Insights of Fe$_2$O$_3$ and MoO$_3$ Electrodes for Electrocatalytic CO$_2$ Reduction in Aprotic Media

Néstor E. Mendieta-Reyes $^{1,*}$, Alejandra S. Lozano-Pérez $^{1,*}$ and Carlos A. Guerrero-Fajardo $^{1,*}$

Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Bogotá 11321, Colombia
* Correspondence: caguerrerofa@una.edu.co; Tel.: +57-3164308909

Abstract: Transition metal oxides (TMO) have been successfully used as electrocatalytically active materials for CO$_2$ reduction in some studies. Because of the lack of understanding of the catalytic behavior of TMOs, electrochemical methods are used to investigate the CO$_2$ reduction in thin-film nanostructured electrodes. In this context, nanostructured thin films of Fe$_2$O$_3$ and MoO$_3$ in an aprotic medium of acetonitrile have been used to study the CO$_2$ reduction reaction. In addition, a synergistic effect between CO$_2$ and the TMO surface is observed. Faradic cathodic processes not only start at lower potentials than those reported with metal electrodes, but also an increase in capacitive currents is observed, which is directly related to an increase in oxygen vacancies. Finally, the results obtained show CO as a product of the reduction.

Keywords: CO$_2$ reduction; TMO electrodes; electrocatalysis; dissociative electroreduction model

1. Introduction

The current atmospheric levels of carbon dioxide and the depletion of fossil fuel reserves raise serious concerns about the resulting effects on the global climate change and on the future of some energy sources [1]. The electrochemical conversion of carbon dioxide is a promising way to address both problems simultaneously; this strategy provides an opportunity for the supply of platform chemicals, which can be used as supplementary raw materials in several industrial processes, or energy sources [2]. A wide variety of methods, such as photocatalysis, electrocatalysis, and heterogeneous catalysis, have all been successful in CO$_2$ reduction [3]. Factors such as solvent, electrolyte, pH, temperature, CO$_2$ concentration, electrode material, surface structure, and electrode potential influence the variety of products obtained [4,5]. Reduction products, including CO, CH$_4$, and CH$_3$OH, among others, have been reported [6–8]. This leads to the development of several reaction mechanisms with different numbers of electrons transferred, which determines the final oxidation state of the carbon atom [9]. However, due to the linear geometry with a closed-shell electronic configuration, the high energy level of its LUMO, and the TMO surface is observed. Faradic cathodic processes not only start at lower potentials than those reported with metal electrodes, but also an increase in capacitive currents is observed, which is directly related to an increase in oxygen vacancies. Finally, the results obtained show CO as a product of the reduction.

In this sense, several reports have shown that the stabilization of the CO$_2$(−) anion radical is an important step for achieving an efficient reduction of CO$_2$. The CO$_2$ molecule can then be activated on a solid-state catalyst, whose function is to adsorb the CO$_2$ molecules by facilitating electron transference from the catalyst, providing favorable conditions for the binding of the molecule and the desorption of the products [10–13]. In this regard, the adduct formation of CO$_2$(δ−) on different metal oxides has been widely reported [16,17]. On the other hand, in an aqueous solution, different factors, such as acid-base equilibria and hydrogen synthesis occurring as a competitive process, act against obtaining
high efficiency and selectivity. In this sense, acetonitrile (ACN) is one of the most widely used non-aqueous aprotic solvents in catalysis and electrochemistry, and has been used to study the electrocatalytic CO\textsubscript{2} reduction [18–20]. Pons et al. studied solutions of tetra-n-butylammonium tetrafluoroborate (TBAF) in dry ACN, finding ACN decomposition at potentials more negative than ~3.0 V vs. Ag/Ag+ (0.01 M) [5]. The ACN solution containing tetrabutylammonium salts, such as the electrolyte system, TBAF (0.1 M), has been used for the study of the electrocatalytic reduction of CO\textsubscript{2}. This non-aqueous system not only offers stability at a potential window more negative than $-1.97$ V vs. SHE, which is needed for the first CO\textsubscript{2} electron transfer, but also that avoids the hydrogen synthesis as a competitive reaction.

