

## Review

# Cu-Based Materials as Photocatalysts for Solar Light Artificial Photosynthesis: Aspects of Engineering Performance, Stability, Selectivity

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**Abstract:** Cu-oxide nanophases (CuO, Cu<sub>2</sub>O, Cu<sup>0</sup>) constitute highly potent nanoplateforms for the development of efficient Artificial Photosynthesis catalysts. The highly reducing conduction band edge of the *d*-electrons in Cu<sub>2</sub>O dictates its efficiency towards CO<sub>2</sub> reduction under sunlight excitation. In the present review, we discuss aspects interlinking the stability under photocorrosion of the (CuO/Cu<sub>2</sub>O/Cu<sup>0</sup>) nanophase equilibria, and performance in H<sub>2</sub>-production/CO<sub>2</sub>-reduction. Converging literature evidence shows that, because of photocorrosion, single-phase Cu-oxides would not be favorable to be used as a standalone cathodic catalyst/electrode; however, their heterojunctions and the coupling with proper partner materials is an encouraging approach. Distinction between the role of various factors is required to protect the material from photocorrosion, e.g., use of hole scavengers/electron acceptors, band-gap engineering, nano-facet engineering, and selectivity of CO<sub>2</sub>-reduction pathways, to name a few possible solutions. In this context, herein we discuss examples and synthesis efforts that aim to clarify the role of interfaces, faces, and phase stability under photocatalytic conditions.

**Keywords:** Cu oxides; CuO; Cu<sub>2</sub>O; Cu<sup>0</sup>; Artificial Photosynthesis; Hydrogen Evolution Reaction (HER); photocatalysis; CO<sub>2</sub> reduction; single-atom; photocorrosion; Z-scheme



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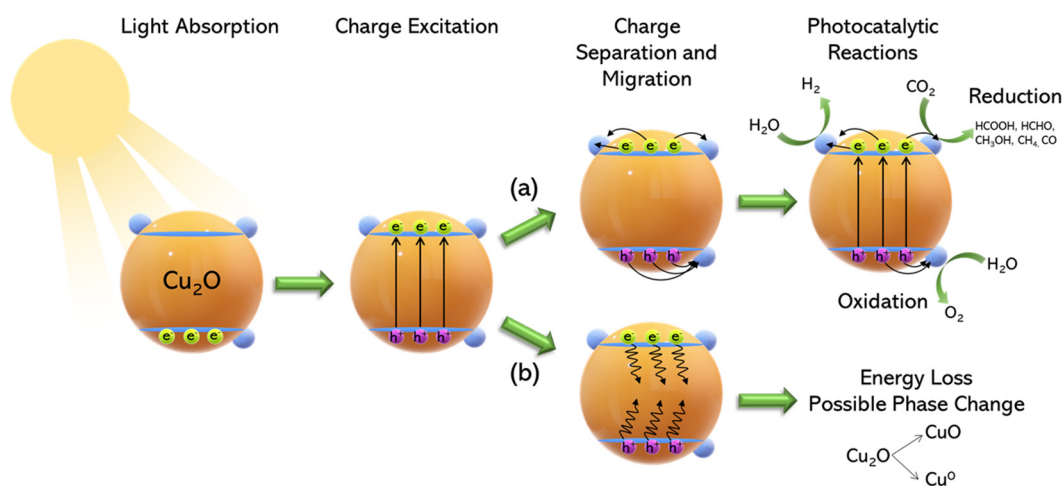


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## 1. Introduction

Over the last decades, the negative impact of greenhouse gas emissions on the environment is strongly correlated with air pollution, climate change, and global warming. Carbon dioxide (CO<sub>2</sub>) is considered one of the main greenhouse gases, thus strategies need to be developed in order to decrease CO<sub>2</sub> levels in the atmosphere. The “Artificial Photosynthesis” approach [1] aims to exploit photocatalytic technology, that is the use of solar photons to produce hydrogen (H<sub>2</sub>) and—ideally—couple it to CO<sub>2</sub> reduction towards carbon-based fuels. Economically and environmentally, this is a sustainable, circular economy approach since CO<sub>2</sub> reduction can result in useful products such as formic acid (HCOOH), formaldehyde (HCHO), methanol (CH<sub>3</sub>OH), methane (CH<sub>4</sub>), and carbon monoxide (CO), to name a few [2].

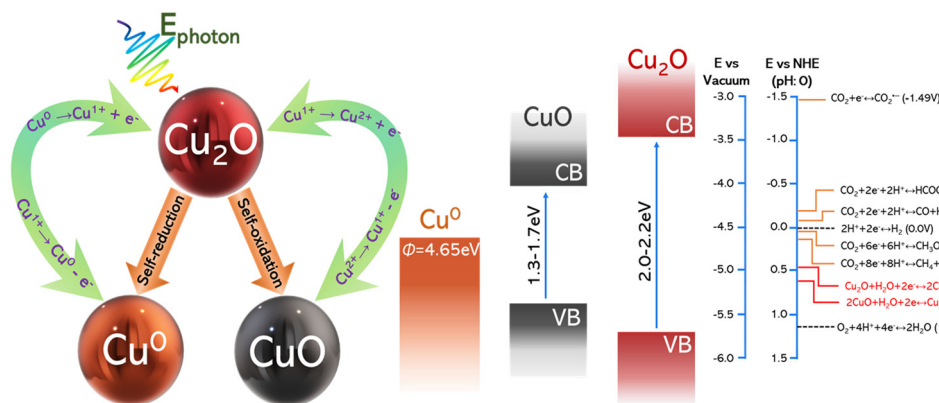
Both photocatalytic H<sub>2</sub> evolution from H<sub>2</sub>O and photocatalytic CO<sub>2</sub> reduction reactions (CO<sub>2</sub>RR) share some common steps, with their difference being on the specific surface reactions of the photogenerated electrons. These steps include, see Figure 1: photon-adsorption by the semiconductor, electron-hole separation and their migration to the semiconductor surface [3], and subsequent incorporation of the electron to a H<sup>+</sup>, leading towards H<sub>2</sub> or to one CO<sub>2</sub> radical, leading towards the HCOOH/HCOH/CH<sub>3</sub>OH/CH<sub>4</sub> chain. H<sub>2</sub> production can be identified as a less-complex process, compared to the CO<sub>2</sub> reduction, the latter involving CO<sub>2</sub> adsorption and activation, product formation, and desorption. Thus, CO<sub>2</sub> reduction is a multi-proton and multi-electron transfer process and selectivity of the products remains a major challenge (see Figure 1).



**Figure 1.** Schematic description of the photoexcitation-related reaction paths in  $\text{Cu}_2\text{O}$  semiconductors in path (a) electron-hole pairs are utilized for “Artificial-Photosynthesis”. In path (b), detrimental phase-transformation can occur due to photocorrosion.

The difficulty in activating the inert  $\text{CO}_2$  molecule lies in its closed-shell electronic configuration, linear geometry, and  $D_{\infty h}$  symmetry [2]. Thus, it requires a highly negative reduction potential of  $-1.9\text{ V}$  (vs. NHE at pH 7) to activate  $\text{CO}_2$  and form the  $\text{CO}_2^-$  radical, which the vast majority of semiconductors cannot provide [2].

Fujishima and Honda in 1972, [4], paved the way for light-induced water splitting by  $\text{TiO}_2$  and, since then, numerous studies on photocatalysts were presented, and in particular  $\text{TiO}_2$  [5–7]. Moreover, research interest in photocatalytic and photo-electrochemical applications has increased, prompting successful engineering of various semiconducting photocatalysts [5,8–10]. So far,  $\text{TiO}_2$  remains the most studied photocatalyst, due to its chemical stability, low cost, and availability [11]. However, the large energy gap of  $\text{TiO}_2$  (3.2 eV) [3] limits its photoactivity exclusively in the ultraviolet radiation range, typically  $\lambda < 360\text{ nm}$ , which accounts for 2–5% of the sunlight [12]. Moreover, the conduction band (CB) edge of  $\text{TiO}_2$  is  $E_{\text{CB}} = -160\text{ mV}$  vs. NHE (pH = 0) or  $E_{\text{CB}} = -50\text{ mV}$  (pH = 7) [3], which disfavors its photoexcited electrons to efficiently achieve reduction of  $\text{CO}_2$  towards the key intermediate  $\text{CO}_2^-$ . In this context, *p*-type  $\text{Cu}_2\text{O}$  is considered as highly promising and attractive since it can absorb visible-light photons,  $E_g$  in the range 2.0–2.2 eV [13–16], and mostly due to the highly reducing energy positioning of its conduction-band edge, which is approximately  $E_{\text{CB}} = -1000\text{ mV}$  vs NHE (pH = 0) (see Figure 2) [10].



**Figure 2.** The photocorrosion pathways can involve either “self-oxidation” or “self-reduction” of  $\text{Cu}_2\text{O}$ . This is related to the positions of the redox couples  $\text{Cu}^{1+}/\text{Cu}^{2+}$  and  $\text{Cu}^{1+}/\text{Cu}^0$  relative to the  $E_{\text{VBand}}$  and  $E_{\text{CBand}}$  edges.

As an element, Cu has high abundance on Earth's crust, ease of handling and manufacturing, low cost, and low environmental toxicity. In the family of stable Cu-oxides,  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  are direct-bandgap semiconductors with  $E_g$  in the range 2.0–2.2 eV ( $\text{Cu}_2\text{O}$ ) and 1.3–1.7 eV ( $\text{CuO}$ ) [13–16], respectively. The variations in  $E_g$  values depend mainly on the particle-morphology and nano- vs. bulk-size [17]. The small bandgap energies allow  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  to absorb the majority of solar-photons while their direct-bandgaps endow the two oxides with large photon-absorption coefficients [18,19]. Additionally, it is reported that copper-based catalysts and the different Cu oxidation states can significantly improve the kinetics and thermodynamics of  $\text{CO}_2$  adsorption, activation, and CO dimerization [20,21]. Li et al. [9] discuss the selectivity of various cocatalysts for the photocatalytic  $\text{CO}_2$  reduction. In this context, metallic  $\text{Cu}^0$  is more favorable for the production of hydrocarbons, primarily  $\text{CH}_4$ , while  $\text{Cu}_2\text{O}$  favors  $\text{CH}_3\text{OH}$  production [2,9].

While  $\text{CuO}$  is known to be the most stable copper oxide, the stability of  $\text{Cu}_2\text{O}$  under photochemical processes, is a matter of concern. The usually reported lack of long-term stability can be attributed to “*photocorrosion*”, a term referring to the occurrence of lattice-destabilization linked to consumption of the photogenerated carriers, see Figure 2, affecting its overall photo-performance [22]. These events, together with eventual enhanced electron-hole recombination rate in  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ , may be detrimental for Hydrogen-Evolution Reaction photocathodes [13,18,23–25]. Pertinent review articles have been published in the literature on the synthesis of Cu-oxides [18,26–28], their use as photocatalysts for pollutant degradation,  $\text{H}_2$ -production from water [6,29], and  $\text{CO}_2$  reduction [10,20,30].

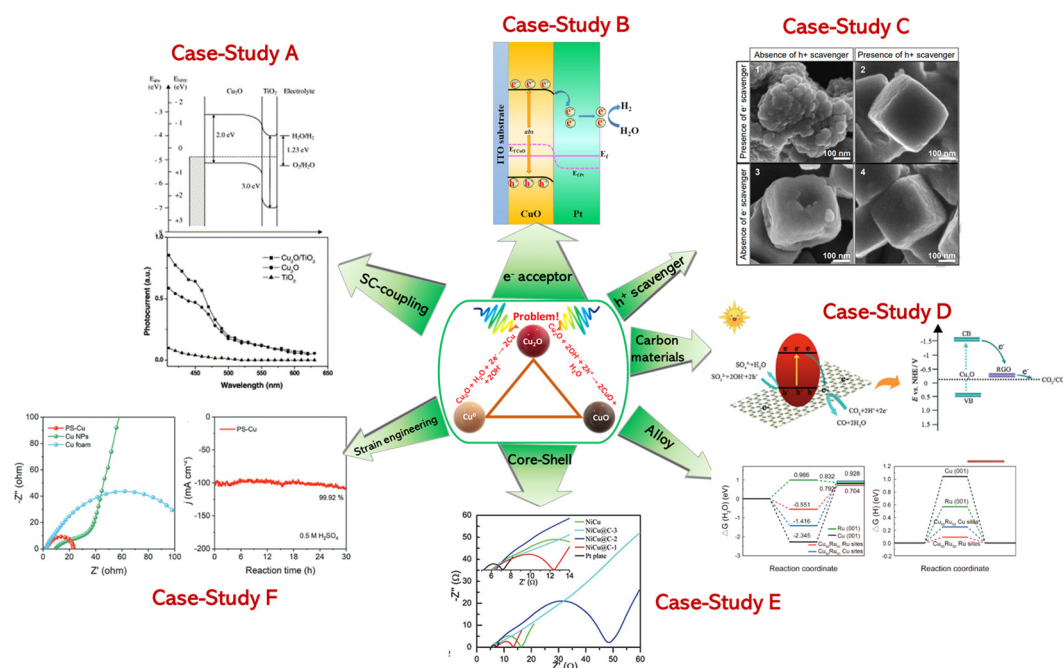
Herein, the aim of this mini-review is to discuss aspects on the photostability of copper oxides,  $\text{CuO}$  and  $\text{Cu}_2\text{O}$ , with focus on some specific, pertinent strategies that have been—so far—reported to improve the photostability. The first part of the review focuses on the photostability problems and the self-decomposition mechanism of  $\text{CuO}$  and  $\text{Cu}_2\text{O}$ . Then, we discuss the different material-engineering approaches such as heterojunctions, core-shell structures, strain engineering, combination with supports. Finally, we provide a targeted overview of some promising Cu-based materials for artificial photosynthesis and discuss the potential strategies employed to enhance the photocatalytic performance. For conciseness, the present review focuses on the reducing process ( $\text{H}_2$ -evolution,  $\text{CO}_2$  reduction). The oxidizing-side (holes) optimization and mechanisms are out of the scope of the present review.

## 2. The Problem of Photocorrosion and Some Specific Approaches to Prevent It

From the redox point of view, photocorrosion of  $\text{Cu}_2\text{O}$  can be explained, see Figure 2, as being triggered either:

- [i] by the oxidation of  $\text{Cu}^{1+}$  to  $\text{Cu}^{2+}$ , by photogenerated holes. Formally, this tends to convert  $\text{Cu}_2\text{O}$  to  $\text{CuO}$ .
- [ii] by the reduction of  $\text{Cu}^{1+}$  to  $\text{Cu}^0$  by photogenerated or electrochemically provided electrons. Formally, this tends to convert  $\text{Cu}_2\text{O}$  to metallic  $\text{Cu}^0$ .

