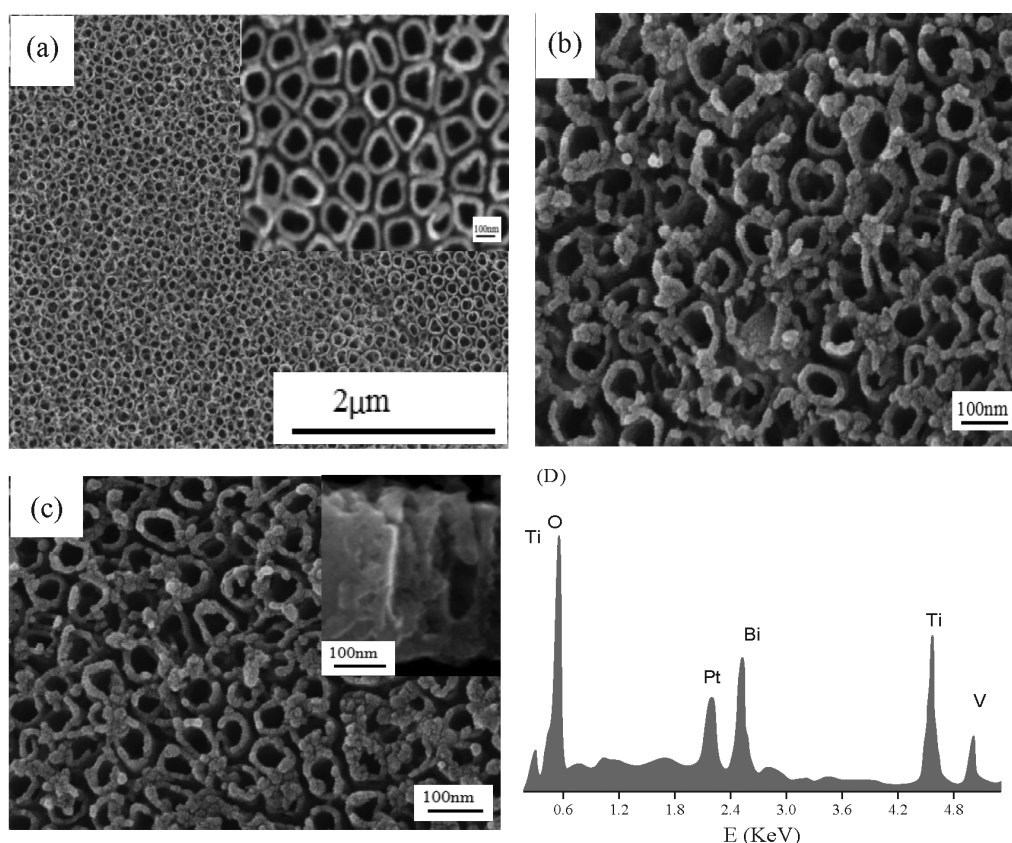


Figure 2: SEM images and EDS analysis of the prepared samples: a) image of Ti/TiO₂ film, b) image of Ti/TiO₂/BiVO₄ film, c) image of Pt-modified Ti/TiO₂/BiVO₄ film, the inset image is the cross-section of the sample, d) EDS analysis of the sample and c)

substrate and anatase TiO₂ were detected (JCPDS No. 84-1285). After the modification of the BiVO₄ layer, new peaks appear, which correspond to the crystalline state of BiVO₄. The observed diffraction peaks are in conformity with the monoclinic scheelite structure (JCPDS 14-0688). From the XRD pattern, it is clear that BiVO₄ could be successfully modified on the Ti/TiO₂ film. Because of a small amount of coatings, the intensity of the diffraction peaks of BiVO₄ is also weak. The XRD spectra of the Pt-modified Ti/TiO₂/BiVO₄ photoanode is not shown here because it is almost identical with the Ti/TiO₂/BiVO₄ photoanode. It is speculated that the reason for this is the fact that the doping content of Pt on the surface of the Ti/TiO₂/BiVO₄ film is low and the dispersion is high.

