Ultrasoundically prepared photocatalyst of W/WO$_3$ nanoplates with WS$_2$ nanosheets as 2D material for improving photoelectrochemical water splitting

Meysam Tayebi, Zohreh Masoumi, Byeong-Kyu Lee

Department of Civil and Environment Engineering, University of Ulsan, Ulsan, South Korea

**ARTICLE INFO**

Keywords: Ultrasonic WS$_2$ nanosheets W/WO$_3$/WS$_2$ electrode Photoelectrochemical

**ABSTRACT**

A sonochemical treatment has been an emerged technique as an interesting method for fabricating different photocatalysts with unique photoelectrochemical (PEC) properties. This study investigated the PEC performance of WO$_3$ with WS$_2$ nanosheets as a 2D material before calcination (WO$_3$/WS$_2$-90) and after calcination (WO$_3$/WS$_2$-450) prepared with sonochemical treatment. The WS$_2$ nanosheets were prepared from a liquid exfoliation phase with few-layer nanosheets, approximately 6.5 nm in thickness. The nanosheets were confirmed by UV–Vis spectroscopy and atomic force microscopy. Further, XPS, RAMAN, and SEM-EDAX analyses indicated that, following calcination of the WO$_3$/WS$_2$ electrode, the WS$_2$ nanosheets initially transformed to 2D-WO$_3$. After depositing the WS$_2$ nanosheets on the WO$_3$, the photocurrent density increased substantially. The WO$_3$/WS$_2$-450 films after calcination showed a photocurrent density of 5.6 mA.cm$^{-2}$ at 1.23 V vs. Ag/AgCl, which was 3.1 and 7.2 times higher, respectively than those of the WO$_3$/WS$_2$-90 before calcination and pure WO$_3$. Mott-Schottky and electrochemical impedance spectroscopy analyses confirmed the fabrication of the WO$_3$/WS$_2$ photoanode after calcination. The deposition of WS$_2$ nanosheets onto pure WO$_3$ increased the donor concentration (24-fold), reduced the space charge layer (4.6-fold), and decreased the flat band potential (1.6-fold), which could all help improve the photoelectrochemical efficiency. Moreover, the incorporation of WO$_3$ with WS$_2$ nanosheets as a 2D material (WO$_3$/WS$_2$-450) enhanced the incident photon current efficiency (IPCE) by 55%. In addition, the applied-bias photon-to-current conversion efficiency of the WO$_3$/WS$_2$-450 films was approximately 2.26% at 0.75 V (vs. Ag/AgCl), which is 5.6 and 9 times higher, respectively than those of WO$_3$/WS$_2$-90 and pure WO$_3$.

1. Introduction

Photoelectrochemical (PEC) water splitting is one of the most promising green approaches for hydrogen generation using solar energy which can meet the global energy challenge [1–5]. Because chemical energy is transportable, storable, and can be efficiently converted to electricity using fuel cells. PEC water splitting is likely to play a significant role in future energysustainability. Moreover, although considerable research has been conducted in this field, progress still needs to be made toward a high-efficiency water-splitting cell for solar-to-hydrogen fuel conversion.

WO$_3$, an n-type semiconductor with a band gap of 2.5–2.8 eV, has attracted considerable attention for photoelectrochemical applications because of its low-cost, non-toxicity, and good charge-carrier transport. However, WO$_3$-photoanode has some limitations, such as a weak visible light response (< 460 nm) and short hole diffusion lengths [6–9]. To date, a range of strategies for constructing heterojunctions have been proposed to alleviate these limitations, such as morphology control [10–12], doping [13–15], combination with other semiconductors [16–19], and graphene-based materials [20–23]. In particular, adopting and designing a suitable semiconductor material to use, as the photoelectrode is key to improving PEC performance.

The unique properties and potential applications of 2D materials have attracted considerable attention for the mass manufacture of thinlinear 2D materials. Further, transition-metal dichalcogenides (TMDs) with 5–10% light absorption in the visible range and a valence band maximum more positive than the water oxidation potential have shown significant promise for the production of H$_2$ or further, to reduce CO$_2$ to hydrocarbon. The high catalytic activity and excellent stability of TMDs, particularly MoS$_2$ and WS$_2$, make them promising 2D materials for energy applications. Theoretical and empirical studies have suggested that TMDs (e.g., MoS$_2$, MoSe$_2$, and WSe$_2$) are promising catalysts...
for CO₂ reduction and water splitting. This can be attributed to two different active sites: active metal sites (W or Mo) and covalent (S or Se) sites [24–26].

WS₂ and other TMDs materials can be prepared through chemical vapor deposition, physical exfoliation, or liquid phase exfoliation (LPE) [27–29]. Liquid phase exfoliation has attracted considerable attention for the production of monolayer or few-layer nanosheets in large quantities compared to the other two routes [30]. Moreover, this method is strongly related to the type of solvent and direct exfoliation method; MoS₂ and WS₂ nanosheets with a monolayer yield as high as 36% can be achieved [31].

The present work showed the roles of 2D-WS₂ nanosheet with few layers prepared by sonochemical method (thickness of about 7.5 nm and average a lateral size of 100–130 nm) in building a 2D-WS₂/WO₃ heterojunction. This study systematically investigated the influence of the PEC performance of the WS₂ nanosheets as a 2D material in WO₃ structure before and after calcination. To further elaborate on the PEC improvement of WO₃/WS₂-450 photoelectrodes, this study used Mott-Schottky, EIS, open current potential (OCP), applied bias photon-to-current conversion efficiency (ABPE) and incident photon current efficiency (IPCE) analyses.

2. Experimental section

2.1. Ultrasonic preparation of WS₂ nanosheets with liquid-phase exfoliation method

The WS₂ sheet was prepared by liquid exfoliation using the sonication method. Mixtures containing 300 mg WS₂ powder and 35 vol% ethanol/water (100 mL) for the preparation of WS₂ sheets were sonicated for five days under continuous ultrasonic bath irradiation (40 kHz, 100 W) and the dispersions were centrifuged at 3500 rpm for 60 min. Finally, a supernatant containing thin WS₂ layers was collected. Fig. 1 shows a schematic diagram of the fabrication procedure of WS₂ nanosheets.

2.2. Ultrasonic fabrication of plate-like tungsten trioxide on the W foil

The substrate which lays the foundation for WO₃ nanostructures plays a very crucial role in determining its PEC efficiency. Metal has high conductivity and good dimensional stability during the processing at elevated temperatures. The WO₃/metal remained stable, maintaining its morphology and good crystallinity. These findings provide crucial information for allowing further developments on the preparation of WO₃ photoanodes, envisaging their commercial application in PEC water splitting cells [32].

