Charge transfer mechanism of WO₃/TiO₂ heterostructure for photoelectrochemical water splitting

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The present study shows how electronic parameters (e.g. band gap energy, band edge positions) on semiconductors affect photoelectrochemical activity in simulated solar light using WO₃, TiO₂ and WO₃/TiO₂ as model systems. Hydrothermal synthesis was conducted to study heterostructure (HE) formation, which the loading of WO₃ in TiO₂ structure were varied to 20, 40 and 80 wt%. Scanning electron microscopy images show that WO₃ and TiO₂ particles are in contact with each other and the synthesis method as well as the deposition method are appropriate for the formation of WO₃/TiO₂ HE film. Important findings were obtained with a hole scavenger during photoelectrochemical characterization of WO₃/TiO₂–40 wt% film. This strategy was effective to clearly distinguish charge transport from charge separation, the essential mechanisms that affect water splitting which are often misinterpreted experimentally for HE. The hole scavenger experiment depicts the increase by 17.5% in photocurrent density for the WO₃/TiO₂–40 wt% film as compared to WO₃ film, corresponding to 210 and 12 μA cm⁻² vs Ag/AgCl respectively. Additionally, this HE film showed water oxidation initiated at lower applied potentials and indicating that coupling of the materials resulted in optimization of band edge properties for water splitting with the increase on light absorption at the visible range. Flat band potential was determined by the Mott-Schottky plot and it indicated the difference of 1.08 V vs Ag/AgCl between TiO₂ and WO₃ potentials, which makes the charge injection from one structure to another effective and thermodynamically stable for charge separation. A charge carrier density of 1.59 × 10¹⁶ was observed for the WO₃/TiO₂–40 wt% and it supports the best photoelectrochemical performance for water oxidation.

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1. Introduction

TiO₂ based catalysts have been extensively investigated for photocatalytic applications. Since the pioneering study of Fujishima and Honda in the early 1970s, where the authors reported water splitting in a photoelectrochemical cell illuminated with near ultraviolet light using TiO₂ as a photoelectrode, several works have been motivated by the promising properties of TiO₂ [1,2]. Despite the advantages associated with the use of TiO₂ such as low cost, nontoxicity and high stability, this oxide suffers from poor utilization of the solar spectrum (band gap energy for anatase crystalline phase is 3.2 eV; ~390 nm) and as a result it makes use of only 2.5–3.5% of the solar light that reaches the Earth [3–6].

In recent literature, significant investigations are underway regarding the optimization of TiO₂ and also the coupling of TiO₂ with other semiconductors (heterostructures or heterojunctions) that present absorption beyond the UV region, in order to improve the light absorption of TiO₂ in the visible regions of sunlight [3,7–9]. These investigations aim to identify the phenomena that occur at the crystalline interface, such as Fermi level alignment, and the influence of band edges (valence and conduction bands) on photocatalytic activity [10–12].

In this context, transition metal compounds, especially tungsten oxide (WO₃), are an abundant material with promising potential for many technological applications. WO₃ presents unique optical and electronic properties that can be explored for the development of a series of functional structural phases [13,14]. To date, WO₃ photoanodes produced by hydrothermal synthesis show high chemical and thermo stability. However, for practical application the photoanodes are still needed best performance for
of TiO₂, the coupling of low band gap materials such as WO₃ with TiO₂ to form heterostructures is one of the most important approaches to band gap engineering, which can enhance photocatalytic or photoelectrocatalytic properties at the visible region [16,17,12,4].

The key parameters for better understanding and optimization of the photocatalytic performance of semiconductors is the determination of their band edge positions [18]. It is well known that the band gap positions and Fermi level energy play important roles in allowing electron transfer in heterostructured systems. Thus, the knowledge derived from energy diagram scans open a window for the characterization of the processes that take place at the surface of semiconductor materials. In this context, photo-electrochemical measurements are ideal techniques that can provide information about the intrinsic electronic properties of semiconductors in contact with electrolyte solutions [19,18]. Several papers describe the development of new catalysts for different applications, but there is a need for further understanding of the main active species and mechanisms for effective water splitting [15].

Several reports have shown the growth of heterostructures using hydrothermal annealing with controlled morphology and crystallinity [20–23]. The observed alignment at the contact interface of semiconductor oxides may be a good strategy for tailoring heterostructures for the study of the charge transfer mechanism for the photoelectrochemical water splitting.