Many nanoengineering approaches aiming to diminish photocorrosion are based on the working hypothesis of the prevention of electron-hole recombination and promoting them out of the Cu-oxide lattice. Hereafter, see Figure 3, we summarize some approaches in this direction.



**Figure 3.** Various Case-Studies exemplifying methods to address the problem of photocorrosion. *Case–Study A:* Energy band diagram of  $\text{Cu}_2\text{O}/\text{TiO}_2$  composite (top) and normalized spectral responses (bottom). Reprinted from [19]. Copyright 2003, with permission from Elsevier; *Case–Study B:* Schematic illustration of charge separation-transfer of  $\text{CuO}/\text{Pt}$  composite photocathode during photoelectrochemical (PEC) water splitting. Reproduced from Ref. [26] with permission from the Royal Society of Chemistry; *Case–Study C:* SEM images of cubic- $\text{Cu}_2\text{O}$  NPs showing the effect of hole and electron scavenger. Reproduced with permission from ref. [31]. Copyright 2018 Wiley–VCH; *Case–Study D:* Charge transfer in  $\text{Cu}_2\text{O}/\text{RGO}$  composites facilitating photocatalytic conversion of  $\text{CO}_2$ . Reproduced with permission from ref. [32]. Copyright 2014 Wiley–VCH; *Case–Study E (Alloy):* Calculated adsorption free energy diagram for the Volmer step (left) and for the Tafel step (right). Reprinted with permission from [28]. Copyright 2020 American Chemical Society; *Case–Study E (Core-Shell):* Nyquist plots of various NiCu catalysts. Reproduced with permission from ref. [33]. Copyright 2017 Wiley–VCH; *Case–Study F:* Nyquist plots and long-term stability (30 h) of PS-Cu, Cu NPs, and Cu foam. Reproduced with permission from ref. [27]. Copyright 2022 Wiley–VCH.

### 2.1. Case–Study A: Photocathode-Heterojunctions (e.g., $\text{Cu}_x\text{O}/\text{TiO}_2$ , $\text{CuO}/\text{BiVO}_4$ , $\text{CuO}/\text{Cu}_2\text{O}$ )

$\text{CuO}$  can be an effective photocatalyst and a photocathode if the self-reduction problem of the  $\text{Cu}^{2+}$  sites to  $\text{Cu}^{1+}$  is solved via a heterojunction with a *n*-type semiconductor such as  $\text{TiO}_2$  [19,34]. This  $\text{TiO}_2@\text{CuO}$  core-shell scheme can act as a protective layer, see Figure 3 (Case-Study A). The efficiency of this approach can be influenced by the preparation method. Masudy-Panah et al. [24], via control of the sputtering power, achieved to optimize the  $\text{TiO}_2$ -layer over  $\text{CuO}$ , and this in turn had a beneficial effect on the photocorrosion stability of  $\text{CuO}$ -based photocathodes [24]. Under five hours of photocorrosion stability tests, increasing the sputtering power was found to significantly suppresses the formation of  $\text{Ti}^{3+}$ , which increased the Hydrogen Evolution Reaction (HER) efficiency of the photocathode [24]. The Nyquist-curves recorded by Electrochemical Impedance Spectroscopy (EIS) of thin  $\text{TiO}_2$ -film indicated easier transfer of photoinduced electrons to the electrolyte solution [24]. Xing et al. [26] reported that a protective layer of  $\text{TiO}_2$  formed by sol-gel method, can be used to protect the  $\text{CuO}$  photocathode [26]. In this case, they had achieved improved photocurrent density by  $\text{TiO}_2@\text{CuO}$  vs. bare  $\text{CuO}$  photocathode. In [26], the long-term stability was impaired due to a less-homogeneous protective  $\text{TiO}_2$  layer on the  $\text{CuO}$  photocathode [26]. Specifically, in the  $\text{TiO}_2@\text{CuO}$  core-shell, it was suggested [26] that photoexcited electrons of  $\text{CuO}$  and  $\text{TiO}_2$  easily migrate to the

CB of  $\text{TiO}_2$  and the holes from VB of  $\text{TiO}_2$  transfer to the VB of  $\text{CuO}$ , while the internal electric field further promotes the separation and transfer of photogenerated carriers in the two components of the Z-heterojunction direction, resulting to a more stable and efficient  $\text{CuO}$  photocathode [26]. Similarly, the results of [35,36] can be understood as being due to a Z-scheme configuration [37] that is considered to improve electron-hole separation and transfer them to the CB of  $\text{TiO}_2$  and VB of  $\text{Cu}_2\text{O}$ , respectively.

In [23], precise control of Oxygen-rich  $\text{CuO}$  and Cu-rich  $\text{CuO}$  regions on the same material was investigated via sputtering on Fluorine Tin Oxide (FTO)-coated glass. It was observed that the stability of  $\text{CuO}$  electrodes was considerably influenced by the precise local balance of Cu or O elements, with O-rich  $\text{CuO}$  electrodes to be most stable against photocorrosion [23]. O-rich materials show higher stability against photocorrosion, which might be a result from slower self-reduction of  $\text{CuO}$  to  $\text{Cu}_2\text{O}$ . EIS data showed that, in O-rich  $\text{CuO}$  electrodes, charge transfer resistance was decreased [23], thus improving interfacial charge transport and photocatalytic performance.

Jeong et al. [38] had fabricated  $\text{BiVO}_4/\text{CuO}$  heterojunction electrodes by spin-coating capping layers of  $\text{BiVO}_4$  on  $\text{CuO}$  photoelectrodes, in order to prevent self-reduction of  $\text{CuO}$  to  $\text{Cu}_2\text{O}$ . Using X-Ray Photoelectron Spectroscopy (XPS) data, they have observed that  $\text{CuO}$  photoelectrodes with poor photostability occurred when self-reduction of  $\text{CuO}$  to  $\text{Cu}_2\text{O}$  was occurring, while after repeated  $\text{BiVO}_4$  deposition cycles, the photocorrosion was suppressed, i.e., a  $> 76\%$  photostability was reported [38].

In conclusion, heterojunction of Cu-oxide semiconductors with appropriate *n*-type semiconductors can be a promising strategy to address the issue of  $\text{Cu}^{2+}/\text{Cu}^{1+}$  self-reduction. Properly accounting for the relative CB and VB positioning, and the ensuing band-bending, is of primary importance in this approach.

## 2.2. Case—Study B: The Case of $e^-$ Capture/Acceptor ( $\text{CuO}/\text{Pt}$ and $\text{CuO}/\text{Pd-Au}$ )

In another approach, to prevent  $\text{Cu}^{2+}$  to  $\text{Cu}^{1+}$  self-reduction [23], an oxygen-rich  $\text{CuO}$  film was coated with a noble-metal nanolayer, e.g., Pt or Pd-Au, using sputtering-technology. Improved stability was confirmed by EIS, showing enhanced  $\text{CuO}$  stability to correlate with decrease of the resistance [23], i.e., photoinduced electrons had higher mobility [23]. Noticeably, in that work, electron-hole generation was improved via the interaction of plasmonic Au with the semiconductor [23]. In a similar approach, adding Pt as an electron accepting catalyst on a  $\text{CuO}$  was reported in [26], using an electro-deposition method [26] (see Figure 3 Case-Study B). By adding a metal with higher work function than  $\text{CuO}$  [ $\Phi = 5.3$  eV] e.g. such as Pt [ $\Phi = 5.65$  eV], the photogenerated electrons can migrate from  $\text{CuO}$  to the Pt layer, thus be trapped there, until thermodynamic equilibrium is established, forming an inner electric-field between  $\text{CuO}$  and Pt [39]. The benefit of this approach, is that, by decreasing electron accumulation on  $\text{CuO}$ , it minimizes the self-reductive corrosion [26].

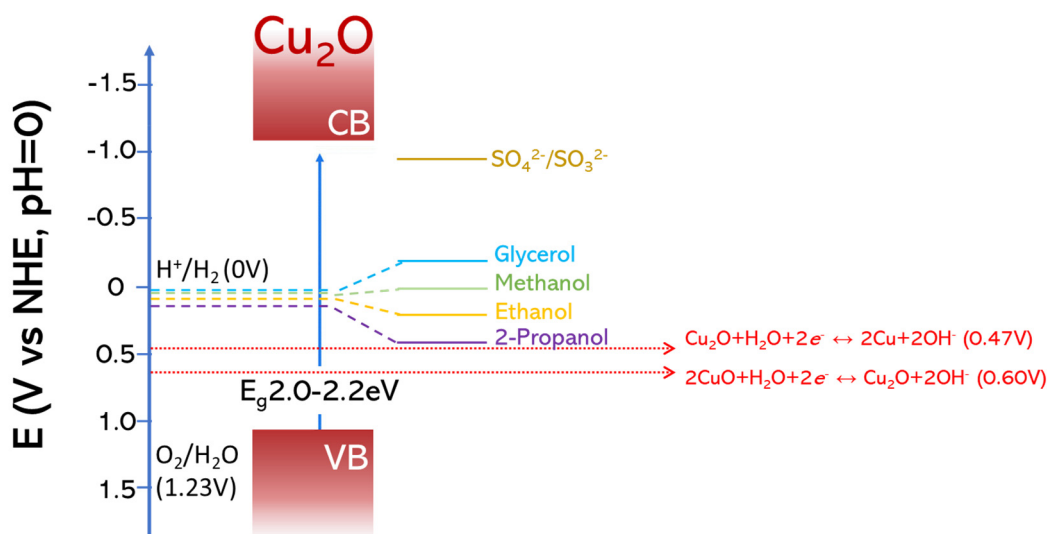
In an alternative approach, Zhang et al. [40] had anchored single Cu-atoms (Cu-SA) on  $\text{TiO}_2$  structure by a bottom-up approach, where a metal organic framework (MOF) MIL-125 was used as a substrate to ensure atomic dispersion of atomic cocatalyst and enabled the highest loading amount of approximately 1.5 wt.% Cu. Anchoring Cu on the  $\text{TiO}_2$  matrix significantly decreased the charge carrier recombination. Loading single Cu-atoms on  $\text{TiO}_2$  versus pristine  $\text{TiO}_2$  indicated that the Cu-SA loading might effectively facilitate the transfer of photogenerated electrons from  $\text{TiO}_2$  to the Cu active sites [40]. This can be attributed to the fact that the redox-potential of  $\text{Cu}^{2+}/\text{Cu}^{1+}$  (0.16 V vs. NHE) is more positive than CB of  $\text{TiO}_2$  (−0.1 V vs. NHE). Electrochemical Impedance Spectroscopy Nyquist curves of  $\text{Cu-SA}/\text{TiO}_2$  verify that the Cu-SA species can act as electron acceptors, thus facilitating the interfacial charge separation [40]. The decreased electron-hole recombination was also evident by the photoluminescence data [40], i.e., in  $\text{Cu-SA TiO}_2$  the recombination of electrons and holes was slower. As a result, long-term stability was reported, i.e., 380 days with minor loss on the catalytic performance [40].



The aforementioned examples, indicate that fast transfer of electrons out from the Cu-oxide matrix, in a non-reversible way, is the key-condition to improve  $\text{Cu}^{2+}$  to  $\text{Cu}^{1+}$  self-reduction. Thus, the redox positioning of the electron-acceptors vs. the CB of the Cu-atoms in Cu-oxides, is one of the key-parameters to be considered.

### 2.3. Case—Study C: The Use of Hole Scavengers

As exemplified in Figure 2, in  $\text{Cu}_2\text{O}$ , self-oxidation of  $\text{Cu}^{1+}$  to  $\text{Cu}^{2+}$  by photogenerated holes, can be a primary photocorrosion source [31]. The highly negative potential CB-edge of  $\text{Cu}_2\text{O}$ , typically  $-1000$  mV vs. NHE ( $\text{pH} = 0$ ) [10] boosts the electron transfer to interfacial  $\text{H}^+$ , towards  $\text{H}_2$  production. Concomitantly,  $\text{h}^+$  are gradually accumulated and this may promote photocorrosion, oxidation of  $\text{Cu}^{1+}$  to  $\text{Cu}^{2+}$ , since the low level of valence band (VB) prevents  $\text{h}^+$  to participate in water oxidation. Thus, an efficient hole scavenger would be required to achieve a rapid withdrawal of  $\text{h}^+$  in order to suppress this  $\text{Cu}_2\text{O}$  self-oxidation (see Figure 3 Case-Study C inset). The presence of a  $\text{h}^+$  scavenger with a suitable oxidizing potential (see Figure 4) facilitates the  $\text{h}^+$  transfer, thus improving the photostability of  $\text{Cu}_2\text{O}$ . In this context, careful selection of a sacrificial hole-scavenger may improve stability by preventing self-photo-oxidation of  $\text{Cu}_2\text{O}$ . This in turn, is expected to enhance the overall photocatalytic  $\text{H}_2$  evolution by  $\text{Cu}_2\text{O}$ , permitting an educing potential to be built-up. In this context, Toe et al. [31] demonstrated that among some hole scavengers, e.g.,  $\text{Na}_2\text{SO}_3$ , methanol, and ethanol,  $\text{Na}_2\text{SO}_3$  was the most effective in photocatalytic  $\text{H}_2$  evolution by  $\text{Cu}_2\text{O}$  catalysts [31].



**Figure 4.** The redox-potential of some commonly used organic hole-scavengers as well as of  $\text{SO}_3^{2-}$ : the more negative potential of the  $\text{SO}_4^{2-}/\text{SO}_3^{2-}$  couple can provide a more efficient protection against self-photo-oxidation of  $\text{Cu}_2\text{O}$  [31,41].