The tungsten foils were cut into 1 × 1.5 cm² squares as a substrate, then cleaned ultrasonically with acetone, ethanol, and deionized water (DI) for 20 min and dried at a room temperature. The rinsed tungsten foil pieces were immersed in 50 mL of a nitric acid solution (1.5 M HNO₃) under continuous ultrasonic bath irradiation (40 kHz, 100 W) for predetermined times of 30 min at 90–95 °C. After the sonication, the samples were then placed in an oil bath for 30 min at 95 °C. The work electrode was put in a furnace at 450 °C for 3 h (See Fig. 2). The color of the WS₂ sheet on the surface of WO₃. For drop casting, 100 μL of a WS₂ nanosheet suspension was dropped on the WO₃ film. The WO₃/WS₂ heat treatment was done without calcination (in an oven at T = 90 °C for 5 min) and with calcination (in a furnace at T = 450 °C for 5 min), and these were which was labeled WO₃/WS₂-90 and WO₃/WS₂-450 respectively. The drop casting and calcination steps were repeated eight times to achieve the desired thickness of the material and improve the crystallinity. After the last drop casting cycle, WO₃/WS₂ was placed at on the center of a furnace or an oven at 450 °C or 90 °C, respectively, for 3 h. Fig. 3 presents a schematic diagram of the preparation procedure for WS₂ nanosheets. Furthermore Table 1 shows the concentration and amount of WS₂ nanosheets on the WO₃ photoelectrode area (mg/cm²).

2.3. Preparation of WO₃/WS₂ photoanodes

WO₃/WS₂ electrodes are prepared by drop casting the 2D-material sheet on the surface of WO₃. For drop casting, 100 μL of a WS₂ nanosheet suspension was dropped on the WO₃ film. The WO₃/WS₂ heat treatment was done without calcination (in an oven at T = 90 °C for 5 min) and with calcination (in a furnace at T = 450 °C for 5 min), and these were which was labeled WO₃/WS₂-90 and WO₃/WS₂-450 respectively. The drop casting and calcination steps were repeated eight times to achieve the desired thickness of the material and improve the crystallinity. After the last drop casting cycle, WO₃/WS₂ was placed at on the center of a furnace or an oven at 450 °C or 90 °C, respectively, for 3 h. Fig. 3 presents a schematic diagram of the preparation procedure for WS₂ nanosheets. Furthermore Table 1 shows the concentration and amount of WS₂ nanosheets on the WO₃ photoelectrode area (mg/cm²).

2.4. Photoelectrochemical measurement

All the PEC measurements were taken in a three-electrode cell under illumination from the front of 100 mW/cm² (AM 1.5G) from a 300 W Xe lamp and a 0.5 M (pH = 7) aqueous Na₂SO₄ solution as the electrolyte. The working electrodes were WO₃, WO₃/WS₂-90 and WO₃/WS₂-450. A Pt electrode was used as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode. The IPCE result was calculated from chronoamperometry measurements at 0.6 V vs. Ag/AgCl. Electrochemical impedance spectroscopy (EIS) was performed under similar conditions, as described above, and over the frequency range of 100 kHz to 0.01 Hz, with an AC voltage with a 10 mV amplitude.

3. Results and discussion

3.1. Materials characterization

Fig. 4a shows the UV–Vis spectra of the few-layer WS₂ nanosheets. The absorption of incident light in the range of the near-infrared (NIR) to ultraviolet (UV) region by the WS₂ film indicates the existence of features known as A, B, and C transitions (Fig. 4a) [34]. The number of layers has a slight effect on the A and B exciton peak shift. These peaks happen at different intensities for monolayered versus multi-layered WS₂ nanosheets. In this case, the C peak in WS₂ is centered at ~425 nm, whereas the B and A transitions are positioned at ~525 nm and ~628 nm, respectively, indicating a dominant contribution from the few-layered nanosheets [35]. Based on these results and equation (2), the thickness of the WS₂ nanosheets, which measured around 6.5 nm, confirm the existence of few-layer nanosheets (thickness N (nm)) and affirms the proper exfoliation from the bulk material.

\[
N(nm) = 6.35 \times 10^{-12} \times \exp\left(\frac{\lambda_a}{8.51}\right) \quad (2)
\]

The thickness of the exfoliated nanosheets was further examined through atomic force microscopy (AFM) by depositing the WS₂ solution on glass or mica substrates by spin coating, then placing them in an oven to dry. AFM can estimate the number of WS₂ nanosheets layers by measuring the height of the deposited flakes (Fig. 4b). The average thickness measured from the height profile diagram (Fig. 4c) was estimated to be approximately 5.5–6.5 nm, which is consistent with there being 8–10 exfoliated WS₂ nanosheets [36,37]. This outcome agreed with the UV–Vis spectroscopy characterization.

Further, the concentration and size of the WS₂ nanosheets, prepared by the liquid exfoliation method, were estimated by equation (3) and (4) to be 0.036 mg/ml and 100–130 nm respectively.
In this equation, \( L \) is the average size of the nanosheets, which is estimated by the \( \text{EXT}_A \) and \( \text{EXT}_{305} \) values from the UV–vis data of WS\(_2\) nanosheets (see Fig. 4a). The concentration of the nanosheets depends on the \( \text{Abs}_{265} \) value. Further, the amount of WS\(_2\) precursor on the WO\(_3\) photoelectrode, which was calculated using equation (5), is summarized in Table 1.

Amount of WS\(_2\) per area of WO\(_3\)

\[
\text{Amount of WS}_2\text{ per area of WO}_3 = \left[ \text{Times of drop} \times \text{amount of droped} \times C \right]/\text{area}
\]

where \( C = \frac{\text{Abs}_{265}}{47.70} \) \( \ast \) Dilution

\[
C (mg/mL) = \frac{\text{Abs}_{265}}{47.70} \ast \text{Dilution}
\]

Average Size of Nanosheets (\( L \) (nm))

\[
\text{Average Size of Nanosheets } L \text{ (nm)} = \frac{(\text{EXT}_A/\text{EXT}_{305}) - 0.0076}{0.00283}
\]

It should be noted that the concentrations reported in the cited references may not be the optimal values, because the experimental parameters (such as ultrasonic time, centrifuge speed and time) would greatly affect the obtained product concentration.

Fig. 5a shows the XRD patterns of the WO\(_3\), WO\(_3/WS_2\)-450 and WO\(_3/WS_2\)-90 from the (002), (020), and (200) planes, respectively, indicating the highly-crystalline monoclinic structure of WO\(_3\) (JCPDS no.72-0677), with the complete transformation of the crystalline phases of monoclinic tungsten trioxides (monohydrate and dehydrate) into tungsten trioxide [38,39]. After adding WS\(_2\) nanosheets because of the low loading of WS\(_2\) nanosheets, no other impurity peaks or different phase-oriented peaks were observed for either the WO\(_3/WS_2\) heterostructure before or after calcination.

The average crystallite sizes of the WO\(_3\), WO\(_3/WS_2\)-450 and WO\(_3/WS_2\)-90 from the (002), (020), and (200) planes were calculated from their XRD profiles using Scherrer’s formula, as given by equation (6):

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

where \( D = \) average crystallite size; \( K = \) Scherrer’s constant (considered to be as 0.9); \( \lambda = 0.15406 \) nm; \( \beta = \) full width at half maximum (FWHM) of the (002) peak; and \( \theta = \) diffraction angle. The obtained information of their crystallite size is summarized in Table 2. The crystalline diameters of the WO\(_3/WS_2\)-450 were slightly larger than those of WO\(_3\) and WO\(_3/WS_2\)-90 for the (002) plane. However, there
was only a small difference between the crystalline diameters because the morphology of WO3 on the W foil is a plate-like structure. Thus, the addition of a small amount of WS2 nanosheets does not affect the crystal size of its corresponding photoanodes.