The present study aims to investigate how the electronic parameters (band edge positions, Fermi level energy and charge migration) affect the photocatalytic activity of heterostructures obtained by hydrothermal synthesis. The as-synthesized materials will be investigated with current-voltage measurements. This work is expected to assist the comprehension of the photochemical mechanism that occurs at the heterostructure interface in order to optimize the material’s electronic properties for photocatalytic applications.

2. Experimental

2.1. Material synthesis

In a typical synthesis procedure, 0.12 mol L⁻¹ solution was prepared by dissolving precursor tungstic acid – H₂WO₄ (Aldrich, 99%) in H₂O₂ (Synth, 29%), to form a stable peroxy-polytungstic acid solution at room temperature. Subsequently, hydrothermal synthesis was conducted to produce the heterostructures where TiO₂ nanopowder (Aldrich, 99.9%) was used as a pre-formed particle to obtain heterostructures utilizing stable peroxy-polytungstic acid solution. The necessary mass of W in the peroxy-complex solution to obtain heterostructures with 20, 40 and 80 wt % of W was calculated.

The solution was placed into a 100 mL micro-controlled hydrothermal cell, which had fine control of temperature and monitoring of the self-generated pressure. The precursors were subjected to hydrothermal treatment at 200 °C under magnetic stirring for 24 h. The same procedure was performed without TiO₂, to obtain only WO₃ particles and for the purpose of checking the properties of the oxide as a comparison of WO₃ with the as-synthesized heterostructures. All materials were separated by centrifugation and dried at 80 °C for 12 h. A summarized denomination of each material is presented in Table 1.

Thin films were produced using the pre-formed oxides and the heterostructures. The paste was prepared for each material by adding 2.67 mL of terpinole (Aldrich) and 3.33 mL of ethyl cellulose solution (Aldrich, 46 cp, 5% in toluene/ethanol 80:20) 10% in pure ethanol (99.9%) and then mixing to obtain a homogenous mixture for film production. The as-prepared homogenous paste was dropped onto the fluorine doped SnO₂ (FTO) substrate and spin-coated for film deposition and to remove residual precursor solution.

2.2. Material characterization

Sample morphology was characterized via field emission scanning electron microscopy (FE-SEM, JEOL JSM 6701F) and energy-dispersive X-ray spectroscopy (EDX) (JEOL SEM 6310 microscope) to evaluate the homogeneity, WO₃ and TiO₂ distribution, and surface quality. X-ray diffraction (XRD) analysis was performed with a Shimadzu XRD 6000 with radiation at 1.54 Å, which corresponds to Cu Kα emission, at a step scan of 0.02° and exposure time of 4 s. The UV–vis spectra were acquired using a Spectrophotometer Cary 5G (Varian) in the diffuse reflectance mode (DRS).

2.3. Photoelectrocatalytic activity

Electrochemical measurements were carried out in a conventional three-electrode system, connected to a computer-controlled potentiostat (Autolab PGSTAT 302N, Metrohm-Eco Chemie controlled by GPES software). The three-electrode system contained thin films as the working-electrode, a Pt wire as the counter-electrode, and Ag/AgCl as the reference electrode. The photoelectrocatalytic activity was measured using simulated solar irradiation 500 W Xenon (Newport, 66902) calibrated to 100 mW cm⁻² and air mass 1.0 global (AM 1.0G) filter.

Linear Sweep Voltammetry (LSV) was carried out using 0.5 mol L⁻¹ aqueous solution of Na₂SO₄ pH 5 at 0.5 mV s⁻¹ with potential range of −0.5 to 1.2 vs Ag/AgCl. Every measurement was repeated three times to ensure equilibrium. In the results section, only the third voltammogram is presented for every measurement. Mott-Schottky plots were obtained at a frequency range of 5–10 kHz, amplitude of 10 mV, in the potential range of −1.0 to 1.0 V vs Ag/AgCl. The Mott-Schottky equation was applied to investigate the flat band potential (Eᶠᵇ) of the electrodes as described elsewhere [19].

3. Results and discussion

The morphology of the as-prepared powders was investigated by SEM images, as shown in Fig. 1.