Metal oxides are used as electrocatalysts for CO\textsubscript{2} reduction [21], and transition metal oxides (TMO) have been theoretically predicted to have efficient active sites for said reduction reaction [22]. In fact, these materials have reactive electrons, empty d orbitals, and crystalline defects, such as oxygen vacancies (OV), grain boundaries, and non-stoichiometry, that are capable of triggering the CO\textsubscript{2} molecule activation, inducing the formation of the CO\textsubscript{2}($\delta$·$-$) adduct [11]. Compared with metal catalysts, TMO can further improve the performance of CO\textsubscript{2} reduction, which has drawn attention in recent studies. Some researchers have proposed that the active sites for CO\textsubscript{2} in metal oxides are due to the reconstruction of their surface, formed by the reduced surface of the metal oxide at highly negative operating potentials [23], whereas others have highlighted metal-oxygen sites as active, leaving an open debate on this topic [24]. In this context and based on the dissociative reduction model previously reported for CO\textsubscript{2} conversion at WO\textsubscript{3} and TiO\textsubscript{2} electrodes, results on Fe\textsubscript{2}O\textsubscript{3} and MoO\textsubscript{3} electrodes are shown for the CO\textsubscript{2} electrochemical reduction. These findings provide an explanation for the electrocatalytic activity seen in other TMOs that have been previously studied, as well as their relationship with surface processes and the formation of OV, in terms of cathodic current and the initial potential that is related to CO\textsubscript{2} reduction [25–27].

2. Results and Discussion

Fe\textsubscript{2}O\textsubscript{3} and MoO\textsubscript{3} thin-film electrodes were coated on Fluorine-doped Tin Oxide (FTO) substrates following two different synthesis routes, as explained in the Supplementary Information, leading to different morphologies. Synthesized Fe\textsubscript{2}O\textsubscript{3} thin-film surface characterization is shown as to hematite, and a highly coated nanostructured electrode surface displaying 50 nm-thick nanoparticles is observed (Figure S2). An oxide film cross-section image, with approximately 500 nm-thickness, shows partially oriented nanobars. FE-SEM images for MoO\textsubscript{3} electrodes, at two different magnification levels of 5000× and 25,000×, are shown in Figure S3. Electrodes prepared by sol-gel process are thoroughly coated, with no uncoated substrate areas (Figure S3a). The morphology of the nanoparticles (Figure S3b) is in accordance with electrodes synthesized by the sol-gel technique. The observed nanoparticles’ diameter is between 20–40 nm, with crystal aggregates well interconnected with each other. The X-ray diffraction pattern of the FTO-coated thin-film electrodes presented in Figure S4 indicates that the as-prepared product presents high-crystallinity.

For electrochemical studies, the prepared electrodes were evaluated in a 0.1 M tetra-n-butylammonium perchlorate (TBAP)/ACN solution as the supporting electrolyte. The electrolyte solution was purged with CO\textsubscript{2} and N\textsubscript{2} for 30 min before the electrochemical procedure. Figure 1 shows the voltammetric response for both the Fe\textsubscript{2}O\textsubscript{3} and MoO\textsubscript{3} working electrodes. The potential window for CO\textsubscript{2} reduction was determined by purging with N\textsubscript{2}. Both Fe\textsubscript{2}O\textsubscript{3} and MoO\textsubscript{3} electrodes show an increase in the cathodic current, with an onset at around $-0.4$ V and $-0.6$ V, respectively, which coincides with the beginning of the accumulation region. From a chemical point of view, such an increase can be seen as corresponding to Fe\textsubscript{(ss)}(III)/(II) and Mo\textsubscript{(ss)}(VI)/(V) redox processes in surface sites for Fe\textsubscript{2}O\textsubscript{3} and MoO\textsubscript{3} (indicated on the figure). Similar behavior has been observed in semiconductor materials such as TiO\textsubscript{2} [28].
The capacitive current has been explained in terms of the increment of OV promoted by generation. This makes the potential at the onset of the reduction of metal atoms at TMO surface density of MoO3 capacitance, even at potentials where CO2 and FeO reduction does not occur. This fact suggests important changes in the electrode state that could be associated with an increase in the surface density of MoO3- and FeO2-reduced species as a result of the enhancement of the OV generation. This makes the potential at the onset of the reduction of metal atoms at TMO and the cathodic current associated with CO2 reduction indistinguishable. The increase in the capacitive current has been explained in terms of the increment of OV promoted by increasingly negative applied potential, which favors CO2 electro adsorption according to the equations:

\[(1 + y)\text{MoO}_3 + y\text{CO}_2 + 2y \, \text{e}^{-} \rightarrow \text{MoO}_3-y\text{(CO}_2)_y + y\text{MoO}_4^{2-} \quad (1)\]

\[(1 + y)\text{Fe}_2\text{O}_3 + 2y \, \text{e}^{-} \rightarrow \text{Fe}_2\text{O}_3-y + 2y\text{FeO}_2^{-} \quad (2)\]

\[(1 + y)\text{Fe}_2\text{O}_3 + y\text{CO}_2 + 2y \, \text{e}^{-} \rightarrow \text{Fe}_2\text{O}_3-y\text{(CO}_2)_y + 2y\text{FeO}_2^{-} \quad (3)\]

In this dissociative model, the partial electroreduction of MO3 and Fe2O3 is limited to the interfacial region, whereas no significant structural damage occurs in the underlying region of the metal oxide film. According to Equations (1) and (3), the partial electroreduction of Mo and Fe lattice atoms from Mo6+ to Mo5+ and Fe3+ to Fe2+ induces the formation of oxygen-deficient metal oxide, MoO3-x and Fe2O3-x. Additionally, this mechanism entails a loss of mass due to the electrodissolution of MoO3 and Fe2O3 by the formation of MoO42- and FeO2- [31].

Under the CO2 purged condition, faradaic currents at −0.6 V and −0.8 V are observed for Fe2O3 and MoO3, respectively. In both cases, the presence of CO2 increased the electrode capacitance, even at potentials where CO2 reduction does not occur. This fact suggests important changes in the electrode state that could be associated with an increase in the surface density of MoO3- and FeO2-reduced species as a result of the enhancement of the OV generation. This makes the potential at the onset of the reduction of metal atoms at TMO and the cathodic current associated with CO2 reduction indistinguishable. The increase in the capacitive current has been explained in terms of the increment of OV promoted by increasingly negative applied potential, which favors CO2 electro adsorption according to the equations:

\[(1 + y)\text{MoO}_3 + y\text{CO}_2 + 2y \, \text{e}^{-} \rightarrow \text{MoO}_3-y\text{(CO}_2)_y + y\text{MoO}_4^{2-} \quad (4)\]

\[(1 + y)\text{Fe}_2\text{O}_3 + y\text{CO}_2 + 2y \, \text{e}^{-} \rightarrow \text{Fe}_2\text{O}_3-y\text{(CO}_2)_y + y\text{FeO}_2^{-} \quad (5)\]

\[(1 + y)\text{Fe}_2\text{O}_3 + y\text{CO}_2 + 2y \, \text{e}^{-} \rightarrow \text{Fe}_2\text{O}_3-y\text{(CO}_2)_y + 2y\text{FeO}_2^{-} \quad (6)\]
The adsorption of CO$_2$ would, thus, promote the generation of non-stoichiometric Fe$_{2(3-y)}$(CO$_2$)$_y$ and MoO$_{3-y}$(CO$_2$)$_y$. In this sense, the adsorption of CO$_2$ induces the stabilization of reduced metal sites. The results show that CO$_2$ binds slightly more strongly to stoichiometrically Ti(III)-deficient sites than to Ti(IV) sites, according to CO$_2$ adsorption studies on TiO$_2$. Therefore, it is reasonable to assume that CO$_2$ adsorption is favored at reduced metal sites (Mo(V) and Fe(II)). Thus, a synergistic effect between CO$_2$ and surface sites is verified. CO$_2$ adsorption not only activates the molecule by the adduct formation, but also induces a promotion of OV and the electron-rich center formation in reduced metal species. By further reducing the applied potential, the resulting high concentration of electrons located in the near-surface region would facilitate charge transfer from the electrode to the adsorbed CO$_2$ molecules, leading to the appearance of faradaic currents. It is worth noting that CO has been detected by gas chromatography analysis (presented in Figure S1 in Supporting Information), and the formation proceeds with two electrons transferred, according to Equations (7) and (8):

\[
(1 + y)\text{MoO}_3 - y(\text{CO}_2)_y + 2ye \rightarrow \text{MoO}_3 - y + y\text{CO} + y\text{MoO}_4^{2-}
\]  

\[
(1 + y)\text{Fe}_2\text{O}_3 + y\text{CO}_2 + 2ye \rightarrow \text{Fe}_2\text{O}_3 - y + y\text{CO} + y\text{Fe}_2\text{O}_4^{2-}
\]