Structural analysis was performed by Raman scattering to detect the atomic vibrations in thin films of W/WO3, WS2, and WO3/WS2-90 films, as well as and WO3/WS2-450 (Fig. 5b). The spectra of WS2 revealed a slight variation in the phonon modes at 356.4 cm⁻¹ and 421.2 cm⁻¹, corresponding to the in-plane vibration of W and sulfur atoms, E₁g mode, and the out-of-plane vibration of sulfur atoms, A₁g mode, respectively. These results are consistent with those of previous studies [40,41]. In the case of WO3/WS2-90, characteristic peaks coexist with WS2 and WO3 peaks with only slight variations in intensity.

On the other hand, after WO3/WS2-450, the peaks disappeared because WS2 converted to WO3, which was consistent with the XPS and SEM-EDAX results (See Figs. 8 and 9).

When the tungsten foil is immersed in a nitric acid solution, which is a strong oxidizing agent, tungsten initially is oxidized to WO2²⁺ [42]. The released WO2²⁺ species are quickly attached to the neighboring water molecules to form the insoluble WO2·H2O or WO3·2H2O nucleus. With acid treatment, WO2²⁺ species are continuously produced, which increases the grain size of the WO3·H2O crystals, leading to a final pure phase of tungsten oxide hydrate deposited on the tungsten foil. Finally, after annealing at about 450 °C, the as-prepared WO3 hydrate (WO3·nH2O) thin films were converted into the WO3 phase with removing the water molecules contained in the films.

![Fig. 2. Schematic illustration of the preparation for WO3 electrode with a ultrasonic method.](image)

Fig. 6 compares the fabrication mechanism of the plate-like tungsten oxide hydrate (WO3·2H2O) electrode without and with ultrasonic treatment. Fig. 6 clearly demonstrates the role of sonification effects for preparing the compact and uniform WO3 electrode. The ultrasonic treatment can expedite the bubbles’ collapse during acoustic cavitation for more formation of the WO3 nanoparticles. Ultrasound irradiation can synergistically increase the nucleation rate and uniform growth of WO3 nanoflakes [43]. When the tungsten foil immersed in nitric acid solution was treated with ultrasound, the solution got more energy by collapsing the bubbles. Therefore, the ultrasonic irradiation can promote the oxidation of tungsten to WO2²⁺ with increasing concentration of soluble W species [44] (see Fig. 6b). The cavitation implosion reduced the surface Gibbs free energy of the crystal nuclei by increasing the temperature at the interface between the collapsing bubbles and the bulk solution. The increased number of crystal nuclei thereby increased the crystal growth rates in a short irradiation time of 15-min [45]. After the ultrasonic treatment for 30 min, the subsequent deposition for another 30 min without ultrasonic treatment with maintaining the previous temperature, led to more WO3·nH2O crystals on the W foil and then formed compact and uniform WO3 films (see the SEM image of Fig. 6b). However, the WO3·H2O without ultrasonic treatment showed an extremely slow crystal growth rate and thus irregular tungstite crystallites were obtained due to the poor adhesion of the WO3 layer onto the W foil (see the SEM image of Fig. 6a).

Fig. 7a shows TEM images of typical WS2 nanosheets prepared using the sonication process in the liquid exfoliation method with a lateral size of 100–130 nm. A high-resolution TEM image (Fig. 7b) shows that the lattice structure of the WS2 nanosheet was not damaged in preparation with the sonication process. The electron diffraction pattern (inset in Fig. 7b) indicates that the WS2 nanosheet has an high
crystallinity. The TEM images clearly confirm that the 2D morphology of WO3/WS2 with the platelike structure morphologies formed due to the sonochemical treatment is perpendicular to the foil substrate (see Fig. 7c and 7d), which is consistent with the SEM result (See Fig. 10). WO3 photoanodes having nanoplate/nanosheet morphology, prepared with a ultrasonic method, led to decreasing the hole diffusion length, improving charge separation, and extending photogenerated carrier lifetimes, which can promote photocatalysis effects [33,43]. The HRTEM (Fig. 7e and f) images of an individual 2D WO3 on the 2D WS2 surface exhibit crystal lattices with an interplanar distance of around 0.37 nm, agreeing well with the lattice spacing of the (200) facet of monoclinic WO3 [46–48]. Moreover, the thin layer of WS2 can be seen from near the surface of WO3 nanoplate. The phase of the thin WS2 layer was amorphous. Based on the information above, the 2D/2D heterojunction between the WO3 nanoplates and the WS2 nanosheets has been successfully prepared, which can be concluded to reflect an increase in the electron-hole transfer.

Fig. 8a and b show the optical properties and the band-gap of the pure WO3 ,WO3/WS2-90 and WO3/WS2-450 by UV/Vis spectroscopy. The band gap was distinguished from the linear part of \((F(R)\times h\nu)^2\) vs. photon energy (\(h\nu\)) plots. The band gap estimated from the plot of the prepared WO3, which was close to the lattice spacing of the (200) facet of monoclinic WO3 [46–48]. Moreover, the thin layer of WS2 can be seen from near the surface of WO3 nanoplate. The phase of the thin WS2 layer was amorphous. Based on the information above, the 2D/2D heterojunction between the WO3 nanoplates and the WS2 nanosheets has been successfully prepared, which can be concluded to reflect an increase in the electron-hole transfer.

Fig. 8a and b show the optical properties and the band-gap of the pure WO3 ,WO3/WS2-90 and WO3/WS2-450 by UV/Vis spectroscopy. The band gap was distinguished from the linear part of \((F(R)\times h\nu)^2\) vs. photon energy (\(h\nu\)) plots. The band gap estimated from the plot of the prepared WO3, which was close to the lattice spacing of the (200) facet of monoclinic WO3 [46–48]. Moreover, the thin layer of WS2 can be seen from near the surface of WO3 nanoplate. The phase of the thin WS2 layer was amorphous. Based on the information above, the 2D/2D heterojunction between the WO3 nanoplates and the WS2 nanosheets has been successfully prepared, which can be concluded to reflect an increase in the electron-hole transfer.

XPS of WO3 and the incorporation of WS2 nanosheets on the WO3 electrodes were investigated for the chemical states of the elements and the surface composition in the films. As illustrated in Fig. 9a, the surfaces of WO3 and WO3/WS2 before and after calcination were composed of W, O, and S with some carbon contamination at 285.7 eV, which was attributed to adventitious carbon. High-resolution XPS of W revealed peaks at 35.3 and 37.5 eV for WO3, WO3/WS2-90, and WO3/WS2-450, which were assigned to W4f7/2 and W4f5/2, respectively (Fig. 9b). This suggests that tungsten (W6+) was deposited in the form of WO3 [53,54]. After the addition of WS2 on the surface of WO3 films (WO3/WS2-90), the sulfur and tungsten peaks indicated the presence of WS2 nanosheets deposited on the surface of WO3 foil (see Fig. 9 b and d). After calcination of the WO3/WS2 photoanode at 450 °C, most of the sulfur atoms vaporized as SO2 while WO3 remained on the surface of the WO3 plate-like sheets. The S 2p core level peaks for WO3/WS2-90 and WO3/WS2-450 confirmed the presence of S, as shown in Fig. 9d. The S 2p peaks appeared at approximately 162.3 and 168.7 eV for WO3/WS2-90, whereas WO3/WS2-450 showed no peak in that region. Overall, the XPS analysis results suggests that the layer structures between WO3 and WS2 in both states before and after calcination were fabricated successfully.