3.2 Morphology analysis

Figure 2 shows SEM images of the Ti/TiO₂ film, Ti/TiO₂/BiVO₄ film and Pt-modified Ti/TiO₂/BiVO₄ film. TiO₂ nanotubes with a pore diameter of 80 nm are shown in **Figure 2a**. The BiVO₄ nanoparticles are uniformly distributed in the voids and surface of the nanotube TiO₂ film (**Figure 2b**).

Figure 2c presents the surface morphology of the Pt-modified Ti/TiO₂/BiVO₄ film fabricated with pulsed potential deposition of Pt on the Ti/TiO₂/BiVO₄ film.

Figure 2d shows the EDS energy spectrum of the Pt-modified Ti/TiO₂/BiVO₄ film. The EDS energy spectrum shows that there are Ti and O in the film, and there is a weak Pt signal, which shows that the Pt doping amount is small and Pt is uniformly dispersed on the surface of the Ti/TiO₂/BiVO₄ film. Bi and V in the energy spectrum show that BiVO₄ is loaded in the composite photoanodes. This structure gives the photoanodes a high surface area, which can greatly increase the contact be-

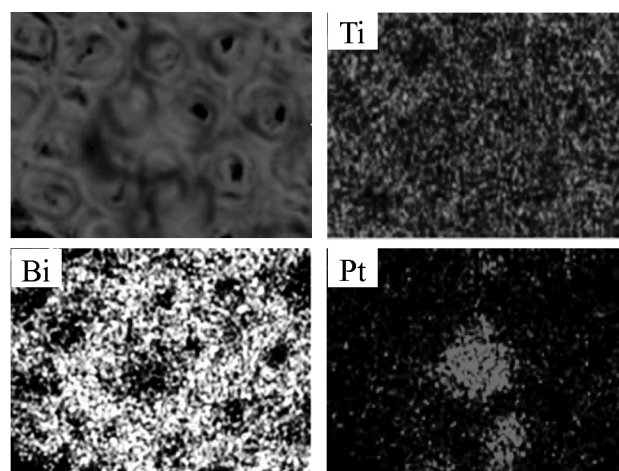


Figure 3: TEM images and EDS analysis, showing the distribution of elements Pt, Bi and Ti

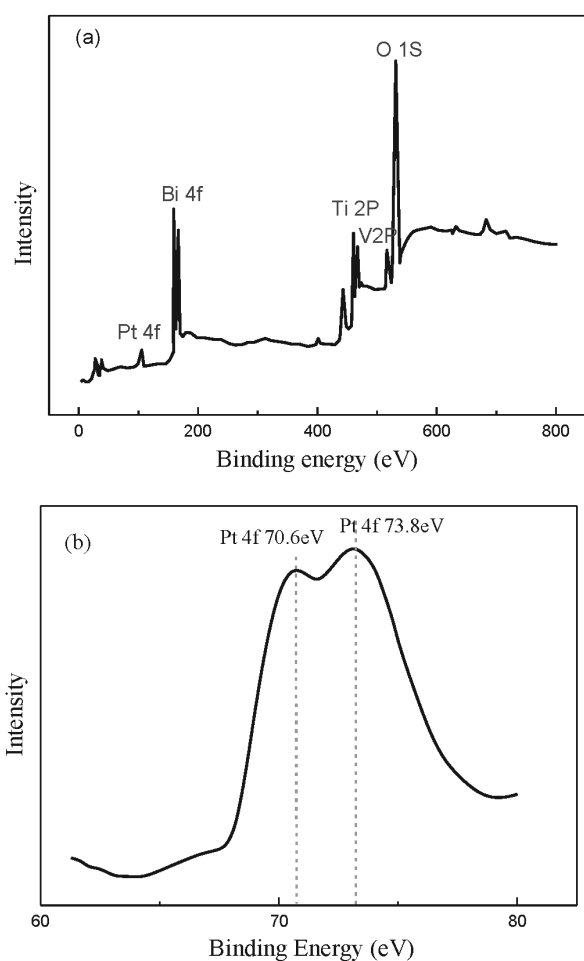


Figure 4: XPS spectrum of the Pt-modified Ti/TiO₂/BiVO₄ films: a) the binding energy is from 0 eV to 800 eV, b) the magnified spectrum at around 60–80 eV

tween the Pt catalyst and solution, resulting in improving the photocatalytic properties of the photoanodes.