In the positive-going scan, a pseudocapacitive peak related to the reoxidation of the reduced metal is observed, and an enhancement in the electrode capacitance related to the increase in reduced metal sites Fe$_{(ss)}$(II)/(III) and Mo$_{(ss)}$(V)/(VI) is evident. Moreover, in the case of Fe$_2$O$_3$, an additional peak, probably related to the reoxidation of some CO$_2$ reduction product, appears at 0.3 V. This fact is intriguing because it demonstrates that each metal oxide has unique electrocatalytic behavior for CO$_2$ reduction and the formation of reduction products. It is important to highlight that carbon dioxide reduction does not proceed when a bare FTO conducting glass electrode is used.

To determinate the nature of the currents associated with CO$_2$ electrocatalytic reduction, a linear sweep voltammetry (LSV) was performed. At a relatively low scan rate (5 mV·s$^{-1}$), the capacitive current decreases, and the faradic currents are mainly observed. Figure 2 shows the initial potential at which the cathodic current for CO$_2$ reduction appears, providing further evidence on the faradaic nature of the cathodic currents linked to CO$_2$ reduction. However, the presence of CO$_2$ generates changes in current profiles, and not only produces faradic currents due to CO$_2$ reduction, but also increases capacitive currents due to the formation of electron-rich centers in reduced metal species. Therefore, to determinate the potential at which the faradaic process starts for the metal oxide materials studied, a double potential step chronoamperometry experiment was performed. A potential step was performed from the 1.0 V as initial potential (Pi), at which no faradaic process occurs, to several negative final potentials (Pf). Each step was applied for 59 s.

The chronoamperometric profiles shown in Figure 3 indicate the potential steps associated with each thin-film electrode. For MoO$_3$, when the applied potential returns to Pi, the current in both CO$_2$ and N$_2$ purged is the same. In contrast, after electrode polarization to the initial potential from each final potential with CO$_2$ electrode saturation, Fe$_2$O$_3$ shows an increase in anodic current. This could possibly be related to a reduction product reoxidation. In this sense, it is worth noting that a wide potential peak at 0.2 V is observed, as can be seen from the cyclic voltammetry results. When a negative potential was applied under N$_2$ and CO$_2$ purging conditions, the currents were not always the same at the end of each step potential. For Fe$_2$O$_3$, an increase in current is observed from $-0.3$ V after 59 s under CO$_2$ purge conditions, the increase being higher at $-0.5$ V. For MoO$_3$, said increase in current becomes evident at $-0.7$ V.
Double potential step chronoamperometry results for the electrocatalytic reduction of CO$_2$ in 0.1 M TBAF/ACN electrolyte solution with thin-film electrodes: (a) Fe$_2$O$_3$, (b) MoO$_3$. The red and black graphs correspond to the electrolyte purged with N$_2$ and CO$_2$, individually. Blue arrow corresponds to initial potential (Pi). Arrows indicate potential steps.

Under CO$_2$ and N$_2$ bubbling conditions, the absolute value of the difference between observed currents as a function of the applied potential step is defined by Equation (9):\[ |j_{\text{CO}_2\text{max}}(v)| - |j_{\text{N}_2\text{max}}(v)| = (V) \] where $|j_{\text{CO}_2\text{max}}(v)|$ and $|j_{\text{N}_2\text{max}}(v)|$ are the cathodic currents obtained 59 s after the electrode polarization occurs at the potential Pf.

A current profile calculated using Equation (9) has an increase in the relationship between faradaic and non-faradaic currents, as shown in Figure 4. In each case, the intercept with the potential axis corresponds to the onset potential for faradaic current related with the CO$_2$ reduction. The onset for electrodes used in this study was −0.4 V for Fe$_2$O$_3$, and −0.6 V for MoO$_3$. Furthermore, Figure 4 reveals not only the decrease of the overpotential for CO$_2$ reduction, but also the higher faradaic currents for the Fe$_2$O$_3$ electrode, being the best electrocatalytic electrode under the experimental conditions. It should be noted that differences in electrode interface area may vary and are desirable for proper electrode performance comparison.
Figure 4. Profile of current associated with CO$_2$ reduction faradaic processes for examined TMO materials as a function of applied potential in square-wave chronoamperometric experiments.