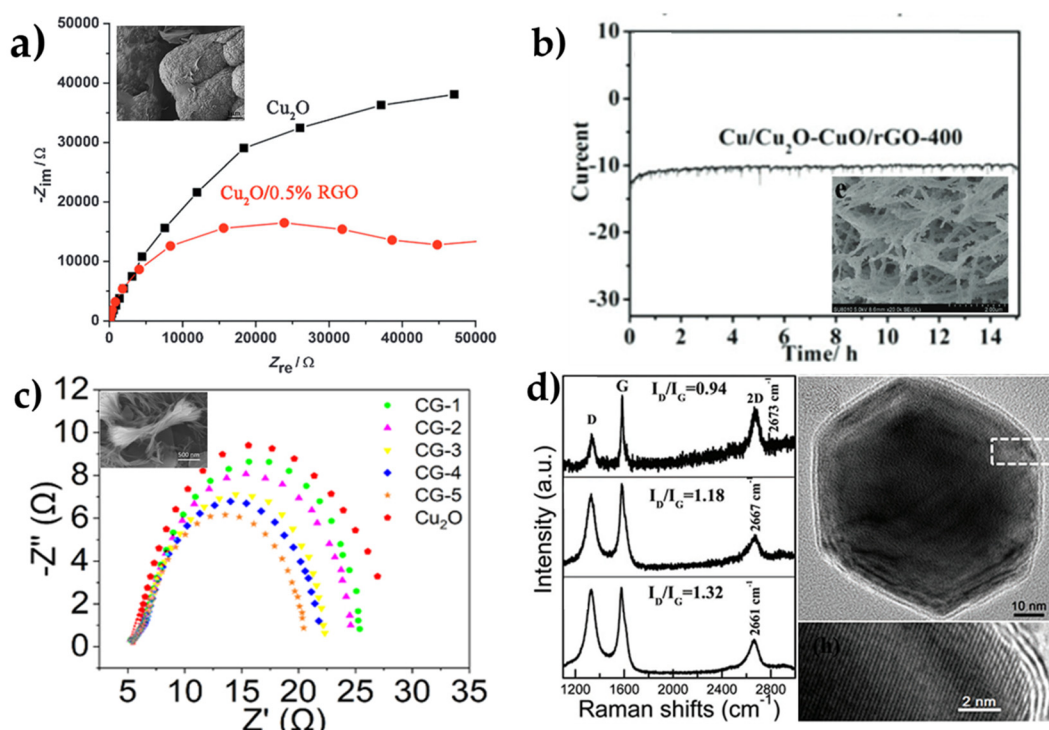
Importantly, this study showed that via this approach [31], photocatalytic  $\text{H}_2$ -production from  $[\text{H}_2\text{O} + \text{scavenger}]$  could be accomplished without any secondary components compared, for example, to the common case of use of alcohols (methanol, isopropanol) as hole scavengers. In [31],  $\text{Na}_2\text{SO}_3$  enabled  $\text{h}^+$  scavenging to oxidize  $\text{SO}_3^{2-}$  into  $\text{SO}_4^{2-}$ , leaving free  $\text{e}^-$  in the conduction band for HER. Importantly,  $\text{Na}_2\text{SO}_3$  allowed an effect 12-fold better than ethanol [31], allowing a 15 h production of  $\text{H}_2$  by the  $\text{Cu}_2\text{O}/\text{Na}_2\text{SO}_3$ , without any signs of photocorrosion [31]. This approach is interesting since it highlights the possibility to engineer  $\text{Cu}_2\text{O}$  without addition of metal or cocatalysts.

### 2.4. Case—Study D: The Effect of Carbonaceous Materials

Reduced graphene oxide (rGO) can act as a protecting agent. An et al. [32] have studied the effect of rGO interfaced with different exposed facets of  $\text{Cu}_2\text{O}$  with (100) to be better for  $\text{CO}_2\text{R}$  than (100) [32]. The proposed mechanism is described in Figure 3

Case-Study D). They measured Cu-leaching using ICP (inductively coupled plasma optical emission spectrometry) and they demonstrated a Cu-atom leaching of  $\sim 3\%$  after 3 h of light-irradiated  $\text{Cu}_2\text{O}/\text{rGO}$  [32]. EIS data showed a smaller resistance indicating better charge-transfer in  $\text{Cu}_2\text{O}/\text{rGO}$  vs.  $\text{Cu}_2\text{O}$ , as can be seen in Figure 5a. In a Mott–Schottky analysis they had a negative slope [32], which indicates *p*-type semiconductor properties in  $\text{Cu}_2\text{O}/\text{rGO}$  and an increased donor-density vs.  $\text{Cu}_2\text{O}$ .

A different carbonaceous substrate, such as  $\text{g-C}_3\text{N}_4$ /Vulcan Carbon, was prepared by Hussain et al. [42], protecting the (111) facets of  $\text{Cu}_2\text{O}$ , resulting in improved stability of  $\text{Cu}_2\text{O}$  nanoparticles. A different approach was given by Sun et al. [43], who developed a heterostructure of  $\text{Cu}_2\text{O}$  quantum dots (QDs) supported on a 3D  $\text{g-C}_3\text{N}_4$  foam. In this work, the authors suggested that the (111) $\text{Cu}_2\text{O}$  facet, when interfaced with  $\text{g-C}_3\text{N}_4$ , allowed creation of additional DOS at the  $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$  interface [43]. In such heterojunction, the photoexcited electrons are suggested to be transferred from  $\text{g-C}_3\text{N}_4$  to  $\text{Cu}_2\text{O}$  QDs, thus avoiding  $\text{Cu}_2\text{O}$  photocorrosion and enhance photocatalytic activity. Enhanced stability was also evidenced by the reusability of this  $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$  heterojunction up to five times [43].



**Figure 5.** (a) EIS of composite electrodes to exploit the charge transfer resistance of pristine  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}/\text{reduced graphene oxide}$  and subplot of SEM image of  $\text{Cu}_2\text{O}/\text{RGO}$  composites. Reproduced with permission from ref. [32]. Copyright 2014 Wiley–VCH. (b) Long–term durability of  $\text{Cu}/\text{Cu}_2\text{O}-\text{CuO}/\text{rGO}-400$  and subplot is a SEM image of the same sample. Reproduced from Ref. [44] with permission from the Royal Society of Chemistry. (c) Electrochemical impedance spectroscopy of CG catalysts and  $\text{Cu}_2\text{O}$  in 1 M KOH with subplot of a SEM image of CG5 after 8 h reaction. Reprinted from [45], with permission from Elsevier. (d) Raman spectra for alloyed Ni–Cu encapsulated in graphitic shells with different thickness with thickness to be increasing downwards and TEM images of the NiCu@C–1 sample. Reproduced with permission from ref. [33]. Copyright 2017 Wiley–VCH.

The protective potential of interfacial carbon was also evidenced by Wang et al., who synthesized  $\text{Cu}_2\text{O}/\text{graphited carbon}$  interfaces, using a polyol-method, to produce  $\text{Cu}_2\text{O}$  nano-flowers on graphene [45]. Increased porosity of the catalyst achieved by  $90^\circ\text{C}$  treatment improved the internal charge transfer, as evidenced by EIS Nyquist data and as can be seen in Figure 5c. [45].

Overall, carbon-nanomatrices can act as protecting agents for Cu-oxides. The enhanced electron-storage capacity of graphitized carbon, together with their high chemical resilience are key-beneficial parameters that renders this approach as highly promising towards industrial exploitability.

### 2.5. Case—Study E: Core-Shell and Alloys

Besides the conventional approach of core-shell structures, in the case of Cu-oxides, one can create core-shell structures by starting from a fully reduced Cu state and result to a reduced metallic-core, with a stable oxidized layer. Yang et al. [18] proposed a two-step method, firstly by electrodeposition of  $\text{Cu}_2\text{O}$  on FTO film and a subsequent thermal oxidation (time was the factor that controlled the thickness of the outer layer) in which the outer film was transformed to  $\text{CuO}$ . The so-formed  $\text{Cu}_2\text{O}/\text{CuO}$  bilayer was tested for its photostability, and Electrochemical Impedance Spectroscopy data showed very small resistance under illumination, while the Mott–Schottky measurements demonstrated large carrier density and a high flat-band potential, evidencing good conductivity and a high degree of band bending [18]. This approach places the  $\text{Cu}_2\text{O}/\text{CuO}$  composite as promising photocathode candidate for HER, according to its good stability in alkaline media, high photocurrent, and the ease of method.

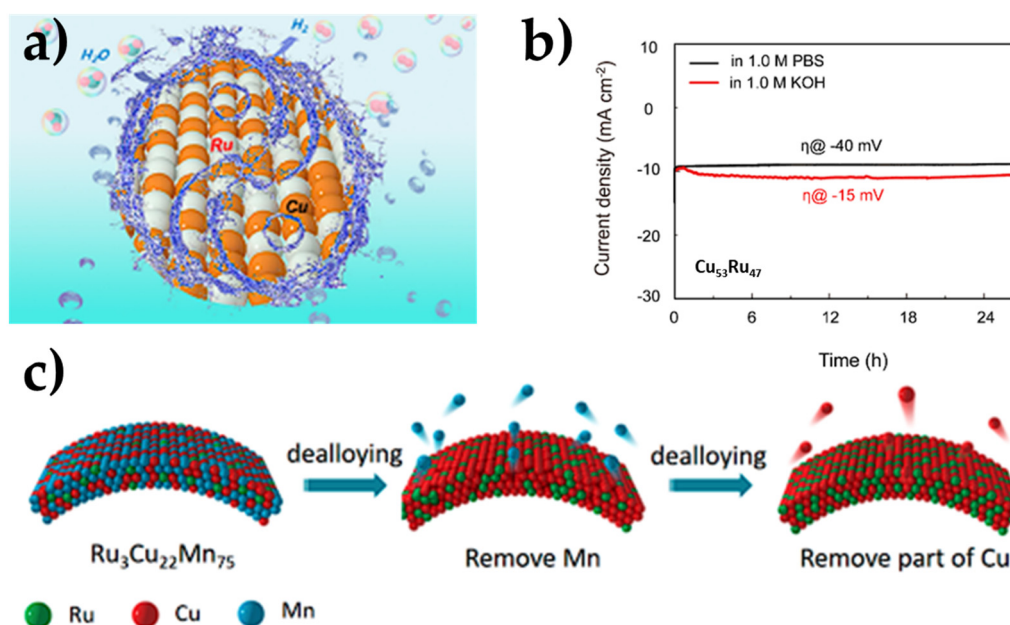
A self-supported  $\text{Cu}/\text{Cu}_2\text{O}-\text{CuO}/\text{rGO}$  nanowire array [44] showed good stability for more than 15 h in alkaline medium, as can be seen in Figure 5b, in accordance with low resistance evidenced by EIS-loops, which indicates fast charge transfer. This provides evidence that the presence of metallic  $\text{Cu}^0$  as a hetero-component—not a standalone one—can offer high-speed paths for electron transportation. In addition, the highly reductive rGO shell also provides a conductive network that may promote charge transfer, which are beneficial for the Hydrogen Evolution Reaction process.

A highly efficient and low cost  $\text{Cu}_2\text{O}-\text{SnO}_2$  core-shell electrocatalyst has been reported in [46] via control of the shell thickness. An optimized 5 nm thick  $\text{SnO}_2$  shell gave the faradaic efficiency, i.e., >90% of  $\text{CO}_2$  to CO reduction [46]. These  $\text{Cu}_2\text{O}-\text{SnO}_2$  electrocatalyst achieved a good stability over 18 h of test at  $-0.6$  V vs. RHE in 0.5 M  $\text{KHCO}_3$  electrolyte.

A three-dimensional nanoporous Cu-Ru alloy as a Pt-free catalyst for HER, was prepared by Wu et al. [28] using a dealloying process, as shown schematically in Figure 6a,c. They demonstrated that the so-obtained nanoporous  $\text{Cu}_{53}\text{Ru}_{47}$  exhibits long-term operation stability for more than 24 h in neutral pH (1.0 M  $\text{PbS}$ ) and, after the first 3 h, fully stable at the alkaline pH (1 M  $\text{KOH}$ ), as can be seen in Figure 6b.

Shen et al. started with a fundamental basis, which relies on electronic modification of a graphitic shell [33]. As reported from other groups too, with a graphitic layer to act as a protective shell for the core, this method can improve significantly the durability of the catalyst. Therefore, this group [33] synthesized a nickel-copper alloy (core) encapsulated in graphitic layer (shell) ( $\text{NiCu}@\text{C}$ ) via chemical vapor deposition method, using  $\text{CH}_4$  as a carbon source. This allowed them to obtain a tunable C-thicknesses. In this way, they had obtained three materials:  $\text{NiCu}@\text{C}-1$  had mostly single-layered (78.4%) C-coating,  $\text{NiCu}@\text{C}-2$  a well-defined, 2–3 nm thickness, core-shell structure, corresponding to 5–10 graphitic layers, and  $\text{NiCu}@\text{C}-3$  with an 8–15 nm shell. Raman Spectroscopy, see Figure 5d, shows the three characteristic peaks, D, G, and 2D, that increased upon increase the graphitic shell (C) [32]. Shift in Raman peaks could be related to the modification of electronic structures of graphitic layers arisen from the interaction of carbon shell  $\text{NiCu}$  core. The stability of the catalyst was evaluated by chronoamperometric measurements, which verify that  $\text{NiCu}@\text{C}$  catalysts show slower decay in both acidic and alkaline pH than in pristine  $\text{NiCu}$ . From EIS, they demonstrated [32] also that the charge transfer resistance follows the same rule, as the thickness is increasing, the resistance increasing too, which can be explained by slower reaction kinetics and electron transport at the thicker graphitic shells (see Figure 3 Case-Study E- *inset*).





**Figure 6.** (a) Schematic representation of a stable alloy of CuRu nanoparticle for Hydrogen Evolution Reaction; (b) Stability tests of the Cu<sub>53</sub>Ru<sub>47</sub> in neutral (1 M PBS) and in alkaline (1 M KOH) environment; (c) Schematic illustration of the preparation procedure by dealloying a single-phase ternary Ru<sub>3</sub>Cu<sub>22</sub>Mn<sub>75</sub> precursor in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution to remove Mn. Reprinted with permission from [28]. Copyright 2022 American Chemical Society.

## 2.6. Case-Study F: Lattice-Size-Shape-Facets

Lattice-strain engineering can be effective on altering the DOS near the Fermi level, thus regulating adsorption energy of catalysts [27]. This was exemplified by Kang et al. [27], who used plasma spraying (PS) to prepare the coating layer in self-supported Cu electrode with intensive strain. The electrode's stability was significant for more than 30 h at 100 mA cm<sup>-2</sup> (see Figure 3 Case-Study F). EIS data show that their PS-Cu had the lowest resistance of all tested samples, and the stability was best at acid medium and the worst at alkaline medium.

In addition, lattice-strain engineering may improve interaction between catalyst and intermediates [47]. For instance, tensile strain [48] could increase the interatomic distance inside the lattice catalyst, thus decreasing the overlap of *d*-orbitals, and/or upshift the *d*-band center and intermediates [49]. In this context, so far, several methodologies have been exploited to generate lattice-strain, such as, introducing interfaces with lattice mismatch [47], creating defects [48], and preparing ultra-thin nanosheets [50].