The TEM images and EDS analysis of the Pt-modified Ti/TiO₂/BiVO₄ film are shown in **Figure 3**. The TiO₂ nanotubes and the deposits are clearly shown. The EDS analysis map shows that the elements are distributed across the nanotubes. Elements Pt, Bi and V are homogeneously distributed on the prepared sample.

3.3 XPS analysis

Figure 4 shows XPS spectra of the Pt-modified Ti/TiO₂/BiVO₄ film. It can be found on the full spectrum (**Figure 4a**) that five elements, Ti, Pt, O, Bi and V, exist in the Pt-modified Ti/TiO₂/BiVO₄ film. The strong peaks at around 460 eV were matched with the data about Ti⁴⁺ in TiO₂.²³ The peaks at around 160 eV were attributed to Bi 4f, and the peaks at around 520 eV were matched with V 2p. These results indicated that the valence states of Bi and V were Bi³⁺ and V³⁺, respectively.²³ The peaks at around 530 eV correspond to O 1s.

Figure 4b is the Pt 4f spectrum of the ternary complex film. It can be seen from the diagram that the peak

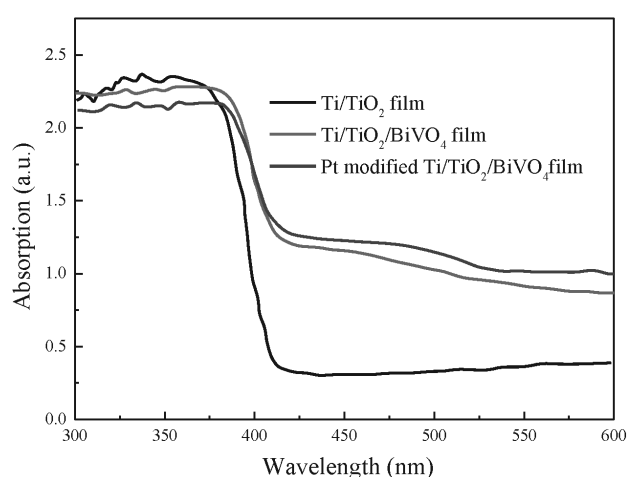


Figure 5: UV-Vis spectra of the three kinds of prepared samples

is at 70.6 eV and 73.8 eV, which means that the valence state of Pt is 0.²⁴ It is proved that Pt was successfully loaded in the Ti/TiO₂/BiVO₄ film using pulsed deposition in the form of a simple metal substance.

3.4 UV-Vis absorption spectrum analysis

UV-Vis spectra of the Ti/TiO₂, Ti/TiO₂/BiVO₄ and Pt-modified Ti/TiO₂/BiVO₄ film are shown in **Figure 5**. The absorption edge of the annealed Ti/TiO₂ film was at around 375 nm, which was in agreement with the band gap of TiO₂ (3.2 eV).²⁵ After being coupled with BiVO₄, the absorption edge of Ti/TiO₂/BiVO₄ was significantly enhanced in a visible-light region between 400 nm and 500 nm. The reason is the fact that the band gap of BiVO₄ is 2.4 eV.^{26,27} According to Equation (1), the band-gap energy of Ti/TiO₂/BiVO₄ was around 2.85 eV. The UV-Vis spectra of the Pt-modified Ti/TiO₂/BiVO₄ film shows that the light-absorption range of the film is not an obvious red shift because Pt has no obvious effect on the light absorption. In addition, the band-gap energy of the Pt-modified Ti/TiO₂/BiVO₄ film was 2.80 eV based on Equation (1).