On the other hand, TMOs, such as Fe$_2$O$_3$ and MoO$_3$, are n-type semiconductors, and their catalytic activity could be related to the conduction band position [32]. The conduction band position could estimate if the electron transfer is thermodynamically feasible. Although several conduction and valence band position diagrams are found in literature for the thin film electrodes studied, these values correspond to conditions different from those applied in this study, and are generally under vacuum conditions [33]. However, the potential at which the conduction band is found depends on factors such as the type of oxide, charge state of the surface, presence of adsorbed species, pH, and isoelectric point of the material [34]. In this way, the flat band potential was estimated via photoelectrochemical measurements in the presence of low oxidation potential species such as methanol [35]. This potential should be very close to the potential of the conduction band lower edge, and related with the apparition of photocurrents. Figure S5 in Supporting Information shows the LSV profile for Fe$_2$O$_3$ and MoO$_3$ electrodes under transitory illumination, in 0.1 M de TBAF/ACN/+3.0 M CH$_3$OH, purged with N$_2$. The results show that photocurrent onset potentials start at $-0.70$ V for Fe$_2$O$_3$, and $0.65$ V for MoO$_3$. Therefore, the electron transference from the TMO to CO$_2$ molecule and the formation of thermodynamically favored C$_1$ products from CO$_2$ reduction are feasible. Scheme 1 represents the conduction band position for TMO under the conditions of this study, and the potentials (versus SHE at pH 7) for some relevant CO$_2$ redox couples (Scheme 1).

The results show a generalized catalytic behavior for CO$_2$ electrocatalytic reduction over the TMO electrodes used. In all cases, a decrease in the overpotential related to that required for the first CO$_2$ electron transfer is evident. According to the dissociative reduction model, in the presence of CO$_2$, the formation of OV caused by the application of increasingly negative potentials appears to be favored by the stabilization of Fe$^{2+}$ and Mo$^{5+}$ species upon CO$_2$ chemisorption. Therefore, it is plausible to think that CO$_2$ could be adsorbed in reduced metal sites, and that the OV generation is favored. Metal reduction is facilitated, causing an increase in capacitive currents in CV profiles, even at potentials where CO$_2$ reduction does not proceed. In this sense, it is reasonable to think that the catalytic surface of the examined TMO materials possesses a different morphology and adsorption energy for CO$_2$, and, therefore, a different activation capability [11,36,37]. Likewise, Tanabe et al. found that basic metal oxides facilitate the transfer of electrons to CO$_2$ molecules adsorbed on the surface by adduct formation [38].
Although the activation of the CO$_2$ molecule by adsorption on the surface of the catalyst favors its reduction, it is not the only factor that determines the electrocatalytic activity of the electrode. The formation of the adsorbed surface does not always lead to CO$_2$ reduction [36]. In this sense, it is important to consider the need of electron-rich active sites giving rise to electron transfer from the TMO surface to the CO$_2$ molecule. Thus, the formation of reduced sites identified as catalytic sites for the reduction of CO$_2$ occurs [21,39]. Density Functional Theory calculations show that OV with n-type semiconductor behavior enhance the surface state near the conduction band [40]. Based on the results obtained, the increment of surface states improves the electrode catalytic activity even at potentials at which CO$_2$ reduction does not occur.

Finally, conduction band position, OV density and their associated energy, as well as surface state density are parameters needed to understand the electrocatalytic behavior of TMO materials. Table 1 presents the initial flat band and faradaic current potentials, $E_{f_b}$ and $E_{f_i}$ for the electrocatalytic reduction of CO$_2$.