Fig. S1 shows the SEM features of the WO3 nanoplates with ultrasonication and the WO3 nanoplates without ultrasonication (See the preparation detail in the supporting information). The WO3 nanoplates prepared without ultrasonic treatment led to some partial cracks or patches or agglomeration in the WO3 nanoplates (Fig. S1a). However, the sonochemically treated WO3 nanoplates (Fig. S1b) exhibited compact and uniform WO3 thin films easily grown on the entire surface of the W substrate.

The morphologies of the WO3 photoanodes with ultrasonic treatment were examined using top-view SEM images and EDAX analysis. SEM images of the WO3 photoanode indicated plate-like morphologies perpendicular to the foil substrate (See Fig. 10a). The ultrasonicated WO3 photoanodes with plate-like sheets showed a narrow size thickness.
and a smooth surface. Element analysis (EDAX) showed that only tungsten and oxygen could be detected on the surface of bare WO₃ foil (See Fig. 10b).

Fig. 10c and 10e show top-view SEM images of WO₃/WS₂ before and after the calcination process, respectively. A rough surface can be observed after the deposition of WS₂ nanosheets on the surface of WO₃ foil, both before and after furnace heating. Importantly, the element analysis (EDAX) results suggested that W, S, and O are the main detectable elements on the surface for WO₃/WS₂-90 (see Fig. 10d). These elements retained the chemical structure of WO₃ and WS₂. A top-view SEM image of the WO₃/WS₂-450 photoanode showed no significant change in morphology. EDAX did not detect sulfur on the surface of the photoanode, which is consistent with the XPS results (S2p core level peaks) (see Fig. 10d). Notably, no apparent change can be distinguished for the top-view morphology of WO₃/WS₂ before and after the furnace treatment. This is because, during the oxidation process, sulfur atoms substitute for oxygen atoms, and the structure is preserved without any distinguishable change.

3.2. Photoelectrochemical (PEC) performance

Fig. 11a and 11b show typical linear scan voltammetry (LSV) and chopped LSV, respectively, of the pure WO₃, WO₃/WS₂-90 and WO₃/WS₂-450 electrodes under continuous and on–off cycling between −0.2–1.75 V vs. Ag/AgCl. As shown in Fig. 11a, pure WO₃ photoanode prepared with the sonication method showed a photocurrent density reaching to 1.25 mA cm⁻² at 1.75 V vs. Ag/AgCl. However, the identified photocurrent density of the WO₃ photoanode without sonication was only 0.7 mA cm⁻², which is much lower than that of the ultrasound treated WO₃ electrode (See Fig. S3). After depositing the WS₂ nanosheets, the photocurrent density increased substantially, particularly for the WO₃/WS₂-450 electrode, showing peaks at approximately 6.6 mA cm⁻² at 1.75 V vs. Ag/AgCl. This behavior was attributed to the role of WS₂ nanosheets in catalyzing the oxygen evolution reaction on the surface of the WS₂ nanosheets [55,56]. In addition, the chopped values (Fig. 11b) are consistent with the photocurrent density of LSV shown in Fig. 11a. This suggests that the WO₃ photoanode shows a quick response to light and promptly generates a photocurrent ranging from zero to its equilibrium value.

Fig. 11c shows the photocurrent response measurements for the pure WO₃, WO₃/WS₂-90 and WO₃/WS₂-450 electrodes at a constant potential of 1.23 V vs. Ag/AgCl. The WO₃/WS₂-450 films showed a photocurrent density of 5.6 mA cm⁻² at 1.23 V vs. Ag/AgCl, which is 3.1 and 7.2 times higher than those of the WO₃/WS₂-90 and pure WO₃, respectively.

The transient decay time of the photocurrent was used to investigate the effect of WO₃/WS₂-450 on the charge recombination behavior of a semiconductor photoelectrode. In general, a longer transient time constant implies a smaller extent of recombination, and the transient time may be treated as the lifetime of the photogenerated carriers which can be calculated from a chronoamperometry plot as follows using equation (7) and (8) [57–59].

\[
D = \frac{I_t - I_\infty}{I_\infty - I_0}
\]  
\[
D = \exp\left(-\frac{t}{\tau_D}\right)
\]

Where \(I_t\) is the photocurrent at time \(t\) (s) and \(I_\infty\) the steady-state photocurrent. The \(\tau_D\) is defined as the time at which \(\ln D = -1\). As shown in Fig. 10d the transient decay times \(\tau_D\) of the photoanodes are evaluated to be 7.4 s, 9.5 s, and 15.2 s for WO₃, WO₃/WS₂-90, and WO₃/WS₂-450, respectively which confirm that the lifetime of the electron-hole pairs in WO₃/WS₂-450 was extended compared to those of the WO₃/WS₂-90 and WO₃ electrodes.

The WO₃/WS₂-450 photoelectrode has a longer transient time than

---

**Table 1** Amount of WS₂ nanosheets on the WO₃ photoelectrode.

| Sample     | Amount of WS₂ nanosheets in precursor (mg/mL) | Concentration of WS₂ in the precursor (mg/mL) | Concentration of WS₂ on WO₃ (mg) | Amount of WS₂ on WO₃ area (mg/cm²) (Wfoil = 1 cm × 1.5 cm) |
|------------|-----------------------------------------------|-----------------------------------------------|---------------------------------|-------------------------------------------------------------|
| WO₃/WS₂   | 0.02                                          | 0.03                                          | 0.056                           | 0.016                                                       |
| WO₃/WS₂-90| 0.016                                         | 0.03                                          | 0.03                            | 0.02                                                        |
| WO₃/WS₂-450| 0.03                                          | 0.056                                         | 0.016                           | 0.02                                                        |
the WO3, WO3/WS2-90 photoelectrodes, suggesting a smaller extent of recombination for the WO3/WS2-450 photoelectrode. This may be because of the faster carrier transit rate for the WO3/WS2-450 photoelectrode, resulting in reduced recombination of the photogenerated carriers.

EIS was performed on a 0.5 M Na2SO4 electrolyte to elucidate the enhanced electron-transfer properties of the WO3, WO3/WS2-90, and WO3/WS2-450 photoanodes.

Table 2
The diameter of crystalline domains, estimated using the Scherrer equation.

| sample         | d(002) (nm) | d(020) (nm) | d(200) (nm) | d(Average) (nm) |
|----------------|-------------|-------------|-------------|-----------------|
| WO3            | 23.93       | 38.45       | 26.43       | 29.6            |
| WO3/WS2-450    | 27.49       | 29.60       | 26.00       | 27.70           |
| WO3/WS2-90     | 27.18       | 20.61       | 21.44       | 23.08           |

Fig. 4. a) UV–vis absorption spectrum of WS2 nanosheets, b) AFM image and c) height profile of the exfoliated WS2 nanosheets.