The different crystallite-facets of metal oxide nanoparticles may affect the activity and stability of photocatalysts for HER and CO<sub>2</sub>RR, thus controlling preferential-facet growth can be a fruitful strategy. In a commonly applied methodology, the differential affinity of certain surfactants for certain Cu<sub>2</sub>O-facets may allow control of surface oxidation extent, oxophilicity, hydrophilicity, and their activity to HER [51]. In a refined work, Gao et al. [52] studied Cu<sub>2</sub>O nanoparticles (NPs) with (100) facets, octahedral Cu<sub>2</sub>O NPs with exposed (111) and *t*-Cu<sub>2</sub>O with both (111) and (100) facets. Studies on these Cu<sub>2</sub>O NPs showed that the types of interfaced crystal facets exhibited different stabilities and different catalytic activities [53]. Shape of Cu<sub>2</sub>O particles has been shown to be correlated with stability during the water splitting process [54]. More specifically, when comparing Cu<sub>2</sub>O cubes with (100) facets, Cu<sub>2</sub>O octahedra with (111) facets and Cu<sub>2</sub>O rhombic dodecahedra with (110) facets, it was concluded that—practically—standalone Cu<sub>2</sub>O, irrespective of the faced exposure, could not be very stable, no matter its facet engineering [53].

From the above-mentioned examples, it may be anticipated that, after finding which facet is best for the catalyst's activity, we should protect that facet, by an appropriate method, e.g., *p-n* heterojunctions or coating or by mixing it with carbon materials as graphene.

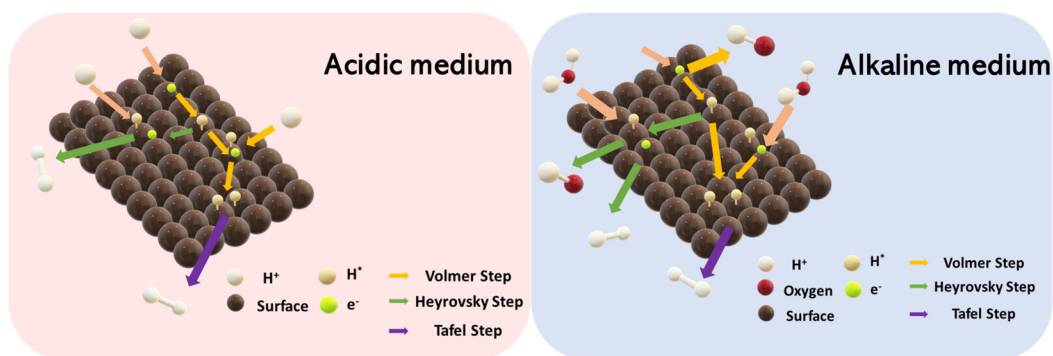
### 3. Hydrogen Evolution by Cu-Oxide Based Materials

Both  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  are *p*-type semiconductors [13–16] with band gaps 2.0–2.5 eV and 1.3–1.7 eV, respectively, see Figure 2, thus, absorbing a significant proportion of the solar-spectrum. However, their stability issues, when combine with fast  $e^-$ - $h^+$  recombination phenomena, make them rather unfavorable photocatalysts for  $\text{H}_2$  evolution from  $\text{H}_2\text{O}$  [54]. Nonetheless, recent studies demonstrate that we can minimize these disadvantages by coupling copper oxides with other, more stable and suitable semiconductors. Doing so, the electrical and optical properties of  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  are significantly changed by the material they are coupled with [24,28,33].

Hydrogen Evolution Reaction (HER) [55] is considered an extraordinary reaction in electrochemistry for two reasons: firstly, for its simplicity, because it is always a  $2e^-$  process, no matter the pH [55], and secondly because it is a direct process to produce high-purity  $\text{H}_2$ , considered to be the key fuel for the future. Mechanistically, the basis of HER is described by the reactions in Table 1 [56]. HER in electrochemistry is a  $2e^-$  process [55], which is divided mainly in two steps: first is the Volmer step (1.i in Table 1) that includes the adsorption of one H-atom on the catalyst surface, by transferring one proton  $\text{H}^+$  from the acid electrolyte which combines with an electron  $e^-$  transferred from the catalyst surface to form an adsorbed hydrogen atom ( $\text{H}^* = \text{H}^+ + e^-$ ); second is the Heyrovsky step (Equation (1.ii)) in which this  $\text{H}^*$  combines with one electron  $e^-$  and one  $\text{H}^+$  to form a  $\text{H}_2$  molecule, see also Figure 7. In addition, there is possibility to form one  $\text{H}_2$  molecule through the Tafel step (1.iii) i.e., the combination of two  $\text{H}^*$  [55].

**Table 1.** Overall reaction pathways for HER in acidic/alkaline mediums.

Overall Reaction (Conditions)	Reaction Pathway	Equations
Acidic Media $2\{\text{H}^+\} + 2\{e^-\} \rightarrow \text{H}_2$	$\{\text{H}^+\} + \{e^-\} + * \rightarrow \text{H}^*$ (Volmer)	1.i
	$\{\text{H}^+\} + \{e^-\} + \text{H}^* \rightarrow \text{H}_2$ (Heyrovsky)	1.ii
	or $\text{H}^* + \text{H}^* \rightarrow \text{H}_2$ (Tafel)	1.iii
Alkaline Media $2\text{H}_2\text{O} + 2\{e^-\} \rightarrow \text{H}_2 + 2\text{OH}^-$	$\text{H}_2 + \{e^-\} \rightarrow \text{H}^* + \text{OH}^-$ (Volmer)	2.i
	$\text{H}_2\text{O} + \{e^-\} + \text{H}^* \rightarrow \text{H}_2 + \text{OH}^-$ (Heyrovsky)	2.ii
	or $\text{H}^* + \text{H}^* \rightarrow \text{H}_2$ (Tafel)	2.iii



**Figure 7.** Electrocatalytic Hydrogen Evolution Reaction in Acidic and Alkaline Conditions. A summary of pertinent Cu-based semiconducting materials is listed on Table 2 (photocatalytic  $\text{H}_2$  production), Table 3 (electrocatalytic  $\text{H}_2$  production) and Table 4 (photoelectrocatalytic  $\text{H}_2$  production). Hereafter, we highlight some engineering aspects related to the control/improvement of hydrogen evolution by such catalysts.

In acidic electrolytes, it has been generally accepted that the differences in reaction rates and activity are closely related to the differences of free-energy of hydrogen-adsorption on

different materials [26]. In alkaline media, due to the lack of  $H^+$ , the reaction must begin from dissociation of  $H_2O$  molecules, see Volmer–Heyrovsky steps (Equations (2.i) and (2.ii)). In addition, in alkaline media, as in the case of acidic media, there is the possibility to form a  $H_2$  molecule through the Tafel step (2.iii), i.e., the combination of two  $H^*$ . This additional step of proton-generation from  $H_2O$  in alkaline media introduces an additional energy barrier and affects the whole reaction kinetics and that is the main reason why acid medium is preferred in this reaction. In alkaline environments, there are two approaches to start with: [i] by the single descriptor of hydrogen binding energy [57], or [ii] the bifunctional nature of HER, a good catalyst needs both a beneficial  $OH_{ad}$  energetics (as it is slower when it has to do with metal; thus, is the rate-limiting step) and beneficial  $H_{ad}$  energetics [51].

A summary of pertinent Cu-based semiconducting materials is listed in Table 2 (photocatalytic  $H_2$  production), Table 3 (electrocatalytic  $H_2$  production) and Table 4 (photoelectrocatalytic  $H_2$  production). Hereafter, we highlight some engineering aspects related to the control/improvement of hydrogen evolution by such catalysts.

**Table 2.** Summary of pertinent Cu-based heterojunctions and photocatalytic  $H_2$  evolution rates.

Photocatalytic Hydrogen Production				
Catalyst	Hole Scavenger	Irradiation Source	$H_2$ Evolution Rate	Ref.
Cubic- $Cu_2O$			Not detected	
Octahedra- $Cu_2O$	Pure $H_2O$ (Water Splitting)	300 W Xe-Lamp	$>0.4 \mu mol g^{-1} h^{-1}$	[54]
Rhombic Dodecahedra- $Cu_2O$			$\sim 1.6 \mu mol g^{-1} h^{-1}$	
$Cu_2O/TiO_2$ (C-1.5/T-2)	30%MeOH ( $H_2O/MeOH$ )	Full-arc Xe Lamp $100 mW cm^{-2}$	$11 mmol g^{-1} h^{-1}$	[58]
	30%MeOH (Seawater/MeOH)		$5.1 mmol g^{-1} h^{-1}$	
$CuO$ (Later $Cu_2O$ )- $TiO_2$	10% Glycerol ( $H_2O/Glycerol$ )	300 W Xe-Lamp	$336 \mu mol g^{-1} h^{-1}$	[59]
$Cu^0-TiO_2$			$\sim 867 \mu mol g^{-1} h^{-1}$	
$Cu_2O/TiO_2$	10% MeOH ( $H_2O/MeOH$ )	300 W Xe-Lamp	$70 \mu mol g^{-1} h^{-1}$	[60]
3 wt.% $Cu-TiO_2$	$\sim 8\%$ MeOH ( $H_2O/MeOH$ 11:1)	125 W Hg-Lamp (325 & 365nm)	$2.07 mmol g^{-1} h^{-1}$	[61]
13.5 wt.% $Cu-TiO_2$			$2.48 mmol g^{-1} h^{-1}$	
Electrodeposited $Cu_2O-WO_3$	Pure $H_2O$ (Water Splitting)	400 W Hg-Lamp	$\sim 7 \mu mol g^{-1}$	[29]
$Cu@Cu_2O/ZnO$	0.75M $Na_2S$ and 1.05M $Na_2SO_3$	300 W Xe-Lamp	$1.47 mmol g^{-1} h^{-1}$	[62]
$ZnO/Cu_2O-CuO$	60mM $Na_2S$	150 W Xe-Lamp	$1092.5 \mu mol g^{-1} h^{-1}$	[63]
$CuSA-TiO_2$ ( $\sim 1.5$ wt%)	$\sim 70\%$ MeOH ( $H_2O/MeOH$ 1:2)	500 W Xe-Lamp	$101.74 mmol g^{-1} h^{-1}$	[40]
0.75% $Cu$ atom- $TiO_2$	25% MeOH ( $H_2O/MeOH$ 3:1)	100 W Xe-Lamp	$16.6 mmol g^{-1} h^{-1}$	[64]
NDs- $Cu_2O$	20% EtOH ( $H_2O/EtOH$ )	300 W Xe-Lamp ( $100 mW cm^{-2}$ )	$1597 \mu mol g^{-1} h^{-1}$	[65]
		Visible Light 420–760 nm $77.5 mW cm^{-2}$	$824 \mu mol g^{-1} h^{-1}$	
$Cu_2O@g-C_3N_4$ (CN5 5wt.%)	Pure $H_2O$	300 W Xe-Lamp ( $\geq 420$ nm)	$795 \mu mol g^{-1} h^{-1}$	[66]

### 3.1. Photocatalytic Hydrogen Production

#### 3.1.1. Facet Engineering

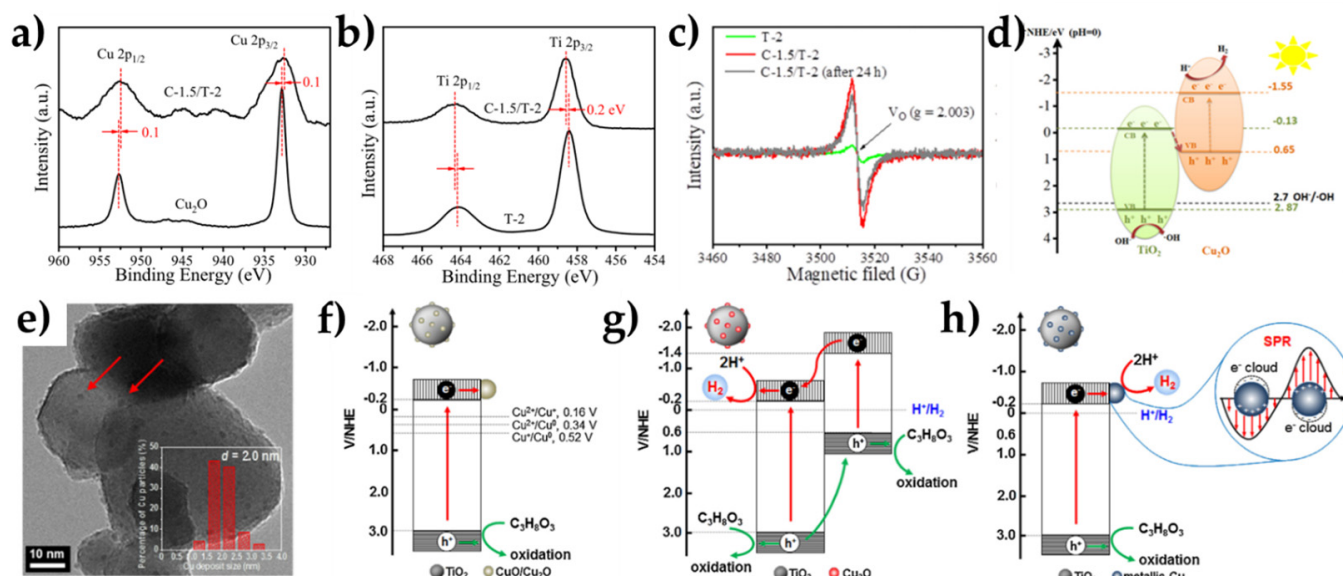
The shape of  $Cu_2O$  nanocrystals can affect the photocatalytic  $H_2$  production performance [54].  $Cu_2O$  nanopowders with different morphologies, i.e., cubes with (100) facets, octahedra with (111) facets, or rhombic dodecahedra with (110) facets, which were evaluated for long-term stability on hydrogen production as well as for overall water-splitting. All materials presented photocorrosion phenomena under irradiation in the form of phase transformation of  $Cu_2O$  to  $CuO$ , verified both by XPS and X-Ray Diffraction (XRD) measurements. Noteworthy, the stability trend was completely different under dark conditions. Moreover, the absence of sacrificial agent during water splitting led to an absence of  $O_2$  production, as normally  $H_2$  and  $O_2$  should have been produced in a 2:1 ratio. Thus, in [54], the photogenerated holes of  $Cu_2O$  that were supposed to oxidize  $H_2O$  and produce  $O_2$  were consumed in the oxidation of  $Cu_2O$  to  $CuO$ . Furthermore, the best performing material, rhombic dodecahedra  $Cu_2O$ , was tested for long-term stability where at 48 h the produced  $H_2$  was 8-fold less and at 72 h no  $H_2$  was detected. To prevent the  $Cu_2O$  oxidation, the nanocrystals were coated with a  $TiIrO_x$  layer [54]. This hybrid  $TiIrO_x/Cu_2O$  material had a better photocatalytic performance with a  $H_2:O_2$  ratio of 2:1, indicating that  $TiIrO_x$

facilitated the hole transfer, thus preventing photocorrosion of  $\text{Cu}_2\text{O}$ , at the same time enabling  $\text{O}_2$ -production from water oxidation.