The heterostructures and the precursor oxides showed different particle morphologies. Pristine WO₃ showed the presence of micro-aggregates in a three-dimensional structure (Fig. 1a) and TiO₂ presented smaller particles at nanometer range (Fig. 1b), formed by agglomerates. For the heterostructures, the presence of micro-aggregates was observed, which is characteristic of WO₃ particles, while smaller particles with spherical and agglomerated morphology possibly correspond to TiO₂. Importantly, SEM images show that WO₃ and TiO₂ particles are in contact with each other and can be indicative of attachment due to the hydrothermal conditions utilized, as indicated in Fig. 1d. Since the hydrothermal method can induce collisions among crystallized particles, under

| Table 1 |
| Synthesized materials W-peroxo/TiO₂ with varying W (mass wt%). |
| Samples | (W-peroxo/TiO₂) |
| Commercial TiO₂ | 0/100 |
| WO₁ | 100/0 |
| WO₁/TiO₂−20 wt% | 20/80 |
| WO₁/TiO₂−40 wt% | 40/60 |
| WO₁/TiO₂−80 wt% | 80/20 |
high pressure and temperature, it is possible to infer that the heterostructures were successfully produced.

With respect to WO$_3$/TiO$_2$–80 wt%, EDX mapping was carried out to confirm the presence of WO$_3$ and TiO$_2$ particles in this heterostructured system. As seen in Supplementary Fig. 1, the particles for both 40 wt% and 80 wt% presented particles in the micrometer range that is correspondent to WO$_3$ with plate-like morphology. The regions with the nanoparticulated agglomerates could be associated to TiO$_2$. It is possible to conclude that the heterostructures were formed by the crystallization of WO$_3$ microparticles attached to TiO$_2$ nanoparticulated agglomerates. Since TiO$_2$ was used as a pre-formed particle during the hydrothermal synthesis, it is expected that the WO$_3$ micro-particles crystallize in contact with the pre-formed TiO$_2$ as a crystalline template.

Since film samples are necessary for the proposed electrochemical characterization experiments, the calcination step (necessary for particle adherence on FTO substrate) may change morphology and, consequently, general properties. The microstructures of the calcined films are presented in Fig. 2. The discrepancy in particle size and morphology between WO$_3$ and TiO$_2$ is evident. The micrograph of TiO$_2$ shows agglomerates formed of uniform spherical particles of approximately 40 nm (Fig. 2a) while WO$_3$ microstructure consists of agglomerates of large irregularly shaped particles. WO$_3$/TiO$_2$–40 wt% film presents small particles believed to be TiO$_2$ on top of large irregularly shaped particles believed to be WO$_3$ due to the sizes of pristine TiO$_2$ and WO$_3$. An important aspect is the similar particle size, mainly of the heterostructure film (Fig. 2c) when compared to the freestanding particles. This reveals that the calcination procedure was not enough to promote significant grain growth, which confirms that the synthesis and film preparation methods are adequate for the proposed study. EDX elemental spectra of WO$_3$/TiO$_2$–40 wt% film shows elemental composition of Ti and W (Supplementary Fig. 2). Sn detection is associated with the FTO substrate. Further, the elemental maps show uniform distribution of Ti and W in the film, an indication that the synthesis method as well as the deposition method are appropriate for the formation of WO$_3$:TiO$_2$ heterostructures (Suppl. Fig. 2b and c).

However, the film preparation procedure was shown as influential on phase composition of heterostructures. Fig. 3a presents XRD patterns for the pristine oxides (TiO$_2$ and WO$_3$) and the heterostructures (20 wt%, 40 wt% and 80 wt%).

The crystallographic properties of as-synthesized powders were determined by XRD measurements (Fig. 3a). The orthorhombic phase of WO$_3$:0.33H$_2$O (JPDS N° 35-0270) was identified as the principal phase for the pristine WO$_3$ sample with WO$_3$ planes showed in Fig. 3a. The main WO$_3$ orthorhombic phase is (002) and (220) planes, similar presented by Li et al. [24]. They obtained diverse micro to nanostructures of WO$_3$ orthorhombic crystallites through microwave heating under different conditions. The anatase phase of TiO$_2$ (JPDS N° 01-086-1157) was identified as the main crystallographic phase in the TiO$_2$ nanoparticle sample.