Fig. 5. (a) X-Ray diffraction patterns and (b) Raman spectra for pure WO3, WO3/WS2-90 and, WO3/WS2-450 photoanodes.
WO$_3$/WS$_2$-450 photoanodes (Fig. 12a). The semicircle radius for both the WO$_3$/WS$_2$-90 and WO$_3$/WS$_2$-450 photoanodes were reduced significantly compared to that of pure WO$_3$ with light irradiation. In addition, the semicircle radius of the WO$_3$/WS$_2$-450 photoanode was substantially smaller than those of the other samples. The reduction of the semicircle radius in an EIS Nyquist plot showed that the charge transfer from WS$_2$ nanosheets to W/WO$_3$ substrate was easier than that from WS$_2$ nanosheets to W/WO$_3$ substrate because the semicircle radius

![Formation mechanism of plate-like WO$_3$ photoanodes (a) without and (b) with sonication.](image)

Fig. 6. Formation mechanism of plate-like WO$_3$ photoanodes (a) without and (b) with sonication.

![TEM images of exfoliated WS$_2$ nanosheets (b) High-resolution TEM image WS$_2$ nanosheet. The inset in (f) is the corresponding SAED pattern. (c, d) TEM image of a 2D-WO$_3$ electrode and (e, f) HRTEM image of a WO$_3$/WS$_2$ electrodes.](image)

Fig. 7. (a) TEM images of exfoliated WS$_2$ nanosheets (b) High-resolution TEM image WS$_2$ nanosheet. The inset in (f) is the corresponding SAED pattern. (c, d) TEM image of a 2D-WO$_3$ electrode and (e, f) HRTEM image of a WO$_3$/WS$_2$ electrodes.
in the Nyquist plot is related to the charge transfer at the interface of the photoanode–electrolyte.

The electron mobility and the charge transport are two important factors, responsible for the recombination rate, which is affected significantly by the donor concentration. Mott-Schottky measurements were taken to evaluate the donor concentration ($N_D$) and flat band potential ($V_{fb}$) of the WO$_3$, WO$_3$/WS$_2$-90, and WO$_3$/WS$_2$-450 photoanodes (Fig. 12b), which are the main factors determining the enhanced PEC performance. The Mott-Schottky plots were obtained using eq. (9) by assuming ideal semiconductor characteristics:

$$\frac{1}{C^2} = \frac{2}{\varepsilon_0 \varepsilon A N_D} (V - V_{fb} - \frac{K_B T}{e})$$

(9)

The donor concentration can be measured from the slope of the Mott-Schottky plot, and $V_{fb}$ is the value of the x-intercept (See Table 3 and Fig. S4). Accordingly, the smaller slope of the electrode represents a higher $N_D$ [62]. The donor concentration of the pure WO$_3$ film was calculated to be approximately $2.17 \times 10^{26}$ m$^{-3}$, which is consistent with those reported in previous studies [63]. By contrast, the $N_D$ of the WO$_3$/WS$_2$ photoanode after calcination showed a higher donor concentration ($5.26 \times 10^{27}$ m$^{-3}$) than WO$_3$/WS$_2$ before calcination and pure WO$_3$ electrodes, which is evidence of the efficient electron

![Fig. 8.](image)

(a) UV–vis reflectance spectra, (b) band gap energies of pure WO$_3$, WO$_3$/WS$_2$-90 and, WO$_3$/WS$_2$-450 photoanodes.

![Fig. 9.](image)

(a) XPS survey spectra and high-resolution XPS spectra for (b) W4f (c) O1s and (d) S2p for pure WO$_3$, WO$_3$/WS$_2$-90 and, WO$_3$/WS$_2$-450.
transport and reduced recombination in the WO$_3$/WS$_2$-450 photoanode. A previous study reported that a negatively shifted flat band potential can supply higher fermi levels of electrons ($V_{fn}$) and greater separation of the fermi level of holes ($V_{fp}$) [64]. Fig. S4 and Table 3 show that the calculated $V_{fb}$ information of pure WO$_3$ is $-0.32$ V, whereas the $V_{fb}$ of the WO$_3$/WS$_2$ photoanode after calcination is $-0.52$ V. This negative shift in the flat band potential suggests a higher concentration of carriers, further confirming that using the hetero-junction WO$_3$ with WS$_2$ nanosheets as a 2D material caused a decreased recombination rate, which helps to enhance the photocurrent density and the photoelectrochemical performance.

The space charge region ($W_{SCL}$) can be estimated using equation (10), which depends on $N_D$ and $V_{fb}$ [65,66].

$$W_{SCL} = \sqrt{\frac{2\varepsilon_0 (V - V_{fb})}{eN_D}}$$  

Table 3 and Fig. S4d show that the outcome of $W_{SCL}$ reduction (by equation (10), the width of the depletion layer is inversely proportional to donor concentration) in WO$_3$/WS$_2$ photoelectrodes (1.58 nm), which is 4.6 times thinner that of the pure WO$_3$ (7.38 nm), leads to an increase in charge carrier transfer and an improvement in PEC performance.

Open current potential (OCP) analysis was conducted to examine the production of photogenerated electrons and the change in voltage (Fig. 12c). The change in open circuit potential ($\Delta$ OCP) was higher for the heterojunction WO$_3$/WS$_2$ photoelectrodes than for the WO$_3$. This indicates either higher photogenerated electron production or low electron-hole recombination.

To quantitatively recognize the PEC activity at different wavelengths, the incident-photon-to-current-efficiencies (IPCE) measurements of the pure WO$_3$, WO$_3$/WS$_2$-90 and WO$_3$/WS$_2$-450 were performed at a bias voltage of 0.6 V (vs. Ag/AgCl) in a 0.5 M aqueous Na$_2$SO$_4$ (pH = 7) solution. The IPCE values were calculated using equation (11)[67,68]:

$$IPCE, \% = \frac{1240 J_{light} - J_{dark}}{P_{light}} \times 100$$  

(11)

Where $J_{dark}$, $J_{light}$, and $P_{light}$ are the dark current density, the steady-state photocurrent density at $\lambda$ (wavelength of incident light), and the light power at the specific wavelengths, respectively. As shown in Fig. 13a, all photoelectrodes displayed incident-photon-to-charge conversion efficiency (IPCE) behavior in the range from 350 to 475 nm, which concurs with the light absorption spectra of the WO$_3$, WO$_3$/WS$_2$ before calcination, and WO$_3$/WS$_2$ after calcination (See Fig. 8). This implies that the absorbed photons successfully convert into a photocurrent in the electrodes. The highest IPCE value (55.2%) was detected at 350 nm for the WO$_3$/WS$_2$-450, which is 2.1 and 2.7 times higher than those of the WO$_3$/WS$_2$-90 film (26.3%) and pure WO$_3$ film (20.1%), respectively. This result was consistent with the improvements
observed in the photocurrent densities (See Fig. 11).