### 3.1.2. Coupling with Semiconductors

#### The case of Cu-TiO<sub>2</sub>

Another strategy is the coupling of CuO or  $\text{Cu}_2\text{O}$  with other semiconductors and the establishment heterojunctions or Z-scheme mechanism [37]. Coupling copper oxides with other semiconductors, such as  $\text{TiO}_2$  or ZnO with lower energy band positions can lead to the formation of Z-Scheme or Type-II electron transfer mechanism between the two materials. Therefore,  $\text{Cu}_2\text{O}/\text{TiO}_2$  hybrid systems have been widely investigated in the fields of photocatalysis for both  $\text{H}_2$  evolution [60] and  $\text{CO}_2$  reduction [67] and degradation of organics [68]. Lv et al. [58] coupled  $\text{Cu}_2\text{O}$  nanoparticles onto the surface of  $\text{TiO}_2$  and showed that, due to the Z-scheme mechanism, carriers with strong oxidation and reduction ability were confined to  $\text{TiO}_2$ , inhibiting the photocorrosion of the  $\text{Cu}_2\text{O}$ . XPS and EPR data, see Figure 8a–c, indicated presence of surface lattice defects, oxygen vacancies ( $\text{O}_\text{V}$ ), which can act both as electron traps and simultaneously enhance the adsorption capability of  $\text{H}^+$  ions in the hydrogen evolution reaction [58].



**Figure 8.** (a,b) XPS spectra of Cu 2p of  $\text{Cu}_2\text{O}$  and C-1.5/T-2 and Ti 2p of T-2 material, respectively. For C-1.5/T-2 nanocomposite we observe a negative shift of 0.1 eV (binding energy of Cu 2p) and a positive shift of 0.2 eV (binding energy of Ti 2p) indicating that the electron density of Ti (IV) decreases and that of Cu(I) increases, which may indicate a directional carrier transfer from  $\text{TiO}_2$  to  $\text{Cu}_2\text{O}$ ; (c) ESR spectra of T-2, C-1.5/T-2 and C-1.5/T-2, where the characteristic  $\text{O}_\text{V}$  signal can be seen confirming the existence of oxygen vacancies; (d) Proposed Z-scheme mechanism of  $\text{Cu}_2\text{O}/\text{TiO}_2$  composite. Reprinted from [58] with permission from Elsevier; (e) Cu nanoparticles with an average size of 2 nm deposited on the surface of  $\text{TiO}_2$ ; (f,g) Proposed  $\text{H}_2$  evolution mechanism for the initial Cu/ $\text{TiO}_2$  composite where photogenerated electron reduce CuO to  $\text{Cu}_2\text{O}$ ; (h) Cu/ $\text{TiO}_2$  composite where under illumination metallic Cu NPs enhance  $\text{H}_2$  production due to SPR. Reprinted from [59] with permission from Elsevier.

Moreover, they notice an upward shift and a downward shift on the XPS spectra of  $\text{Ti}_{2p}$  and  $\text{Cu}_{2p}$ , respectively [58], indicating a directional carrier transport from  $\text{TiO}_2$  to  $\text{Cu}_2\text{O}$  (Figure 8a,b). Regarding the photocatalytic activity, their  $\text{Cu}_2\text{O}/\text{TiO}_2$  composite exhibited high  $\text{H}_2$  production rates,  $11 \text{ mmol g}^{-1} \text{ h}^{-1}$  in water and  $5.1 \text{ mmol g}^{-1} \text{ h}^{-1}$  in seawater [57]. Compared with the pristine  $\text{Cu}_2\text{O}$ , yielding  $0.5 \text{ mmol g}^{-1} \text{ h}^{-1}$  and  $0.3 \text{ mmol g}^{-1} \text{ h}^{-1}$  in water and seawater, respectively, the  $\text{Cu}_2\text{O}/\text{TiO}_2$  composite showed a clear improvement. This significant improvement of photocatalytic activity and stability



is attributed on the consumption of the highly oxidizing holes of  $\text{Cu}_2\text{O}$  from the  $\text{O}_\text{V}$ 's of  $\text{TiO}_2$  and the Z-scheme mechanism [58] (Figure 8d). Generally, stabilizing  $\text{CuO}$  or  $\text{Cu}_2\text{O}$  nanoparticles on  $\text{TiO}_2$  is a common approach, Tian et al. have prepared a  $\text{TiO}_2$  photocatalyst loaded with  $\text{Cu}$  NPs through an ion exchange (IE) process, where they report the co-existence of  $\text{Cu}^{2+}$ ,  $\text{Cu}^{1+}$ , and  $\text{Cu}^0$ , based on XPS-data. The final composite material gave a purple hue which persisted during the photocatalytic experiments, indicating that copper was at the metallic state [60]. In another study, Jung et al. also used  $\text{TiO}_2$  as a substrate to deposit small, finely-dispersed  $\text{CuO}$  NPs (0.5–2.5 nm) [59] (Figure 8e). During  $\text{H}_2$  generation, they made two observations, [i] there was a color change from dark-grey to deep-violet, attributed to change of the  $\text{Cu}$  oxidation state, and [ii] there was an initial delay of the hydrogen production. XPS and AES profile at different illumination times show the slow transformation of  $\text{Cu}$  oxidation states from  $\text{Cu}^{2+}$  to  $\text{Cu}^{1+}$ . The authors [59] suggest that the photogenerated electrons are consumed to reduce  $\text{CuO}$  to  $\text{Cu}_2\text{O}$  instead of reducing  $\text{H}^+$  and produce  $\text{H}_2$  (Figure 8f,g). When the reduction of copper has been accomplished, these photogenerated electrons participate in  $\text{H}_2$  production. In the case of  $\text{Cu}^0$ , as in the cases of noble metal cocatalysts, there is a continuum of states within the  $\text{TiO}_2$  energy gap where  $\text{Cu}^0$  attracts the photogenerated electron from  $\text{TiO}_2$ , thus facilitating electron transfer to protons (see Figure 8h).

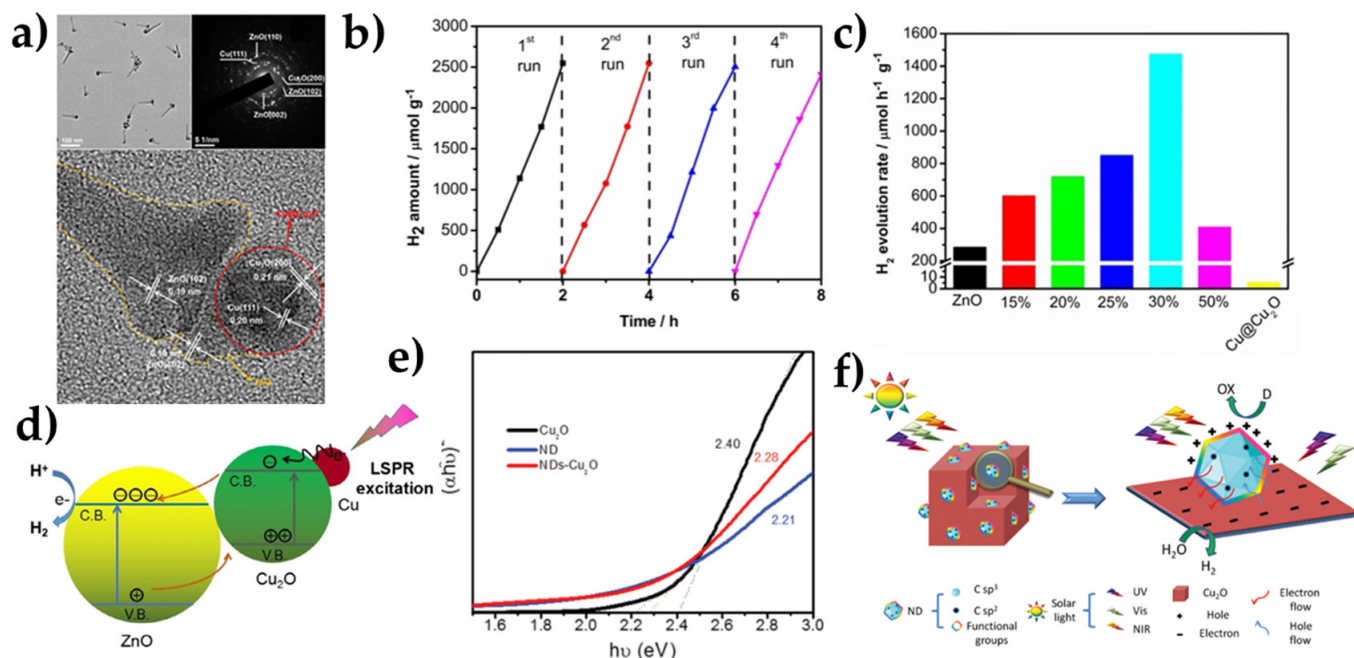
#### *Coupling of Cu with Non- $\text{TiO}_2$ Semiconductors*

Besides  $\text{TiO}_2$ , other semiconductors, especially *n*-type, have been also used for the stabilization of  $\text{Cu}$  NPs. In this context, Hu et al. coupled *p*-type  $\text{Cu}_2\text{O}$  with *n*-type  $\text{WO}_3$ , forming a *p-n* heterojunction [29]. Unlike pristine  $\text{Cu}_2\text{O}$ , which did not produce  $\text{H}_2$  during water splitting,  $\text{Cu}_2\text{O}/\text{WO}_3$  heterojunction facilitated  $\text{H}_2$  production, due to efficient charge separation. Lou et al. designed a  $\text{Cu}^0@\text{Cu}_2\text{O}/\text{ZnO}$  heterostructure in order to stabilize the plasmonic  $\text{Cu}$  core, by decorating it with  $\text{Cu}_2\text{O}$  shell, and finally stabilizing this core-shell structure onto  $\text{ZnO}$  nanorods [62] (See Figure 9a). This hybrid nanostructure exhibited better stability even after four catalytic cycles (Figure 9b), and superior photocatalytic performance, i.e.,  $1472 \mu\text{mol g}^{-1} \text{h}^{-1}$  compared with the pristine  $\text{Cu}@\text{Cu}_2\text{O}$  material which yields  $5 \mu\text{mol g}^{-1} \text{h}^{-1}$  (See Figure 9c). This improvement on the photocatalytic activity was attributed on the Localized Surface Plasmon Resonance (LSPR) caused by photoexcitation of metallic  $\text{Cu}^0$  particles [69]. Arguably, the LSPR was suggested to be linked with hot-electron transfer, as evidenced by Photoluminescence (PL) data. Specifically, the PL emission spectra indicated that  $\text{Cu}@\text{Cu}_2\text{O}/\text{ZnO}$  nanocomposites could delay the recombination rate of  $\text{e}^-$ - $\text{h}^+$  pairs. In the proposed model, see Figure 9d, surface plasmons are photoexcited upon irradiation and the hot electrons occupy the surface plasmon states above the Fermi energy. A fraction of these hot electrons are injected onto the CB of  $\text{Cu}_2\text{O}$ , by overcoming the Schottky barrier formed at the  $\text{Cu}_2\text{O}$ - $\text{Cu}^0$  interface, and finally they leap on the CB of  $\text{ZnO}$ . This mechanistic path for the electrons is believed to intercept photocorrosion phenomena [62].

#### 3.1.3. Carbon-Based Materials and Core-Shell Structures

Use of carbonaceous materials is another interesting approach towards the stabilization and the improvement of the photocatalytic performance of copper nanocatalysts. Lin et al. has decorated 50 nm  $\text{Cu}_2\text{O}$  with small  $\sim 3$  nm nanodiamonds (NDs), and the optimal loading was found to be 3 wt.% enabling a  $\text{H}_2$  production rate of  $1597 \mu\text{mol g}^{-1} \text{h}^{-1}$  with a solar-to-hydrogen efficiency of 0.85%. This nanocomposite exhibited high photocatalytic stability attributed to the narrower band gap, compared with pristine  $\text{Cu}_2\text{O}$ , which improves the ability to harvest solar light [65] (See Figure 9e). As for the proposed photocatalytic mechanism, the photoexcited electrons from the NDs surface were injected into the  $\text{Cu}_2\text{O}$  and at the same time the photogenerated holes of  $\text{Cu}_2\text{O}$  migrated to the NDs (See Figure 9f). The excess of electrons on  $\text{Cu}_2\text{O}$  performed the reduction of  $\text{H}_2\text{O}$  to  $\text{H}_2$  and the excess of holes on the NDs oxidized the ethanol. Another material of great interest is graphitic carbon nitride (*g*- $\text{C}_3\text{N}_4$ ). Liu et al. synthesized a  $\text{Cu}_2\text{O}@g\text{-C}_3\text{N}_4$  core-shell structure onto the  $\text{Cu}_2\text{O}$  octahedra with exposed (111) facets. The efficiency of the composite material

under visible light irradiation was attributed to the synergistic effect at the interface of  $\text{Cu}_2\text{O}$  and  $g\text{-C}_3\text{N}_4$ , i.e., transfer of the photogenerated electrons of  $\text{Cu}_2\text{O}$  to the  $g\text{-C}_3\text{N}_4$  shell. In contrast, UV irradiation on the  $\text{Cu}_2\text{O}$  crystals had a negative effect, and this was attributed to a mechanism where  $\text{O}_\text{V}$  in  $\text{Cu}_2\text{O}$  act as electron traps, leading to the reduction of  $\text{Cu}_2\text{O}$  to  $\text{Cu}^0$  exhibiting lower photocatalytic activity [66].



**Figure 9.** (a) TEM–SAED–HRTEM images of the Cu@Cu<sub>2</sub>O/ZnO nanocomposite; (b) Photocatalytic stability experiments of the Cu@Cu<sub>2</sub>O/ZnO (30wt%) where after four catalytic runs there was no significant decrease of the performance; (c) H<sub>2</sub> production rates of Cu@Cu<sub>2</sub>O/ZnO catalysts where 30% copper loading shows the best photocatalytic performance; (d) Proposed photocatalytic H<sub>2</sub> production mechanism of the Cu@Cu<sub>2</sub>O/ZnO under visible light irradiation. Reproduced with permission from ref. [62], Copyright 2018 Wiley–VCH; (e) Tauc plots of Cu<sub>2</sub>O, ND and NDs–Cu<sub>2</sub>O where the addition of NDs decreases the energy gap of Cu<sub>2</sub>O. (f) Schematic representation of the photocatalytic mechanism of NDs–Cu<sub>2</sub>O; Reproduced with permission from ref. [65], Copyright 2015 Wiley–VCH.