**Table 1. Initial and flat band potential for TMO electrodes.** Potentials were measured versus an Ag/AgCl/KCl$_{sat}$ reference electrode.

| Electrode | $E/V$ ($E_{f_b}$) | $E/V$ ($E_{f_i}$) |
|-----------|------------------|------------------|
| Fe$_2$O$_3$ | −0.70            | −0.4             |
| WO$_3$    | −0.50            | −0.6             |
| MoO$_3$   | −0.60            | −0.6             |
| TiO$_2$   | −1.55            | −1.3             |

The initial faradaic onset potential for Fe$_2$O$_3$ electrodes is less negative than those at the conduction band position. This fact reveals a high density of surface states near the conduction band; from which, electron transfer to the adsorbed CO$_2$ molecules occurs. In the case of MoO$_3$, $E_{f_b}$ and $E_{f_i}$ are very close to each other. The initial potential for MoO$_3$ is 0.05 V, which is less negative than its flat band potential. This could be related to the fact that the metal Mo has different oxidation numbers; therefore, the excess charge from the formation of OV can be distributed on both surface and bulk atoms, causing the excess charge to delocalize, and the density of electron-rich sites to decrease. The migration
capability for OV in TMO such as TiO\(_2\) and WO\(_3\) is predicted by DFT studies, as well as (0 0 1)-orientation activation energies of 0.76 V and 0.14 V, respectively [41,42]. This means that excess electrons resulting from OV formation in TMO such as MoO\(_3\) may migrate to the bulk structure more seamlessly than Fe\(_2\)O\(_3\) [43], which suggests a greater availability of Lewis basic active sites on the TMO surface for CO\(_2\) reduction when the OV migration energy is higher.

3. Materials and Methods

The preparation of Fe\(_2\)O\(_3\) and MoO\(_3\) electrodes was carried out by chemical bath deposition and the sol-gel method, respectively [28]. Experimental details for oxide thin-film synthesis and the characterization are presented in the Supporting Information.

A computer-controlled micro-Autolab potentiostat was used for all electrochemical experiments. A conventional three-electrode glass cell was used with an Ag/AgCl(s)/KCl (aq,sat) reference electrode and a Pt wire as a counter electrode in all the experiments. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAP) (≥99.0% from Sigma-Aldrich, Madrid, Spain) in ACN (99.88% anhydrous from Scharlau, Multisolvent, HPLC grade, Barcelona, Spain). In all the experiments, the electrolyte was purged for 30 min with either N\(_2\) (Alphagaz 99.999%, Madrid, Spain) or CO\(_2\) (Air Liquid, 99.98%, Madrid, Spain). A conversion of potentials measured to SHE scale is the same as previously reported, and according to Pavlishchuk and Addison. Detailed information about materials, methods, and the potential conversion scale are presented in the Supporting Information.

4. Conclusions

Based on the results obtained, TMOs present an electrocatalytic behavior for the reduction of CO\(_2\) in ACN medium. In this sense, it could be affirmed that the location of the conduction band, the ability to generate OV, and charge accumulation in surface states are factors that can modify the charge transfer from TMO to CO\(_2\). The results obtained show that, in general terms, the less negative (in potential) the conduction band position is, the more positive the potential at which the processes of faradic reduction of CO\(_2\) are initiated. This behavior is expected, since there is a correlation between the location of the edge of the conduction band and the electronic surface states responsible for the CO\(_2\) activation. In this sense, future studies that allow obtaining information on the generation energy and the migration of OVs may be relevant for the evaluation of a TMO as a possible (photo)cathode for CO\(_2\) reduction. Finally, it should be noted that carbon monoxide was obtained as a reduction product, which is in accordance with what is expected for aprotic systems.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ijms232113367/s1. References [44,45] are cited in the Supplementary Materials.

Author Contributions: Conceptualization, N.E.M.-R. and C.A.G.-F.; methodology, N.E.M.-R. and A.S.L.-P.; formal analysis, N.E.M.-R. and A.S.L.-P.; investigation, N.E.M.-R.; data curation, A.S.L.-P.; writing—original draft preparation, A.S.L.-P.; writing—review and editing, N.E.M.-R.; supervision, C.A.G.-F.; project administration, C.A.G.-F. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by MINCIENCIAS through National Doctoral Scholarship (567-2019), and (848-2019) postdoctoral fellowship.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: We would like to acknowledge the support of the Universidad Nacional de Colombia, its facilities, and the use of its equipment.