Fig. 13b shows the applied bias photon-to-current conversion efficiency (ABPE) under different applied potentials, which were calculated based on LSV. The ABPE was determined using equation (12) [69,70], where \( J \) is the net photocurrent density at different potentials, \( V \) is the applied potential, and \( P \) is the power density of the incident light, which is 100 mW cm\(^{-2}\) (AM 1.5G).

\[
\text{ABPE}(\%) = \frac{J(\text{at } V_{\text{bias}})}{P(\text{incident light})} \times 100
\]

The ABPE of WO\(_3\)/WS\(_2\) after calcination was higher than that of WO\(_3\)/WS\(_2\) before calcination and pure WO\(_3\) over the measured potential range in a 0.5 M (pH = 7) aqueous solution of Na\(_2\)SO\(_4\). The maximum ABPE was approximately 2.26% at 0.75 V (vs. Ag/AgCl) for the WO\(_3\)/WS\(_2\)-450, which is 5.5 and 9 times higher than those of WO\(_3\)/WS\(_2\) before calcination (0.41%) and pure WO\(_3\) film (0.25%), respectively. Overall, the WO\(_3\)/WS\(_2\) photoanode after calcination showed the highest photoelectrochemical properties.

It is well known that WO\(_3\) suffers from weak visible light response, and the low absorption coefficient for photons is a commonly known disadvantage of metal oxide photocatalysts. Here, to circumvent this drawback, we use WS\(_2\) nanosheets with 5–10% of light absorption in visible range. However, the key question regards the mechanism in which adding WS\(_2\) nanosheets can suppress the recombination rate and increase the charge separation.

In this study, we proposed a photocurrent enhancement of heterojunction WO\(_3\) and WS\(_2\) nanosheets by referring to electron-hole transfer (See Fig. 14). After illumination light, electron-holes are generated in both electrodes. Holes move from WO\(_3\) to WS\(_2\) nanosheets and electrons move from the valence band of WS\(_2\) nanosheets to the conduction band of WO\(_3\). The conduction band of WS\(_2\) nanosheets is more negative than the conduction band of WO\(_3\), so the accumulated electrons can easily be passed into WO\(_3\) and then assembled by W as the substrate conductor. A remarkable improvement can be seen in the PEC performances when WS\(_2\) nanosheets are added to WO\(_3\) to form the WO\(_3\)/WS\(_2\) photoelectrode. The photocurrent generated by the heterojunction WO\(_3\)/WS\(_2\)-450 films shows a photocurrent density 7.2 times higher than that of the pure WO\(_3\) (See Fig. 11). The increased photocurrent density of WO\(_3\)/WS\(_2\)-450 can be attributed to because of electron/hole separation, which occur when WO\(_3\) and WS\(_2\) nanosheets are interfaced, thus making a type II heterojunction. In addition, the photocurrent onset potentials of WO\(_3\) shift toward the anodic direction from the corresponding V\(_{\text{fb}}\), which is commonly observed for the n-type semiconductors and is usually caused by surface recombination.

3.3. Conclusion

WS\(_2\) nanosheet was prepared using the LPE method with ultrasonication. WO\(_3\) nanoplates were synthesized on tungsten foil by a sonochemically assisted method. WO\(_3\) electrode prepared with ultrasonic showed compact and uniform films which were easily grown on
the entire surface of the W substrate. The ultrasonicated WS₂ had an average film thickness of 6.5 nm, confirming that there were approximately 10 layers of exfoliated WS₂ nanosheets. The WO₃/WS₂-450 films showed a photocurrent density of 5.6 mA.cm⁻² at 1.23 V vs. Ag/AgCl, respectively, which is 3.1 and 7.2 times higher than those of the WO₃/WS₂-90 and pure WO₃, respectively. WO₃/WS₂-450 plate-like structure prepared with ultrasonication increased charge separation and reduced recombination of the photogenerated carriers. The enhanced PEC performance of the WO₃/WS₂ electrodes was attributed to the following: the role of WS₂-2D nanosheets acting as a photosensitizer by increasing light harvesting in the visible region of the solar spectrum, a charge separator through suitable energy band alignment, and a charge transporter. The fabricated WO₃/WS₂ electrodes are therefore promising candidates as a photoanode for PEC cells.

Table 3
Summarized the Vfb, ND and WSCl values obtained Mott-Schottky plots.

| sample           | slope   | intercept | N_D (m⁻³) | V_FB (V) | W_SC (nm) |
|------------------|---------|-----------|-----------|----------|-----------|
| WO₃              | 3.25 × 10¹⁰ | -0.30     | 2.17 × 10⁶ | -0.32    | 7.34      |
| WO₃/WS₂-450      | 1.34 × 10⁸  | -0.50     | 5.26 × 10⁷ | -0.52    | 1.58      |
| WO₃/WS₂-90       | 1.25 × 10⁹  | -0.45     | 5.88 × 10⁶ | -0.47    | 4.60      |

Fig. 12. (a) EIS Nyquist plot (b) Mott–Schottky plot and (c) open current potential (OCP) of the pure WO₃, WO₃/WS₂-90 and, WO₃/WS₂-450, under 100 mWcm⁻²; the supporting electrolyte was a 0.5 M (PH = 7) aqueous solution of Na₂SO₄.

Fig. 13. (a) The IPCE result at 0.6 V vs. Ag/AgCl (b) Applied bias photon-to-current efficiency (ABPE) value for pure WO₃, WO₃/WS₂-90 and, WO₃/WS₂-450, under 100 mWcm⁻²; the supporting electrolyte was a 0.5 M (PH = 7) aqueous solution of Na₂SO₄.


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MIST: Ministry of Science and ICT) (No. 2019R1A2C2085250).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultraschon.2020.105339.