### 3.1.4. The Case of Cu-Single Atoms

Lastly, single-atom catalysts (SACs) are gaining more and more interest owing to their ability in maximizing reaction active sites [70]. These isolated metal atoms anchored in the surface of photocatalysts may offer more reaction active sites, but their stability and tendency to aggregate during photocatalysis is still an issue to address. Very recently, Lee et al. [64] designed atomically-dispersed Cu on TiO<sub>2</sub> by incorporating site-specific single atoms of Cu. Interestingly, it was shown that photogenerated electrons can be transferred from the CB of TiO<sub>2</sub> to the *d*-orbitals of the isolated Cu<sup>2+</sup> atoms. These trapped electrons induced a polarization field resulting in lattice distortion of TiO<sub>2</sub>, that was suggested to be linked with the enhanced photocatalytic H<sub>2</sub> activity. This phenomenon was reversible when the material was exposed to O<sub>2</sub> without irradiation. They also report a change of color during photocatalysis, in accordance with other studies on TiO<sub>2</sub>-based nanocatalysts [58,59]. In another very recent study, Zhang et al. managed to deposit higher amounts of CuSA (>1 wt%) on TiO<sub>2</sub>, at this point we should note that normally the loading percentages of SACs is near 0.1–0.3 wt% [40]. Their optimized material exhibited the impressive H<sub>2</sub> evolution rate of 101.7 mmol g<sup>-1</sup> h<sup>-1</sup>, which in their case was higher than PtSA-TiO<sub>2</sub> (95.3 mmol g<sup>-1</sup> h<sup>-1</sup>). This impressive photocatalytic performance is attributed to the larger amount of Cu SACs as well as to the high dispersion onto the TiO<sub>2</sub> surface. Regarding the photocatalytic mechanism, efficient electron transfer is attributed to the reversible

redox process between  $\text{Cu}^{2+}$  and  $\text{Cu}^{1+}$  atoms. These findings are supported by Electron Paramagnetic Resonance (EPR) data, showing a strong  $\text{Cu}^{2+}$  EPR signal before irradiation, which during irradiation was converted to  $\text{Cu}^+$ , which was re-oxidized to  $\text{Cu}^{2+}$  after exposure to air  $\text{O}_2$  [40]. This in situ self-healing process enables CuSA-TiO<sub>2</sub> to achieve these remarkable H<sub>2</sub> production rates. Furthermore, long-term H<sub>2</sub> evolution experiments, i.e., 380 days later, showed no loss of the photocatalytic performance [40].

### 3.2. Electrocatalytic Hydrogen Production

Electrochemistry permits quantitative comparisons of activity stability, while photo-electrochemistry permits more advanced parameters to be monitored, i.e., photocurrent density, photo-response, photostability and photocorrosion. In brief, the tools used can be [56]:

- [i] exploring the intrinsic activity of catalysts by measuring the capacitance of double layer Cdl to detect the electrochemical active surface area (ESCA) [71],
- [ii] overpotential needs to be the lowest possible, at 10 mA/cm<sup>2</sup> [72],
- [iii] the Tafel slope shows the rate of adsorption–desorption kinetics, where the electrochemical desorption step is rate-determining according to the Volmer–Heyrovsky mechanism [73].
- [iv] through EIS measurements the charge transfer resistance can easily be found [56].
- [v] Mott–Schottky plots can provide information about flat band potential and the populations of donors and acceptors [74].

The double-layer capacitance which can be determined by cyclic voltammetry measurements, the electrochemically active surface area, current density [56], and the faradaic efficiency of the sample [75]. Linear Sweep Voltammetry (LSV) provides a measure of overpotentials necessary to achieve  $j = 10 \text{ mA/cm}^2$ , and after 2 h to check the stability, or even a long-term stability test which can last up to 24 h [76].

In Table 3, we summarize pertinent values for these electrochemical parameters for selected Cu-oxide catalysts.

**Table 3.** Summary of Electrocatalytic Parameters, related to Hydrogen Evolution Reaction, for Cu-based catalysts.

Electrocatalytic Hydrogen Production					
Catalyst	Electrolyte or pH	$C_{at}$ (mF/cm <sup>2</sup> )	$\eta$ (mV) @ $-10$ mA/cm <sup>2</sup>	Tafel Slope (mV dec <sup>-1</sup> )	Ref.
Cu/Cu <sub>2</sub> O-CuO/rGO-400	1 M KOH	130	105	124	[44]
PS-Cu	0.5 M H <sub>2</sub> SO <sub>4</sub>	8.77	182	99.16	[27]
	1 M PBS	10.01	261	143.58	
	1 M KOH	13.56	121	136.54	
	0.5 M H <sub>2</sub> SO <sub>4</sub>	4.86	411	192.22	
Cu-foam	1 M PBS	5.60	429	211.95	
	1 M KOH	5.91	473	230.27	
	0.5 M H <sub>2</sub> SO <sub>4</sub>	6.87	530	132.17	
Cu-NPs	1 M PBS	6.47	707	285.99	
	1 M KOH	9.72	454	148.86	
	0.5 M H <sub>2</sub> SO <sub>4</sub>		78	79.09	
Pt-foil	1 M PBS		186	194.05	
	1 M KOH		178	167.84	
NiCu@C-1	pH = 0		48	94.5	[33]
	pH = 7		164	94.6	
	pH = 14		74	74	
Graphene coated Cu	0.5 M H <sub>2</sub> SO <sub>4</sub>		252	67	[77]
Cu@NC NT/CF-500	1 M KOH	101	123	61	[78]
Cu <sub>53</sub> Ru <sub>47</sub>	1 M KOH	59	15	30	[28]
	1 M PbS	59	41	35	
Cu-m/Cu-W/NiCo-LDH	0.5 M H <sub>2</sub> SO <sub>4</sub>		15	79.4	[79]
	1 M KOH	19.8	27	50.5	

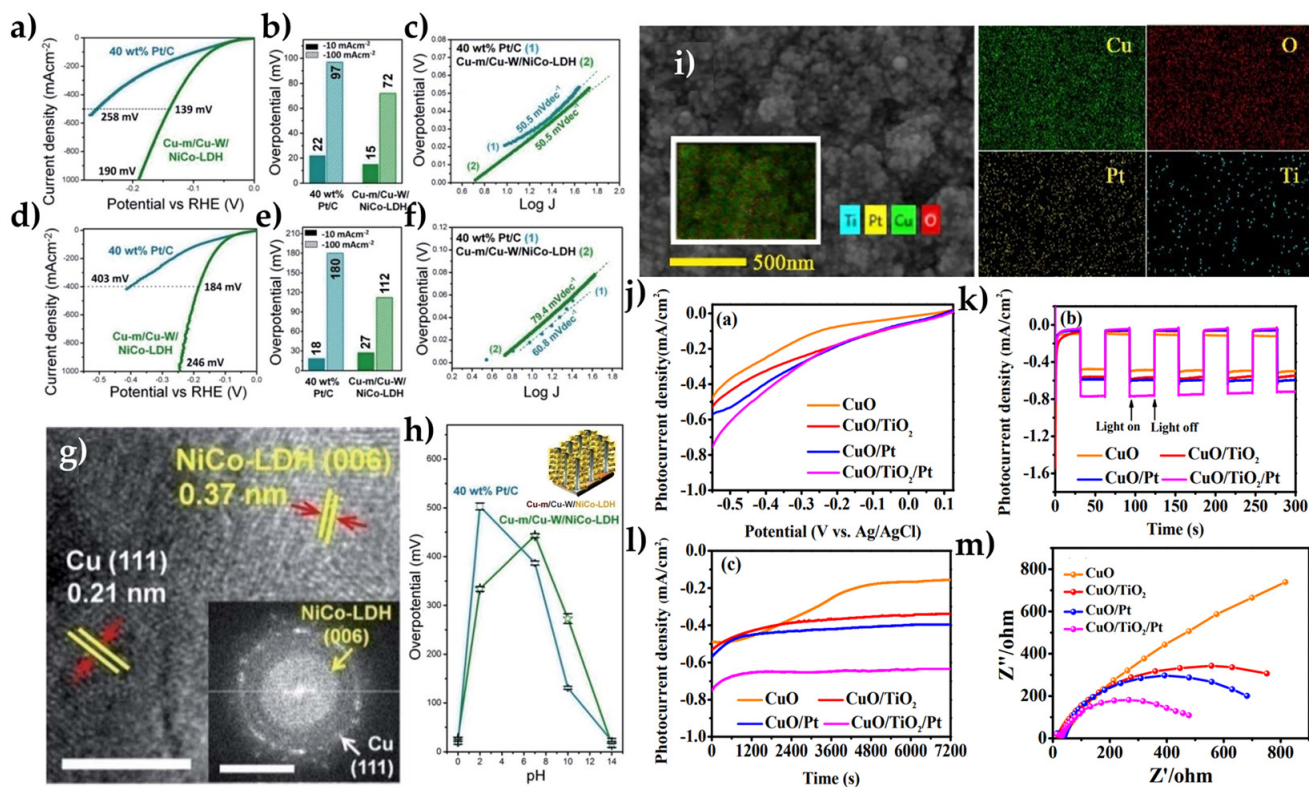
In Table 3, pertinent literature works are presented. In all cases, we mention works where they did not use noble metals as co-catalysts, but use only Cu-based electrocatalysts. Some of them had merged the electrolytes with graphene as a core-shell structure in order to protect them from corrosion [77], while others [44,78] used carbon nanotubes with Cu or Cu/Cu<sub>2</sub>O/CuO structures merged in reduced graphene oxide. An important contribution is a strain-activated copper catalyst [27], operating under a wide pH range. In [27] the current density achieved was 1.987 A cm<sup>-2</sup> at  $-1.2$  V vs. RHE, which is 2.85 times vs. a reference Pt foil.

Moreover, a three-dimensional nanoporous Cu-Ru alloy as an outstanding Pt-free catalyst for HER has been prepared by a dealloying process by Wu et al. [28]. This catalyst had a good activity with a very low overpotential and very low Tafel slopes in alkaline and neutral environments. By alloying those two metals, Cu and Ru, the incorporation of Ru atoms in the Cu matrix enhanced the strength of the Cu-H interaction, while it weakened the Ru-H interaction, but improved the overall activity [27]. The Electrochemical impedance spectroscopy measurements of np-Cu<sub>53</sub>Ru<sub>47</sub> further confirmed that the incorporation of Ru atoms into the Cu matrix brings about small internal resistance and fast charge-transfer behavior. The same group, [27], demonstrated with Density Functional Theory (DFT) that the incorporation of Ru atoms into the Cu matrix could effectively optimize the *d*-electron domination of Cu and Ru atoms and decrease the energy barrier and improving the HER activity.

Another approach [79] presented a complex heterostructure of NiCo layered double hydroxide wrapped around Cu nanowires grown on top of commercially available Cu mesh (Cu-m). This Cu-m/Cu-W/NiCo-LDH material outperformed the benchmark 40 wt% Pt/C at a wide pH range [79]. As shown in Figure 10a,b, the required overpotential was smaller for alkaline medium than 40%Pt/C, confirmed by the Tafel plots at Figure 10c. While in acidic environment, as shown in Figure 10d,e, the Cu-m/Cu-W/NiCo-LDH had increased



overpotential versus 40%Pt/C at  $-10 \text{ mA cm}^{-2}$ , while the Tafel slope in Figure 10f shows a decreased value for Cu-m/Cu-W/NiCo-LDH. Figure 10h shows the required potential across the pH range to reach  $-10 \text{ mA cm}^{-2}$  for Cu-m/Cu-W/NiCo-LDH versus 40 wt% Pt/C. In Figure 10g, high-resolution transmission electron microscopy (HRTEM) shows the (111) exposed facets of Cu-m and Cu-Ws, and the latter's growth direction is along (111).