3.5 Photoelectrocatalytic performance

Figure 6 gives photoelectrochemical performance plots for the Ti/TiO₂ film, Ti/TiO₂/BiVO₄ film and Pt-modified Ti/TiO₂/BiVO₄ film under a 150 W Xe-lamp illumination. The photocurrent density of the Ti/TiO₂ film was 0.0308 mA/cm² at 0.6 V (vs SCE). These results clearly indicated that the modification of the Ti/TiO₂ film with BiVO₄ effectively reduced the recombination of electrons and holes generated in the Ti/TiO₂/BiVO₄ film due to the formation of a heterojunction.²⁸ The photocurrent density of the Pt-modified Ti/TiO₂/BiVO₄ film was 0.3845 mA/cm² at 0.6 V (vs SCE), which was almost 2.3 times higher than that of the Ti/TiO₂/BiVO₄ film. The dramatic enhancement of the photocurrent response of the Pt-modified Ti/TiO₂/BiVO₄

film was an indication that Pt may have positively modulated the surface kinetics of the photoelectrode during solar water splitting.²⁹

The *i-t* curves of the prepared samples under a constant bias of 0.6 V vs SCE are shown in **Figure 6b**. The photocurrent densities of all the photoanodes dropped rapidly to nearly zero when the simulated sunlight was

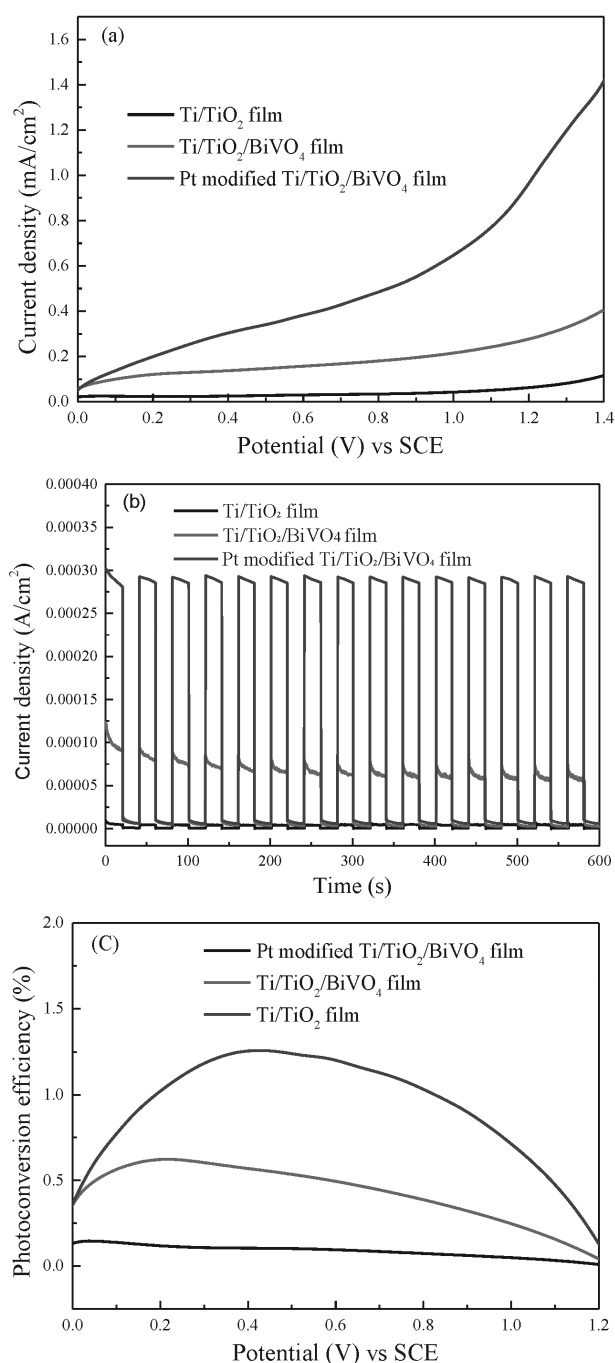


Figure 6: Photoelectrochemical measurements of photoelectrodes in a 0.2 M Na₂SO₄ solution under 150 W (25 mW/cm²) Xe-lamp illumination: a) LSV curve under simulated sunlight illumination, b) *i-t* curves measured at 0.6 V vs SCE, c) calculated photoconversion efficiency of the prepared samples