References

[1] B.S. Kalanur, H. Seo, S.S. Kalanur, Recent developments in photoelectrochemical water-splitting using WO3/BiVO4 heterojunction photoanode: a review, Materials Science for Energy Technologies 1 (2018) 49-62.
[2] X. Shi, I.Y. Choi, K. Zhang, J. Kwon, D.Y. Kim, J.K. Lee, S.H. Oh, J.K. Kim, J.H. Park, Efficient photoelectrochemical hydrogen production from bismuth vanadate-decorated tungsten trioxide helix nanostuctures, Nat. Commun. 5 (2014) 4775.
[3] A. Yadav, Y. Hunge, S. Kulkarni, Synthesis of multifunctional FeCo2O4 electrode using ultrasonic treatment for photocatalysis and energy storage applications, Ultrason. Sonochem. 58 (2019) 104663.
[4] A. Yadav, Y. Hunge, S. Kulkarni, C. Terashima, S.-W. Kang, Three Dimensional Nanoflower-like Hierarchical Array of Multifunctional Copper Cobaltate Electrode as Efficient Electrocatalyst for Oxygen Evolution Reaction and Energy Storage Application, J. Colloid Interface Sci. (2020).
[5] M. Tayebi, B.-K. Lee, Recent advances in BiVO4 semiconductor materials for hydrogen production using photoelectrochemical water splitting, Renew. Sustain. Energy Rev. 111 (2019) 332–343.
[6] T. Soltani, A. Tayyebi, B.-K. Lee, Sonoochemical-driven ultrafast facile synthesis of WO3 nanoparticles with controllable morphology and oxygen vacancies for efficient photoelectrochemical water splitting, Ultrason. Sonochem. 50 (2019) 230–238.
[7] T. Soltani, A. Tayyebi, H. Hong, M.H. Mirfaisi, B.-K. Lee, A novel growth control of nanoparticles WO3 photoanodes with dual oxygen and tungsten vacancies for efficient photoelectrochemical water splitting performance, Sol. Energy Mater. Sol. Cells 191 (2019) 1–13.
[8] L. Sun, Y. Wang, F. Razig, Y. Ou, L. Bai, L. Jing, Enhanced photoelectrochemical activities for water oxidation and phenol degradation on WO 3 nanofibers by transferring electrons and trapping holes, Sci. Rep. 7 (2017) 1303.
[9] M.H. Mirfaisi, C. Li, A. Tayyebi, Q. Cao, J. Yu, J.-J. Delaunay, Oxygen-vacancy-induced photoelectrochemical water oxidation by platelike tungsten oxide photoanodes prepared under acid-mediated hydrothermal treatment conditions, RSC Adv. 7 (2017) 26992–27000.
[10] S.L. Wang, Y.-L. Mak, S. Wang, J. Chai, F. Pan, M.L. Foo, W. Chen, K. Wu, G.Q. Xu, Visible-Near-Infrared-Light-Driven Oxygen Evolution Reaction with Noble-Metal-Free WO2-WO3 Hybrid Nanorods, Langmuir : the ACS journal of surfaces and colloids 52 (2016) 13046–13053.
[11] A. Hammad, H.M. El-Bery, A. El-Shazly, M. Elkady, Effect of WO3 Morphological Structure on its Photoelectrochemical Properties, Int. J. Electrochem. Sci 13 (2018) 362–372.
[12] J.Y. Zheng, Z. Haider, T.K. Van, A.U. Pawar, M.J. Kang, C.W. Kim, Y.S. Kang, Tuning of the crystal engineering and photoelectrochemical properties of crystalline tungsten oxide for optoelectronic device applications, CrystEngComm 17 (2015) 6070–6093.
[13] M. Tayebi, A. Tayyebi, B.-K. Lee, J.-H. Lee, D.-H. Lim, The effect of silver doping on photoelectrochemical (PEC) properties of bismuth vanadate for hydrogen production, Sol. Energy Mater. Sol. Cells 200 (2019) 109943.
[14] S.S. Kalanur, H. Seo, Influence of molybdenum doping on the structural, optical and electronic properties of WO3 for improved solar water splitting, J. Colloid Interface Sci. 509 (2018) 440–447.
[15] W. Li, F. Zhan, J. Li, C. Liu, Y. Yang, Y. Li, Q. Chen, Enhancing photoelectrochemical water splitting by aluminum-doped plate-like WO3 electrodes, Electrochim. Acta 160 (2015) 57–63.
[16] L. Xia, Y. Bai, J. Li, Q. Zeng, X. Li, B. Zhu, A highly efficient BiVO4/WO3/W heterojunction photoanode for visible-light responsive dual photoelectrode photocatalytic fuel cell, Appl. Catal. B 183 (2016) 224–230.
[17] S.S. Kalanur, J.-H. Yoo, J. Park, H. Seo, Insights into the electronic bands of WO 3/BiVO 4/TiO 2, revealing high solar water splitting efficiency, J. Mater. Chem. A 5 (2017) 1455–1461.
[18] P.M. Adamopoulos, I. Papagiannis, D. Raptis, P. Lianos, Photoelectrocatalytic hydrogen production using a TiO2/WO3 bilayer photocatalyst in the presence of ethanol as a fuel, Catalysis 9 (2019) 976.
[19] Y. Hunge, A. Yadav, V. Mathe, Ultrasound assisted synthesis of WO3-ZnO nanocomposites for brilliant blue dye degradation, Ultrason. Sonochem. 45 (2018) 116–122.
[20] J. Lin, P. Hu, Y. Zhang, M. Fan, Z. He, C.K. Ngaw, J.S.C. Loo, D. Liao, T.T.Y. Tan, Understanding the photoelectrochemical properties of a reduced graphene oxide-WO 3 heterojunction photoanode for efficient solar-light-driven overall water splitting, RSC Adv. 3 (2013) 9339–9336.
[21] M. Tayebi, M. Kolaei, A. Tayyebi, Z. Manoumi, Z. Belbasi, B.-K. Lee, Reduced graphene oxide (RGO) on TiO2 for an improved photoelectrochemical (PEC) and photocatalytic activity, Sol. Energy 190 (2019) 185–194.
[22] Y. Hunge, A. Yadav, A. Dhodamani, N. Suzuki, C. Terashima, A. Fujishima, V. Mathe, Enhanced photocatalytic performance of ultrasound treated GO/TiO2 composite for photocatalytic degradation of salicylic acid under sunlight illumination, Ultrason. Sonochem. 61 (2020) 104849.
[23] M. Tayebi, A. Tayyebi, Z. Manoumi, B.-K. Lee, Photoinduced corrosion suppression and photoelectrochemical (PEC) enhancement of ZnO via hybridization with graphene nanosheets, Appl. Surf. Sci. 502 (2020) 144189.
Y. Tang, Z. Zheng, X. Sun, L. Li, K.P. Loh, H. Zhang, The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets, Nat. Chem. 5 (2013) 263.

L. Li, J.A. Robinson, R.E. Schaal, D. Sun, Y. Sun, T.E. Mallouk, M. Terrones, Transition metal dichalcogenides and beyond: synthesis, properties, and applications of single- and few-layer nanosheets, Acc. Chem. Res. 48 (2014) 56–64.

Y.H. Lee, X.Q. Zhang, W. Zhang, M.T. Chang, C.T. Lin, K.D. Chang, Y.C. Yu, J.T.W. Wang, C.S. Chang, L.J. Li, Synthesis of large-area MoS2 atomic layers with chemical vapor deposition, Adv. Mater. 24 (2012) 2220–2225.

K. Chang, X. Hai, J. Ye, Transition Metal Disulfides as Noble-Metal-Alternative Co-Catalysts for Solar Hydrogen Production, Adv. Energy Mater. 6 (2016) 1502555.

X. Hai, W. Zhou, K. Chang, H. Fang, H. Liu, L. Shi, F. Ichihara, J. Ye, Engineering the MoS2 of MoS2 monolayers for highly efficient solar hydrogen production, J. Mater. A. Chem. 5 (2017) 8591–8598.

J. Shen, Y. He, J. Wu, C. Gao, K. Keyshar, X. Zhang, Y. Yang, M. Ye, R. Vajtai, J. Lou, Liquid phase exfoliation of two-dimensional materials by directly probing and matching surface tension components, Nano Lett. 15 (2015) 5449–5454.

T. Lopes, L. Meda, L. Andrade, A. Mendes, Photoelectrochemical water splitting using WO3 photoanodes: the substrate and temperature roles, PCCP 18 (2016) 5252–5243.