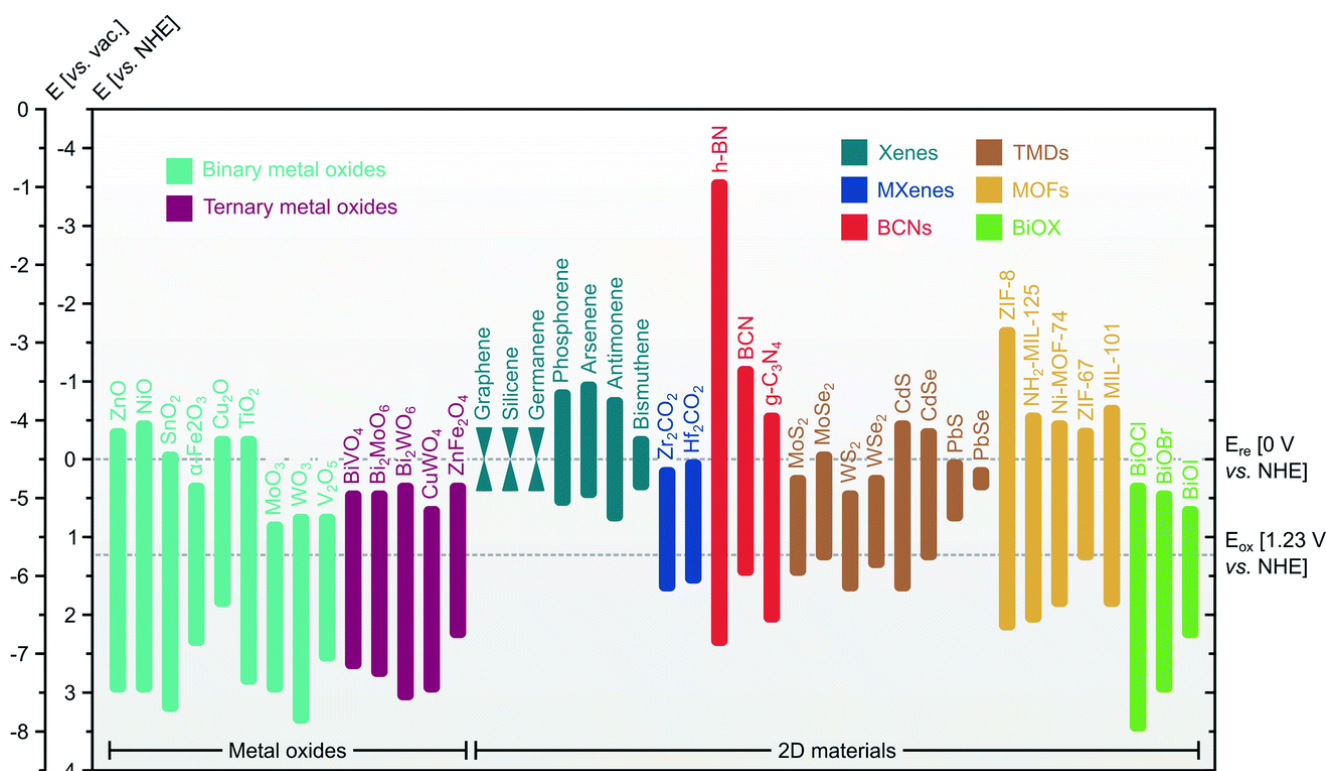
**Figure 10.** Electrocatalytic HER performance of Cu-m/Cu-W/NiCo-LDH as a competitive catalyst against the state of art 40% Pt/C. Alkaline conditions (1 M KOH) (a) HER polarization curves in 1 M KOH (iR-corrected); (b) overpotentials at  $-10$  and  $-100 \text{ mA cm}^{-2}$ ; (c) Tafel plots for Cu-m/Cu-W/NiCo-LDH and 40 wt% Pt/C. For acidic conditions (0.5 M H<sub>2</sub>SO<sub>4</sub>): (d) HER polarization curves (iR-corrected); (e) overpotentials at  $-10$  and  $-100 \text{ mA cm}^{-2}$ ; (f) corresponding Tafel plots; (g) high resolution TEM images of Cu-m/Cu-W/NiCo-LDH; (h) Required overpotential across the pH spectrum to reach  $-10 \text{ mA cm}^{-2}$  for Cu-m/Cu-W/NiCo-LDH and 40 wt% Pt/C. Reproduced from Ref. [79] with permission from the Royal Society of Chemistry; Photo-electrochemical HER of CuO with CuO, CuO/TiO<sub>2</sub>, CuO/Pt and CuO/TiO<sub>2</sub>/Pt photocathodes. (i) SEM image of the last sample CuO/TiO<sub>2</sub>/Pt is presented with elemental mapping images of Cu, O, Ti and Pt of CuO/TiO<sub>2</sub>/Pt. (j) Photocurrent density versus Applied Voltage, with the CuO/TiO<sub>2</sub>/Pt to behave better of all other samples. (k) The photo-response of samples measured at  $-0.55 \text{ V vs. Ag/AgCl}$  under illumination with 30 s light on/off cycles, while (l) presents Photocurrent density-time curves measured in 1 M NaOH electrolyte at  $-0.55 \text{ V vs. Ag/AgCl}$  under simulated sunlight illumination for 2 h, indicating a stable sample and (m) Nyquist plots by Electrochemical Impedance Spectroscopy measured at  $-0.55 \text{ V vs. Ag/AgCl}$  of photocathodes with the CuO/TiO<sub>2</sub>/Pt to has the smaller arc-radius. Reproduced from Ref. [26] with permission from the Royal Society of Chemistry.

### 3.3. Photoelectrochemical Hydrogen Evolution Reaction

Photoelectrochemical cells (PEC) are widely considered potent for solar water splitting devices [80] because they combine solar energy collection with water electrolysis and because they spatially separate two half-cell reactions, HER and OER. For a PEC cell, the process depends on three steps [55]: (i) light absorption by a semiconductor material, (ii) electron-hole pair generation, and, as a result, (iii) photoinduced electrons (or holes) are

driven, by space-charge field, to the semiconductor/solution interface where they reduce or oxidize water.

Usually, a PEC cell has a *n*-type semiconductors, such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{BiVO}_4$ ,  $\text{WO}_3$ ,  $\text{Fe}_2\text{O}_3$  [4,81–83] whose valence band edges are more positive than the potential of the  $\text{H}_2\text{O}/\text{O}_2$  redox couple, that makes them ideal for OER photoanodes. On the other hand, *p*-type semiconductors such as *p*-CdS, *p*-WSe, *p*-InP and *p*-type Copper Oxides [25,84,85], whose conduction band edge is more negative than the  $\text{H}_2\text{O}/\text{H}_2$  potential, are ideal for HER photocathodes (see Figure 11). In Table 4, we selected some interesting works from several groups, who have presented durable and stable photocathodes for a PEC cell. In addition, very important for these catalysts is to have good light response and photocurrent to benchmark their photocatalytic activity.



**Figure 11.** Band positions of various metal oxide and non-oxide semiconductors and 2D materials. Reproduced from Ref. [86] with permission from the Royal Society of Chemistry.

In order to explore the photocorrosion of  $\text{CuO}$ , Xing et al. [26] had tested heterojunctions  $\text{CuO}:\text{CuO}/\text{TiO}_2$ ,  $\text{CuO}/\text{Pt}$ , and  $\text{CuO}/\text{TiO}_2/\text{Pt}$  as photocathodes. Under increased protection of the photocathodes, allowed increase of the photocurrent density at  $-0.55\text{ V}$ , as shown in Figure 10j. The composite of  $\text{CuO}/\text{TiO}_2/\text{Pt}$  had the highest photocurrent density. In addition, according to the Figure 10k,  $\text{CuO}/\text{TiO}_2/\text{Pt}$  seems to have a very good photo-response, at  $-0.55\text{ V}$  vs.  $\text{Ag}/\text{AgCl}$  applied under 30 s light on/off cycles for more than 300 s. This electrode was stable against photocorrosion in 1 M  $\text{NaOH}$  electrolyte at  $-0.55\text{ V}$  vs.  $\text{Ag}/\text{AgCl}$  under simulated sunlight illumination for 2 h, Figure 10l. The EIS Nyquist plot, shown in Figure 10m, reveals that the  $\text{CuO}/\text{TiO}_2/\text{Pt}$  has decreased resistance in charge transfer phenomena, which indicates easier transfer of photoinduced electrons to the electrolyte solution.

As general conclusion, photocorrosion must be scrutinized as another important phenomenon in PEC for solar hydrogen production. This aspect is considered using molecular components such as linkers, non-oxide material modifiers, or catalysts. The most common method, as mentioned in Table 4, is by using  $\text{TiO}_2$  as a matrix where  $\text{CuO}$ ,  $\text{Cu}_2\text{O}$  can be protected by photocorrosion through the Z-scheme mechanism. In the case of

single-Cu atoms, there is a different approach, where Cu(II) transforms reversibly to Cu(I) during photoelectrocatalysis as described before.

**Table 4.** Pertinent Cu-based materials for PhotoElectrochemical Hydrogen Evolution Reaction based on their catalytic activity.

Photoelectrochemical Hydrogen Production				
Catalyst	Environment	Light Source	J @ Applied Potential	Ref.
CuO/TiO <sub>2</sub>	1 M KOH	500 W Xe-Lamp	−0.54 mA/cm <sup>2</sup> @ −0.55 V vs. Ag/AgCl	[26]
CuO/Pt	1 M KOH		−0.57 mA/cm <sup>2</sup> @ −0.55 V vs. Ag/AgCl	
CuO/TiO <sub>2</sub> /Pt	1 M KOH		−0.75 mA/cm <sup>2</sup> @ −0.55 V vs. Ag/AgCl	
Cu <sub>2</sub> O/CuO Bilayered composite	0.5 M Na <sub>2</sub> SO <sub>4</sub> + 1 M KOH	300 W Xe-Lamp (1000 mW m <sup>−2</sup> )	−3.15 mA/cm <sup>2</sup> @ 0.40V vs. RHE	[18]
Cu <sub>2</sub> O/Ga <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub> /Ru <sub>x</sub>	0.5 M Na <sub>2</sub> SO <sub>4</sub> + 0.1 M phosphate solution	300 W Xe-Lamp (1000 mW m <sup>−2</sup> )	−10 mA/cm <sup>2</sup> @ 0V vs. RHE	[87]
3D CuO		150 W solar simulator (1000 mW m <sup>−2</sup> )	−3.15 mA/cm <sup>2</sup> @ 0.42V vs. RHE	[88]
CuO/thin film	0.1 M Na <sub>2</sub> SO <sub>4</sub>	Sunlight (1000 mW m <sup>−2</sup> )	−3.1 mA/cm <sup>2</sup> @ 0V vs. RHE	[23]
Au-Pd decorated CuO thin film	0.1 M Na <sub>2</sub> SO <sub>4</sub>	Sunlight (1000 mW m <sup>−2</sup> )	−3.88 mA/cm <sup>2</sup> @ 0V vs. RHE	
CuSA-TiO <sub>2</sub>	0.2 M Na <sub>2</sub> SO <sub>4</sub>	150 W Xe-Lamp	−10 mA/cm <sup>2</sup> @ −0.72V vs. NHE	[40]

#### 4. CO<sub>2</sub> Reduction by Cu-Based Materials

From an economic and environmental point of view, (electro)photocatalytic CO<sub>2</sub> reduction is a forward-looking realm in catalytic technology. Inspired by natural-photosynthesis, scientists are trying to realize “Artificial-Photosynthesis”, convert CO<sub>2</sub> into useful and high value chemical fuels, using the highly abundant solar energy (see Figure 1). Inoue together with Fujishima and Honda pioneered the idea of the feasibility of catalytic conversion of CO<sub>2</sub> to C1-fuels using semiconductors [4,89]. Since then, many efforts were made to improve the overall performance and tune the selectivity towards a specific product [9]. In this context, Cu-oxides and metal-Cu particles emerge among the most promising photocatalysts thanks to good electron transfer properties and loosely bound *d*-electrons, thus having great potential for facilitating CO<sub>2</sub> photoreduction [20]. Herein, we focus on Cu-based semiconductors coupled with other oxide semiconductors, carbon-based materials or plain copper catalysts with facet modifications and discuss stability issues and product selectivity (see Table 5).

**Table 5.** Pertinent Cu-based semiconductors used for the photocatalytic CO<sub>2</sub> conversion into various chemical fuels.

Photocatalytic CO <sub>2</sub> Reduction				
Catalyst	Hole Scavenger/ Reaction Conditions	Irradiation Source	Main Products	Ref.
(110) Cu <sub>2</sub> O	Saturated H <sub>2</sub> O in CO <sub>2</sub>	300 W Xe-Lamp	CH <sub>3</sub> OH: 1.2 mol g <sup>−1</sup> h <sup>−1</sup>	[90]
Dodeca-Cu <sub>2</sub> O/rGO	Saturated H <sub>2</sub> O in CO <sub>2</sub>	300 W Xe-Lamp (λ ≤ 420 nm)	CH <sub>3</sub> OH: 355.3 μmol g <sup>−1</sup> h <sup>−1</sup>	[91]
Pt-Cu <sub>2</sub> O/TiO <sub>2</sub>	Saturated H <sub>2</sub> O in CO <sub>2</sub> (71kPa)	500 W Xe-arc Lamp (300 nm < λ < 400 nm) (20.5 mW cm <sup>−2</sup> )	CH <sub>4</sub> : 1.42 μmol g <sup>−1</sup> h <sup>−1</sup> CO: 0.05 μmol g <sup>−1</sup> h <sup>−1</sup>	[92]
Octa-Cu <sub>2</sub> O/TiO <sub>2</sub>	Water vapor—1atm CO <sub>2</sub> (g)	1 kW Hg (Xe) arc lamp (λ ≥ 305 nm)	CO: 2.11 μmol g <sup>−1</sup> h <sup>−1</sup>	[67]
1% Cu/TiO <sub>2</sub> (H <sub>2</sub> )	Mixed gas CO <sub>2</sub> /H <sub>2</sub> O	150 W solar simulator (90 mW cm <sup>−2</sup> , 200 ≤ λ ≤ 1000 nm)	CH <sub>4</sub> : 25 μmol g <sup>−1</sup> h <sup>−1</sup> CO: 4.4 μmol g <sup>−1</sup> h <sup>−1</sup>	[93]
2%CuO-19%ZnO/TiO <sub>2</sub>	Saturated H <sub>2</sub> O in CO <sub>2</sub> , 0.2 M NaOH	18 W Hg-Lamp (λ = 254 nm)	CH <sub>4</sub> : 184 μmol g <sup>−1</sup> (after 24 h)	[94]
ZnO-Cu <sub>2</sub> O	Saturated H <sub>2</sub> O in CO <sub>2</sub> , 0.2 M Na <sub>2</sub> CO <sub>3</sub>	300 W Xe-Lamp	CH <sub>4</sub> : 1080 μmol g <sup>−1</sup> h <sup>−1</sup>	[95]
5wt% CuO/NaTaO <sub>3</sub>	CO <sub>2</sub> , Isopropanol	250 W Hg-Lamp (365 nm)	CH <sub>3</sub> OH: 1302.22 μmol g <sup>−1</sup> h <sup>−1</sup>	[96]
Cu <sub>2</sub> O	Saturated H <sub>2</sub> O in CO <sub>2</sub> , NaOH, Na <sub>2</sub> SO <sub>3</sub>	500 W Xe-arc Lamp (400 nm < λ < 700nm)	CH <sub>3</sub> OH: 104 μmol g <sup>−1</sup>	[97]
Cu <sub>2</sub> O-SiC			CH <sub>3</sub> OH: 191 μmol g <sup>−1</sup>	



Table 5. Cont.