Fig. 1. FE-SEM images of WO$_3$ (a), TiO$_2$ (b), WO$_3$/TiO$_2$–20 wt% (c), WO$_3$/TiO$_2$–40 wt% (d) and WO$_3$/TiO$_2$–80 wt% (e).

Fig. 2. FE-SEM images of films (a) TiO$_2$ (b) WO$_3$ and (c) WO$_3$/TiO$_2$–40 wt%.
WO$_3$/TiO$_2$–40 wt% corresponds to the best performance composition expected, as based on recent reports \cite{20,21}, and it is a representative material to evidence the heterojunction effect on semiconductor properties. It is well known that heteroaggregation process is driven by collisions between different nanoparticles during hydrothermal annealing and it was studied for different semiconductor oxide models in our research group. \cite{20,21}. The best composition was chosen based on these recent publications and considering FE-SEM images of WO$_3$/TiO$_2$ 40 wt% with the indication of heterostructure formation in Fig. 1d for further characterization.

The electronic structure of the films was investigated using UV–vis spectra in reflectance mode. The indirect transition model was used to estimate the band gap energy ($E_g$) of the semiconductors by Tauc equation \cite{20} and it is presented in Fig. 4.

TiO$_2$ film showed an absorption edge at 380 nm and a band gap of 3.26 eV, which is in agreement with its band gap energy reported in literature with a characteristic absorption in the UV region of the spectrum \cite{2}. For WO$_3$ film, the band gap energy is observed at 3.03 eV and equivalent to 409 nm, thus the light absorption is extend for photocatalytic reactions. The WO$_3$/TiO$_2$–40 wt% film presented intermediate band gap energy between pristine TiO$_2$ and WO$_3$ values (3.23 eV). Also, FTO substrate presented a band gap energy at 3.36 eV and one can see that it is not an interference at the estimated band gap for the as-prepared films.

\section*{4. Photoelectrochemical characterization}

The photoelectrochemical performance of the produced films was investigated for water oxidation as shown in Fig. 5a. The LSV characteristics under dark and under simulated solar irradiation at 50 mW cm$^{-2}$ is shown, using the produced films and Na$_2$SO$_4$ 0.5 mol L$^{-1}$. A summary of the results is presented in Table 2.

The films presented no significant current in dark conditions, in the potential range from −0.5 to 1.2 V (vs Ag/AgCl reference electrode) and the higher current density observed is of WO$_3$/TiO$_2$ film but it still negligible compared to the data collected underillumination. With simulated solar irradiation, the current reached 29.5 μA cm$^{-2}$ for WO$_3$ film at 0.75 V vs Ag/AgCl. On the other hand, TiO$_2$ film current does not deviate from zero significantly. This is expected since the band gap energy observed for TiO$_2$ film is in the order of UV region (3.26 eV).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{XRD patterns of powder samples (a) and the films (b). Main peaks are labelled for TiO$_2$ and WO$_3$ crystal planes with corresponded JCPDS card numbers.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{UV–vis diffuse reflectance spectra of the (a) WO$_3$ film, (b) TiO$_2$ film, (c) WO$_3$/TiO$_2$–40 wt% film and (d) FTO substrate. The intersection between the horizontal and vertical short dash dotted curves are the reference value of estimated $E_g$ for the films.}
\end{figure}

The powder heterostructures exhibit TiO$_2$ anatase phase peaks (JCPDS N° 01-086-1157) and WO$_3$-0.33H$_2$O orthorhombic phase peaks (JCPDS N° 35-0270) as the main crystalline phases. The powder heterostructures exhibit XRD patterns correspondent to TiO$_2$ anatase (JCPDS N° 01-086-1157) and WO$_3$-0.33H$_2$O orthorhombic (JCPDS N° 35-0270) as the main crystalline phases. The intensity of the (101) anatase TiO$_2$ plane is reduced with W loading and it may indicates the preferential WO$_3$ attachment at TiO$_2$ (101) crystal orientation to obtain the heterostructures.