S. Adhikari, D. Sarkar, Hydrothermal synthesis and electrochromism of WO3 nanocubes, RSC Adv. 4 (2014) 1–10.

M. Guo, Z. Xing, T. Zhao, Z. Li, S. Yang, W. Zhou, WS2 quantum dots/MoS2@WO3-x core-shell hierarchical dual Z-scheme tandem heterojunctions with wide-spectrum light illumination, Chem. Eng. J. 368 (2019) 448–458.

Z. Zheng, X. Li, L. Li, Y. Yang, Photoelectrocatalytic degradation of amoxicillin over quaternary ZnO/ZnSe/CSx/Cds/MoS2 hierarchical nanorods, Int. J. Hydrogen Energy 44 (2019) 20826–20838.

P. Cheng, C. Deng, X. Dai, B. Li, D. Liu, J. Xu, Enhanced energy conversion efficiency of TiO2 electrode modified with WO3 in dye-sensitized solar cells, J. Photochem. Photobiol., A 195 (2008) 144–150.

P. Chatzichai, Y. Murakami, S.-Y. Kishioka, A.Y. Nosaka, Y. Nosaka, Efficient photocatalytic activity of water oxidation over WO3/BiVO4 composite under visible light irradiation, Electrochim. Acta 54 (2009) 1147–1152.

W. Zhao, Y. Liu, Z. Wei, S. Yang, H. He, C. Sun, Fabrication of a novel p-n heterojunction photocatalyst BiVO4@MoS2 core-shell structure and its excellent-visible light photocatalytic reduction and oxidation activities, Appl. Catal. B 185 (2016) 242–252.

L. Zheng, S. Han, H. Liu, P. Yu, X. Fang, Hierarchical MoS2 nanosheet@TiO2 nanotube array composites with enhanced photocatalytic and photocurrent performances, Small 12 (2016) 1527–1536.

C. Liu, Y. Yang, W. Li, J. Li, Y. Li, Q. Chen, In situ synthesis of Bi 2 S3 sensitized WO3 nanoplate arrays with less interfacial defects and enhanced photocatalytic performance, Sci. Rep. 6 (2016) 23451.

J. Nong, G. Lan, W. Jin, P. Luo, C. Guo, X. Tang, Z. Zang, W. Bai, Wei, Eco-friendly and high-performance photoelectrochemical anode based on AgInS2 quantum dots embedded in 3D graphene nanowalls, J. Mater. Chem. C 7 (2019) 9830–9839.

M. Radecka, P. Sobas, M. Wierzbicka, M. Bekas, Photoelectrocatalytic properties of undoped and Ti-doped WO3, Physica B 364 (2005) 85–92.

M. Tayebi, A. Tayyebi, T. Soh, B.-K. Lee, pH-Dependent photocatalytic performance of modified bismuth vanadate by bismuth ferrite, New J. Chem. 43 (2019) 9106–9115.

M. Tayebi, A. Tayyebi, B.-K. Lee, Photocharged molybdenum-doped BiVO4 photoanodes for simultaneous enhancements in charge transport and surface passivation, Sol. Energy 191 (2019) 427–436.

C. Liu, Y. Yang, W. Li, J. Li, Y. Li, Q. Chen, Construction of novel Bi2S3 nanobelts@WO3 nanoplate arrays on FTO glass with high photoelectrocatalytic activity, Int. J. Hydrogen Energy 41 (2016) 5878–5886.

Y. Yang, F. Zhan, H. Li, W. Liu, S. Yu, In situ Sn-doped WO3 films with enhanced photoelectrochemical performance for reducing CO 2 into formic acid, J. Solid State Electrochem. 21 (2017) 2231–2240.

C. Liu, J. Li, Y. Li, W. Li, Y. Yang, Q. Chen, Epitaxial growth of Bi 2 S 3 nanowires on BiVO4 nanocubes for enhancing photoelectrochemical performance, RSC Adv. 5 (2015) 71692–71698.

J. T. W. Wang, C. S. Chang, L. J. Li, Synthesis of large-area MoS2 atomic layers with chemical vapor deposition, Electrochim. Acta 43 (1998) 2773–2780.

M. Tayebi, A. Tayyebi, B.-K. Lee, Improved photoelectrochemical performance of molybdenum (Mo)-doped monoclinic bismuth vanadate with increasing donor concentration, Catal. Today 328 (2019) 35–42.

Z. Masoumi, M. Tayebi, B.-K. Lee, The role of doping molybdenum (Mo) and back-front side illumination in enhancing the charge separation of α-Pc0303 nanorod photoanode for solar water splitting, Sol. Energy 205 (2020) 126–134.

M. Tayebi, B.-K. Lee, The effects of W/Mo-co-doped BiVO4 photoanodes for improving photoelectrochemical water splitting performance, Catal. Today (2020).

S. Adhikari, D. Sarkar, Hydrothermal synthesis and electrochemical of WO3 nanocubes, RSC Adv. 4 (2014) 20415–20453.

L. Sun, B. Li, X. Chu, N. Sun, Y. Qu, X. Zhang, I. Khan, L. Bai, L. Jiang, Synthesis of Si-O-Bridged g-CN3/WO3 2D-Heterojunction Nanocomposites as Efficient Photocatalysts for Alcohol Oxidation and Mechanism Insight, ACS Sustainable Chem. Eng. 7 (2019) 9916–9927.

P. Zhou, Q. Xu, H. Li, W. Yang, B. Yan, Y. Zhou, J. Chen, J. Zhang, K. Wang, Fabrication of Two-Dimensional Lateral Heterojunctions of WS2/WO3 H2O Through Selective Oxidation of Monolayer WS2, Angew. Chem. 127 (2015) 15441–15445.

G. Gopakumar, S.V. Nair, M. Shambag, Plasma driven nano-morphological evolution of SnO2 nanostructures for enhancing photoelectrochemical performance, RSC Adv. 9 (2019) 5492–5500.

K.-H. Ye, H. Li, D. Huang, S. Xiao, W. Qiu, M. Li, Y. Hu, W. Mai, H. Ji, S. Yang, Enhanced photocatalytic activity of water splitting by combining work function tuning and heterojunction engineering, Nat. Commun. 10 (2019) 1–9.

N. Huo, Q. Yue, J. Yang, S. Yang, J. Li, Abnormal photocurrent response and enhanced photocatalytic activity induced by charge transfer between WS2 nanosheets and WO3 nanoparticles, ChemPhysChem 14 (2013) 4069–4073.

G. Gopakumar, S.V. Nair, M. Shambag, Plasma driven nano-morphological changes and photovoltaic performance in dye sensitized 2D-layered dual oxalyl-sulfide phase WS2 films, Nanoscale 12 (2020) 239–247.

S. Ma, L. Zeng, L. Tao, C.Y. Tang, H. Yuan, H. Long, P.K. Cheng, Y. Chai, C. Chen, K.H. Fang, Enhanced photocatalytic activity of WS 2 film by laser drilling to produce porous WS 2/WO 3 Heterostructure, Sci. Rep. 7 (2017) 1–9.

M. Guo, Z. Xing, T. Zhao, X. Li, W. Yang, W. Zhou, WS2 quantum dots/MoS2@W03 core-shell hierarchical dual Z-scheme tandem heterojunctions with wide-spectrum response and enhanced photocatalytic performance, Appl. Catal. B 257 (2019) 117913.