turned off, and the photocurrent density quickly recovered when the light was turned on. The rapid rising and falling of the photocurrent density indicated a fast charge-carrier transport in the Pt-modified Ti/TiO₂/BiVO₄ photoelectrode, which was attributed to a high penetration path for ion diffusion facilitated by Pt.²⁹ The transient photocurrent response generated in the Pt-modified Ti/TiO₂/BiVO₄ photoelectrode was nearly 3 times greater than that of the Ti/TiO₂/BiVO₄ photoanode. The photoconversion efficiency was calculated using Equation (2) and the results are shown in **Figure 6c**. The Pt-modified Ti/TiO₂/BiVO₄ photoanode also achieved the maximum conversion efficiency of 1.26 % at 0.4 V vs SCE, which was about 2.1 times higher than that of the Ti/TiO₂/BiVO₄ photoanode (0.6 % at a bias of 0.2 V vs SCE) and 8.4 times greater than that of the Ti/TiO₂ photoanode (0.15 % at a bias of 0.01 V vs SCE). The improvement in the photoconversion efficiency was mainly attributed to the enhanced bulk-charge separation and more efficient surface-charge transfer in the Pt-modified Ti/TiO₂/BiVO₄ photoelectrode due to the weak effect of Pt on the light absorption.

EIS measurement was used to characterize the photoelectrochemical interfacial reaction of the three kinds of prepared samples for water splitting under light irradiation. **Figure 7** shows the Nyquist plots for the Ti/TiO₂, Ti/TiO₂/BiVO₄ and Pt-modified Ti/TiO₂/BiVO₄ photoelectrodes in a 0.2 M Na₂SO₄ aqueous solution at 0.1 V vs SCE. The Nyquist plots of all the samples were fitted to a simple equivalent circuit (the inset in **Figure 7**). The proposed equivalent circuit consists of the charge-transfer resistance (R_{ct}), which is in parallel with the constant-phase element (CPE). And the solution resistance (R_s) is also shown here.

The diameter of a semicircle usually equals the R_{ct} parameter, which relates to the efficiency of the charge transfer at the electrode interface.³⁰ As it can be seen in **Figure 8**, the Pt-modified Ti/TiO₂/BiVO₄ photoelectrode generated the smallest semicircle, indicating a low

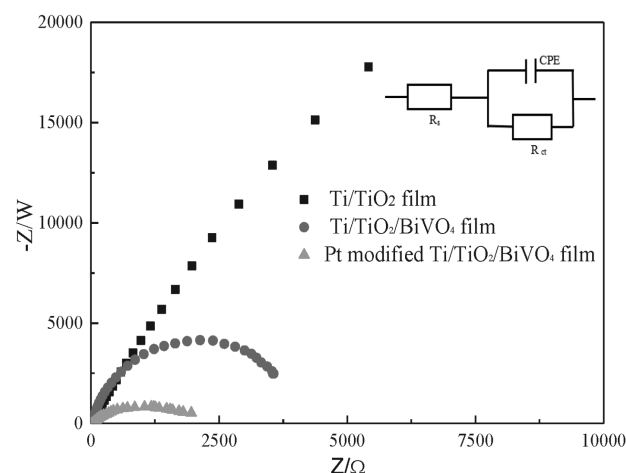


Figure 7: EIS curves measured in a 0.2 M Na₂SO₄ aqueous solution at 0.1 V vs. SCE under light irradiation