Fig. 3b shows XRD patterns for the produced films deposited over the FTO substrate. As one can see, crystalline phase was not changed after TiO$_2$ film. However, during calcination, WO$_3$ changed from orthorhombic structure to hexagonal, as confirmed by JCPDS N° 01-085-2460. Ramana et al. \cite{25} confirms that the WO$_3$ phase transitions in thin films occur as the temperature increases, starting as monoclinic phase, then orthorhombic phase at 350 °C and, finally, hexagonal phase at 500 °C. There is no evidence of heterostructure detachment, i.e., by SEM images it is possible to assume that the heterostructure was preserved even after the WO$_3$ phase modification.
The heterostructure (WO$_3$/TiO$_2$–40 wt% film) showed a photocurrent density of 35.9 $\mu$A cm$^{-2}$ at 0.75 V vs Ag/AgCl, which is higher than the photocurrent observed for WO$_3$ film. Additionally, the HE film presented a step increase above −0.24 V while for WO$_3$ film it is observed at approximately 0.1 V vs Ag/AgCl. It is usually assumed the onset potential where the water oxidation reaction takes place at the electrode film surface and it could be observed by the step increase in photocurrent, Fig. 5a. As a result, the WO$_3$/TiO$_2$–40 wt% film is showed to initiate water oxidation process at lower applied potentials as compared to WO$_3$ film. Indeed, the photoexcited electrons and holes generated at the electrode surface upon illumination occur at lower voltages for the
heterostructured film and the negative shift of the onset potential represents a good response for photoelectrochemical water splitting.

For a better comprehension of the electronic mechanism in the photoelectrochemical cell, there are two main aspects to be considered: i) effective charge transport and ii) effective charge separation. By employing Na$_2$SO$_3$ 0.5 mol L$^{-1}$, Na$_2$SO$_4$ 0.5 mol L$^{-1}$, pH 6.0, the electrolyte (a hole scavenger) can completely suppress surface recombination without affecting charge separation within the space charge layer of the electrode. With this strategy we can differentiate between the two mechanisms that may be acting at the heterostructured material and to elucidate the electronic mechanism for water oxidation process. From Fig. 5b, WO$_3$/TiO$_2$–40 wt% film shows the best performance with 210 $\mu$A cm$^{-2}$ at 0.75 V vs Ag/AgCl. The isolated oxide films reached a photocurrent density of approximately 12 $\mu$A cm$^{-2}$ at the same conditions. Thus, the mechanism occurring on the heterostructured film is actually effective charge separation at the electrode surface, as indicated by the hole scavenger test in Fig. 5b. The increase in photocurrent density for the isolated oxide films in the presence of the hole scavenger is correlated to the decrease in surface charge recombination, since the sulfite electrolyte acts as a hole collector with 100% efficiency.

Apart from the hole scavenger test, the effect of the band edge alignment was investigated by Mott-Schottky plots, Fig. 6. It is assumed that for n-type semiconductors such as WO$_3$ and TiO$_2$, the difference between the flat band potential (E$_{fb}$) and the conduction band edge is very small [26]. Also, for a heterostructured system it is well established that electrons can flow from one semiconductor structure to another, when the Fermi level $E_f$ of semiconductor 1 > $E_f$ of semiconductor 2, until equilibrium is reached and $E_f$ semiconductor 1 is similar to $E_f$ semiconductor 2. Based on these statements, we can estimate the band energy levels for the produced films as a comparison with the observed photoelectrochemical performance for water oxidation.

According to Mott-Schottky plot (Fig. 6), the $E_{fb}$ of TiO$_2$ is estimated as $-1.34$ V and for WO$_3$ is $-0.26$ V vs Ag/AgCl. When the semiconductors are excited with appropriate light intensity, electrons can be transferred from the conduction band of TiO$_2$ to WO$_3$, since the $E_{fb}$ of TiO$_2$ is 1.08 V higher than for WO$_3$, until thermodynamic equilibrium is established where $E_f$ levels are the same across the heterojunction [27]. An opposite flow of holes ($h^+$) from the valence band of WO$_3$ to TiO$_2$ is expected. As a result, the photogenerated electrons and holes can be spatially distributed in two different crystalline phases of TiO$_2$ and WO$_3$ and charge recombination is inhibited, which can explain the efficient photocatalytic activity towards water oxidation in the photoelectrochemical cell, as compared to the performance of the isolated oxides [28]. This is in agreement with the hole scavenger test in Fig. 8b, where the increase in photocurrent density of WO$_3$/

Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>$J (\mu A cm^{-2})$</th>
<th>$J (\mu A cm^{-2})$ with hole scavenger</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial TiO$_2$</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>WO$_3$</td>
<td>29.5</td>
<td>12</td>
</tr>
<tr>
<td>WO$_3$/TiO$_2$–40 wt%</td>
<td>35.9</td>
<td>210</td>
</tr>
</tbody>
</table>

Fig. 6. Mott-Schottky plots without illumination at 10 kHz in 0.5 M Na$_2$SO$_3$ electrolyte. (a) TiO$_2$ film (b) WO$_3$ film and (c) WO$_3$/TiO$_2$–40 wt% film.
TiO\(_2\) 40 wt\% film is observed as a consequence of the effective charge separation mechanism and transference. Also, it is possible to calculate the donor density (\(N_0\)) which is derived from Mott-Schottky plots as described elsewhere [19]. The films presented \(N_0\) values of 2.59 \(\times\) 10\(^{10}\) and 1.17 \(\times\) 10\(^{18}\) cm\(^{-2}\) for TiO\(_2\) and WO\(_3\) respectively. For the heterostructured film \(N_0\) is much higher (1.59 \(\times\) 10\(^{20}\)) and it is in accordance to the best photoelectrochemical performance for water oxidation as exhibited by WO\(_3\)/TiO\(_2\)-40 wt\% film.

To elucidate the band edge level for the films and to establish a correlation between heterojunction formation and enhanced photocurrent as observed through photocurrent-voltage measurements, the conduction band edge (\(E_{CB}\)) can be estimated with a small shift of the \(E_0\) from the Mott Schottky plot [18]. The valence band edge (\(E_{VB}\)) can be determined with respect to \(E_{CB}\), as \(E_{VB} = E_{CB} + E_{v}\), where \(E_v\) is obtained by DRS analysis. The experimentally determined energy diagram is presented in Fig. 7. It is consistent with the formation of a type II heterojunction between TiO\(_2\) and WO\(_3\) and it correlates well to recent reports in the literature for the improvement of spatial charge separation and consequently increase in photocatalytic response [29,20]. Those results provide substantial arguments to explain the mechanisms that occur at the electrode surface for the photoassisted water splitting.

When the heterojunction is illuminated with simulated solar irradiation, WO\(_3\) is able to produce electron-hole pairs due to its electronic structure, where the holes at the \(E_{VB}\) of WO\(_3\) are spontaneously injected into the \(E_{CB}\) of TiO\(_2\) because of the work function and chemical potential difference between these semiconductors at the interface of a type II band alignment. On the other hand, the electrons at the \(E_{CB}\) of WO\(_3\) are not allowed to be injected into the \(E_{CB}\) of TiO\(_2\) due to thermodynamics as indicated in Fig. 6, which prevents charge recombination at the electrolyte solution and contributes to the migration of electrons to the outer circuit. Hence the WO\(_3\)/TiO\(_2\) heterojunction is expected to exhibit the improved photocatalytic performance under simulated solar irradiation.

5. Conclusion

WO\(_3\) and TiO\(_2\) particles are in contact with each other, which show different particle morphologies of the heterostructures and the precursor oxides. The heterostructures were formed by the crystallization of WO\(_3\) micro-particles attached to TiO\(_2\) nanoparticles with agglomerate structure. The synthesis method as well as the deposition method is appropriate for the formation of WO\(_3\)/TiO\(_2\) heterostructures due to the uniform distribution of Ti and W elements in the deposited film. Film preparation procedure was shown to influence phase composition of the heterostructures, where crystalline phase was not changed after film production for TiO\(_2\) film (mainly anatase phase), but WO\(_3\) changed from orthorhombic structure to hexagonal structure after calcination. WO\(_3\)/TiO\(_2\)-40 wt\% film presented intermediate band gap energy (3.23 eV) between pristine TiO\(_2\) (3.26 eV) and WO\(_3\) values (3.03 eV). More evidence of the effective charge separation at the heterojunction is showed using a hole scavenger during the photoelectrocatalytic tests where the photocurrent is much higher than the pure oxides (210 \(\mu\)A cm\(^{-2}\) for the heterostructure and around 12 \(\mu\)A cm\(^{-2}\) at 0.75 V vs Ag/AgCl for pure oxides). This is a clear evidence of heterostructures' photocatalytic efficiency toward water oxidation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2017.02.024.

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