Conflicts of Interest: The authors declare no conflict of interest.
30. Foley, J.K.; Korzeniewski, C.; Pons, S. Anodic and cathodic reactions in acetonitrile/tetra-n-butylammonium tetrafluoroborate: An electrochemical and infrared spectroelectrochemical study. *Can. J. Chem.* 1988, 66, 201–206. [CrossRef]

31. Hepel, M.; Wickham, D. Large Cation Model of Dissociative Reduction of WO$_{3-x}$ Lattice Studied by EQCN and AFM. *ECS Trans.* 2009, 19, 11–23. [CrossRef]

32. Chava, R.K.; Son, N.; Kang, M. Band structure alignment transitioning strategy for the fabrication of efficient photocatalysts for solar fuel generation and environmental remediation applications. *J. Colloid Interface Sci.* 2022, 627, 247–260. [CrossRef]

33. Jian, J.; Sun, J. A Review of Recent Progress on Silicon Carbide for Photoelectrochemical Water Splitting. *Sol. RRL* 2020, 4, 2000111. [CrossRef]

34. Wang, D.; Liu, Z.P.; Yang, W.M. Proton-Promoted Electron Transfer in Photocatalysis: Key Step for Photocatalytic Hydrogen Evolution on Metal/Titania Composites. *ACS Catal.* 2017, 7, 2744–2752. [CrossRef]

35. Ismael, M. Highly effective ruthenium-doped TiO$_2$ nanoparticles photocatalyst for visible-light-driven photocatalytic hydrogen production. *New J. Chem.* 2019, 43, 9596–9605. [CrossRef]

36. Breyer, C.; Reichert, D.; Seidel, J.; Hüttl, R.; Mertens, F.; Kureti, S. Kinetic modeling of the adsorption and desorption of CO$_2$ on α-Fe$_2$O$_3$. *Phys. Chem. Chem. Phys.* 2015, 17, 27011–27018. [CrossRef]

37. Liu, L.; Lin, M.; Liu, Z.; Sun, H.; Zhao, X. Density functional theory study of CO$_2$ and H$_2$O adsorption on a monoclinic WO$_3$(001) surface. *Chem. Res. Chin. Univ.* 2017, 33, 255–260. [CrossRef]

38. Wicke, E.J.R., Anderson, M., Boudart. (Eds.): Catalysis, Science and Technology. Vol. 4, Springer-Verlag, Berlin, Heidelberg, New York 1983. 289 Seiten, Preis: DM 132,-. *Ber. Bunsenges. Phys. Chem.* 1984, 88, 586. [CrossRef]

39. Rao, C.N.R. Transition Metal Oxides. *Annu. Rev. Phys. Chem.* 1989, 40, 291–326. [CrossRef]

40. Di Valentin, C.; Pacchioni, G.; Selloni, A. Reduced and n-Type Doped TiO$_2$: Nature of Ti$^{3+}$ Species. *J. Phys. Chem. C* 2009, 113, 20543–20552. [CrossRef]

41. Cheng, H.; Selloni, A. Energetics and diffusion of intrinsic surface and subsurface defects on anatase TiO$_2$ (101). *J. Chem. Phys.* 2009, 131, 054703. [CrossRef] [PubMed]

42. Le, H.M.; Vu, N.H.; Phan, B.T. Migrations of oxygen vacancy in tungsten oxide (WO$_3$): A density functional theory study. *Comput. Mater. Sci.* 2014, 90, 171–176. [CrossRef]

43. Yin, W.J.; Wen, B.; Zhou, C.; Selloni, A.; Liu, L.M. Excess electrons in reduced rutile and anatase TiO$_2$. *Surf. Sci. Rep.* 2018, 73, 58–82. [CrossRef]

44. Hasani-Sadrabadi, M.M.; Dashtimoghadam, E.; Nasseri, R.; Karkhaneh, A.; Majedi, F.S.; Mokarram, N.; Renaud, P.; Jacob, K.I. Cellulose nanowhiskers to regulate the microstructure of perfluorosulfonate ionomers for high-performance fuel cells. *J. Mater. Chem. A* 2014, 2, 11334. [CrossRef]

45. Pavlishchuk, V.V.; Addison, A.W. Conversion constants for redox potentials measured versus different reference electrodes in acetonitrile solutions at 25 °C. *Inorg. Chim. Acta* 2000, 298, 97–102. [CrossRef]