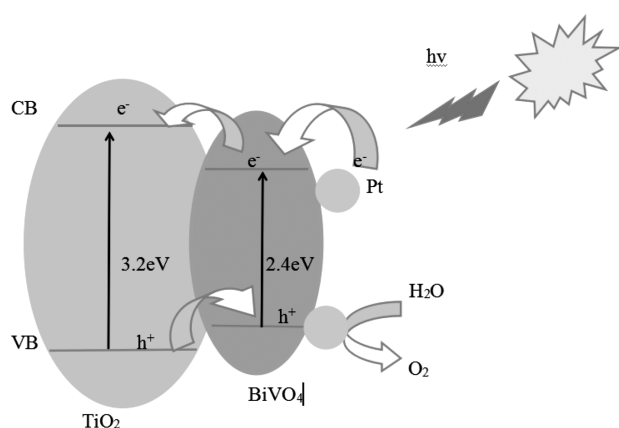


Figure 8: Schematic illustration of water-oxidation photocatalytic mechanism using the Pt-modified Ti/TiO₂/BiVO₄ film under simulated sunlight irradiation

charge-transfer impedance. However, the charge-transfer impedance was high for the Ti/TiO₂ and Ti/TiO₂/BiVO₄ photoanodes. A reduction in the charge-transfer resistance of the Pt-modified Ti/TiO₂/BiVO₄ film causes a higher carrier-separation efficiency. Moreover, Pt at the BiVO₄ surface also enhances the charge transfer at the interface of the photoelectrodes and electrolyte.³¹

Based on the analysis, a schematic diagram of the charge-transfer processes on the Pt-modified Ti/TiO₂/BiVO₄ photoelectrode for water splitting under light irradiation is shown in **Figure 8**. Photogenerated electrons can easily transfer from the conduction band of BiVO₄ to that of TiO₂ because of the matching of the conduction-band energy levels. Moreover, TiO₂ nanotubes act as the barrier for the hole of BiVO₄ to get to the Ti substrate and thus decrease the recombination of electrons and holes, as described in a previous study.¹⁶ The hole-transfer rate at the interface between the electrolyte and photoanode was highly improved by the presence of noble-metal Pt particles. The improvement of the photocatalytic property could be explained with the fact that the Pt nanoparticles act as a catalyst, enhancing the transfer rate of electrons from the electrolyte to BiVO₄ and the transfer rate of the holes from BiVO₄ to electrolyte.³² Therefore, holes can reach the BiVO₄ surface easily without any recombination, which results in efficient photocatalytic properties.

The photosensitive electrons were separated with the assistance of the TiO₂ nanotube layer from the holes. The holes could reach the BiVO₄/electrolyte interface to oxidize water to form oxygen. In the whole process, the Pt nanoparticles at the BiVO₄ surface act as the catalyst, improving the oxidation reaction with the holes because of the suppression of charge recombination. Consequently, the Pt-modified Ti/TiO₂/BiVO₄ photoelectrodes reported in the present work provide an improved efficiency of the photocatalytic system. It may be useful for other photocatalytic applications such as the degradation of an organic pollutant in an aqueous solution.

4 CONCLUSIONS

Pt-modified Ti/TiO₂/BiVO₄ films were successfully fabricated with the pulsed-potential-electrodeposition technique. In a composite photoanode system, TiO₂, BiVO₄ and Pt perform their own functions required for a high photocatalytic efficiency of water splitting. A significant enhancement in both the photocurrent and energy-conversion efficiency for water oxidation is observed after the deposition of a small amount of Pt nanoparticles on the Ti/TiO₂/BiVO₄ photoelectrode, suggesting that charge separation was improved by BiVO₄ and the water-oxidation kinetics was accelerated due to the Pt catalysts in the composite system. The analysis of the electrochemical-impedance spectra for the photoanodes indicates that Pt nanoparticles act as a catalyst, enhancing the charge-transfer rate at the interface of Ti/TiO₂/BiVO₄ and the electrolyte photoelectrode for water splitting under light irradiation.

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