Photocatalytic CO <sub>2</sub> Reduction				
Catalyst	Hole Scavenger/ Reaction Conditions	Irradiation Source	Main Products	Ref.
BiVO <sub>4</sub> /C-coated Cu <sub>2</sub> O	Saturated H <sub>2</sub> O in CO <sub>2</sub>	300 W Xe-Lamp (100 mW cm <sup>-2</sup> ) ( $\lambda > 420$ nm)	CO: $\sim 3 \mu\text{mol g}^{-1} \text{h}^{-1}$	[98]
3%Cu/TiO <sub>2</sub>			HCOOH: $> 4500 \mu\text{mol g}^{-1} \text{h}^{-1}$ (Visible) // CH <sub>3</sub> OH: $\sim 300 \mu\text{mol g}^{-1} \text{h}^{-1}$ (Visible) HCOOH: $> 2000 \mu\text{mol g}^{-1} \text{h}^{-1}$ (UV) // CH <sub>3</sub> OH: $> 75 \mu\text{mol g}^{-1} \text{h}^{-1}$ (UV)	
3% Cu/g-C <sub>3</sub> N <sub>4</sub>	Saturated H <sub>2</sub> O in CO <sub>2</sub> , 1 M NaOH	UV-Lamp (254 nm, 5.4 mW cm <sup>-2</sup> ) Visible: 500 W Xe-arc Lamp	HCOOH: $> 3500 \mu\text{mol g}^{-1} \text{h}^{-1}$ (Visible) // CH <sub>3</sub> OH: $\sim 350 \mu\text{mol g}^{-1} \text{h}^{-1}$ (Visible) HCOOH: $> 3750 \mu\text{mol g}^{-1} \text{h}^{-1}$ (UV) // CH <sub>3</sub> OH: $> 200 \mu\text{mol g}^{-1} \text{h}^{-1}$ (UV)	[99]
(g-C <sub>3</sub> N <sub>4</sub> )/(3%Cu/TiO <sub>2</sub> ) (30:70)			HCOOH: $5069 \mu\text{mol g}^{-1}$ (Visible) // CH <sub>3</sub> OH: $2574 \mu\text{mol g}^{-1}$ (Visible) HCOOH: $6709 \mu\text{mol g}^{-1}$ (UV) // CH <sub>3</sub> OH: $614 \mu\text{mol g}^{-1}$ (UV)	
rGO-CuO	DMF, Saturated H <sub>2</sub> O in CO <sub>2</sub>	20 W LED (85 W m <sup>-2</sup> )	CH <sub>3</sub> OH: $1228 \mu\text{mol g}^{-1}$	[100]
rGO-Cu <sub>2</sub> O			CH <sub>3</sub> OH: $862 \mu\text{mol g}^{-1}$	
c-Cu <sub>2</sub> O-gCN	$\sim 1$ bar CO <sub>2</sub> with moisture	8 W LED Lamp	CO: $0.002 \mu\text{mol g}^{-1} \text{h}^{-1}$	[101]
g-C <sub>3</sub> N <sub>4</sub> /CuO@MIL-125(Ti)	H <sub>2</sub> O 0.3%CO <sub>2</sub> (1 MPa)	300 W Xe-Lamp (326.1 W m <sup>-2</sup> ) ( $\lambda = 420$ nm)	CO: $180.1 \mu\text{mol g}^{-1}$ CH <sub>3</sub> OH: $997.2 \mu\text{mol g}^{-1}$ C <sub>2</sub> H <sub>5</sub> OH: $531.5 \mu\text{mol g}^{-1}$ CH <sub>3</sub> CHO: $1505.7 \mu\text{mol g}^{-1}$	[102]

#### 4.1. Photocatalytic CO<sub>2</sub> Reduction

##### 4.1.1. Facet Dependency of CO<sub>2</sub> Reduction

As in the case of photocatalytic H<sub>2</sub> evolution, see Section 3.1.1, facet engineering of Cu oxides shows high promise towards increased performance in photocatalytic CO<sub>2</sub> reduction [10]. Recently, Wu et al. reported the photocatalytic reduction of CO<sub>2</sub> on facet specific active sites of Cu<sub>2</sub>O [90]. They demonstrated that the (110) facet of a single Cu<sub>2</sub>O particle was the photoactive site towards CO<sub>2</sub> reduction to CH<sub>3</sub>OH, while the (100) facet remained inert [90]. This observation can be attributed to electron-density difference on Cu active sites on the (110) facet and a shift from Cu(I) to Cu(II) due to CO<sub>2</sub> and H<sub>2</sub>O adsorption [90]. In this way, during CO<sub>2</sub> reduction, the Cu<sub>2</sub>O catalyst manages to oxidize H<sub>2</sub>O accompanied with a lattice expansion due to the CO<sub>2</sub> adsorption. This process showed a selectivity towards methanol yielding  $1.2 \text{ mol CH}_3\text{OH g}^{-1} \text{h}^{-1}$  and reaching an internal quantum yield of  $\sim 72\%$  [90].

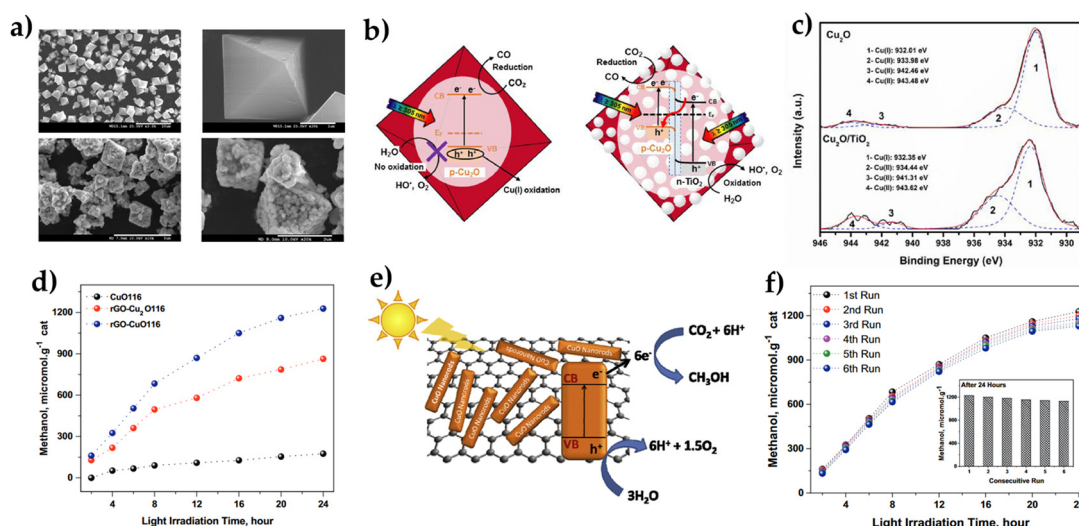
##### 4.1.2. Coupling with Semiconductors

##### The Case of Cu-TiO<sub>2</sub>

Cu<sub>2</sub>O coupling with TiO<sub>2</sub> has been explored as an efficient strategy to enhance photocatalytic performance. More specifically, Aguirre et al. synthesized a *p-n* Cu<sub>2</sub>O/TiO<sub>2</sub> heterojunction, where the Z-scheme mechanism of electron transfer [37] enhances the stability of Cu<sub>2</sub>O [67] (see Figure 12a,b). The energetics of this example are educative. TiO<sub>2</sub> alone exhibits very low CO<sub>2</sub>-to-fuel-conversion efficiency under UV excitation, while Cu<sub>2</sub>O possesses a more favorable  $E_{\text{CB}} = -1.4 \text{ eV}$  vs. NHE (pH = 7) [103]; however, it suffers from photostability issues [13]. In the *p-n* Cu<sub>2</sub>O/TiO<sub>2</sub> scheme, Cu(0) was not observed during photocatalytic experiments. In contrast, compared with pure Cu<sub>2</sub>O, an increase of Cu(II)/Cu(I) ratio [67] was observed (see Figure 12c). Liu et al. had prepared a Cu/TiO<sub>2</sub> catalyst tailoring Cu valence and oxygen vacancies of the composite [93]. By thermal treatment under reducing atmosphere (H<sub>2</sub> and He) they exhibit the formation of defect sites, i.e., O<sub>V</sub>'s and Ti<sup>3+</sup> centers which affected the CO production. Moreover, during the reduction process through calcination, there was a change on the Cu oxidation states from Cu<sup>2+</sup> to Cu<sup>1+</sup> or Cu<sup>0</sup>. These Cu<sup>1+</sup> species can effectively trap electrons due to the more positive reduction potential of Cu<sup>+</sup>/Cu<sup>0</sup> (+0.52 eV) couple vs. that of Cu<sup>2+</sup>/Cu<sup>0</sup>



(+0.34 eV) [104]. The  $\text{Cu}^+/\text{Cu}^0$  couple can play a dual role where  $\text{Cu}^{1+}$  species trap electrons, and  $\text{Cu}^0$  species can effectively trap holes [93]. Xiong et al. had used  $\text{TiO}_2$  crystals as a matrix to deposit Pt and  $\text{Cu}_2\text{O}$  NPs where  $\text{Cu}_2\text{O}$  promoted  $\text{CH}_4$  production but suppressed  $\text{H}_2$  evolution [92]. In that case, Pt favored the activation of  $\text{H}_2\text{O}$  while  $\text{Cu}_2\text{O}$  performed the  $\text{CO}_2$  reduction. After the photocatalytic reaction, most of the  $\text{Cu}_2\text{O}$  phase was reduced to  $\text{Cu}^0$ , indicating that Pt promotes  $e^-$ -transfer to  $\text{Cu}_2\text{O}$  during photocatalysis. Afterwards, the so-formed metallic  $\text{Cu}^0$  enhanced the selective  $\text{CH}_4$  production, a well-known property of metallic Cu [92].



**Figure 12.** (a) SEM images of  $\text{Cu}_2\text{O}$  (top) and  $\text{Cu}_2\text{O}/\text{TiO}_2$  composite (bottom) where the surface of  $\text{Cu}_2\text{O}$  octahedral particles is covered with  $\text{TiO}_2$  NPs; (b) Schematic presentation of the proposed  $\text{CO}_2$  reduction mechanism induced by  $\lambda \geq 305$  nm; (c) XPS spectra for Cu  $2p_{3/2}$  for pristine  $\text{Cu}_2\text{O}$  (top) and  $\text{Cu}_2\text{O}/\text{TiO}_2$  (bottom). Reprinted from [67], with permission from Elsevier; (d)  $\text{CH}_3\text{OH}$  yields of  $\text{CuO}$ ,  $\text{rGO-CuO}$  and  $\text{rGO-Cu}_2\text{O}$  composites; (e) Schematic representation of the  $\text{CO}_2$  conversion mechanism to  $\text{CH}_3\text{OH}$  using the  $\text{rGO-CuO116}$  composite under visible light irradiation; (f) Stability/recycling experiments of  $\text{rGO-CuO116}$ . Inset figure shows  $\text{CH}_3\text{OH}$  yields after 6 consecutive catalytic runs. Reprinted from [100] with permission from Elsevier.

### The Case of Cu Coupling with Non- $\text{TiO}_2$ Semiconductors

As we have already stated,  $p$ - $n$  junctions of  $\text{Cu}_2\text{O}$  with appropriate  $n$ -type metal-oxides can exhibit better charge separation and enhanced photocatalytic activity for  $\text{CO}_2$  reduction.  $\text{ZnO}$  as an  $n$ -type semiconductor possesses a large energy gap of 3.2–3.3 eV with high electron mobility and low dielectric constant, e.g., compared to  $\text{TiO}_2$ . Bae et al. [95] used  $\text{ZnO-Cu}_2\text{O}$  nanohybrids to reduce  $\text{CO}_2$  to  $\text{CH}_4$  in an  $\text{CO}_2$ -saturated aqueous medium without use of hole scavenger [95]. Once again, the Z-scheme was the proposed mechanism and when compared to  $\text{TiO}_2(\text{P25})\text{-Cu}_2\text{O}$ , the  $\text{ZnO-Cu}_2\text{O}$  exhibited superior reaction activity and selectivity. Another work [96] reported the synthesis of a  $\text{CuO-NaTaO}_3$  hybrid with the ability to reduce  $\text{CO}_2$  to  $\text{CH}_3\text{OH}$  with a maximum yield of  $1302 \mu\text{mol CH}_3\text{OH g}^{-1} \text{ h}^{-1}$ . As expected, smaller, and more uniform distribution of  $\text{CuO}$  NPs exhibited better catalytic performance. Noteworthy, in that work [96],  $\text{CuO}$  was suggested to be the  $\text{CO}_2$  reduction site, while  $\text{NaTaO}_3$  was the hole-scavenging site, and oxidized isopropanol to acetone. XPS analysis indicated the presence of  $\text{Cu}^{2+}$  species only, i.e., by  $\text{CuO}$ ; however, a post catalytic analysis was missing.

#### 4.1.3. Carbon-Based Materials and Core-Shell Cu-Oxide Structures

Incorporating copper oxide in carbon-based materials such as  $\text{rGO}$ ,  $\text{g-C}_3\text{N}_4$ , or carbon coating, is a widely used strategy in photocatalytic  $\text{CO}_2$  reduction. Graphene-based materials are gaining attention, due to their characteristics, high specific area and adsorption

capacity, as well as excellent electron mobility and chemical stability [105]. Gusain et al. prepared rGO-CuO/Cu<sub>2</sub>O nanohybrids and used them for photocatalytic conversion of CO<sub>2</sub> to CH<sub>3</sub>OH [100] (see Figure 12d). rGO interfaced with semiconducting materials can serve as an electron bridge and enhance the electron transfer process, a step crucial for the photocatalytic reactions [106]. In that work [106], it was suggested that the photo-generated electrons of CuO can be efficiently transferred to rGO, inhibiting in this way the electron hole recombination (see Figure 12e). Moreover, the high surface area and the defects of rGO can enhance CO<sub>2</sub> adsorption [100]. Noticeably, CuO (Cu<sup>2+</sup>) nanorods grafted on rGO exhibited better photocatalytic activity than a rGO/Cu<sub>2</sub>O (Cu<sup>1+</sup>) nanocomposite. Stability experiments indicated that after six catalytic runs, there were no significant changes in the morphological and chemical characteristics of the nanocomposite [100] (see Figure 12f). In another work, Chang et al. fabricated Cu<sub>2</sub>O/gCN nanocomposites with different Cu<sub>2</sub>O morphologies [101]. The main gaseous product of CO<sub>2</sub> reduction was CO with c-Cu<sub>2</sub>O/gCN being the best performing photocatalyst. The high activity of c-Cu<sub>2</sub>O/gCN was suggested to be linked with the improved CO<sub>2</sub> adsorption as well as the formation of CuO [101].

## 5. Conclusions

Herein, we discuss cases of pertinent Cu-based materials, that under appropriate coupling and engineering (facet and strain) aimed to resolve stability problems (corrosion and photocorrosion). There are many factors to be taken into consideration, such as the catalytic environment, the wavelength and intensity of irradiation source, and primarily the Cu oxidation state, which is proven to be a crucial factor determining the catalytic performance. Fundamental steps towards the stabilization and durability of Cu-based materials include the selection of a proper semiconductor coupling, suitable sacrificial agents, surface protection through core-shell structures and stabilization on defect sites of the substrate matrix. Z-scheme mechanisms could lead to the stabilization of Cu<sub>2</sub>O through enhanced charge-separation of the photogenerated carriers. In addition, the proper selection of Cu oxidation states can tune the selectivity towards specific CO<sub>2</sub> reduction products. It is important to mention that the vast majority of Cu-based nanocatalysts discussed herein were noble-metal free. To conclude, the reviewed works indicate that the Cu-oxide nanophases constitute highly potent nanoplatforms for development of efficient artificial photosynthesis catalysts. There is converging evidence that—probably—pure Cu-phases would be difficult to be used as standalone cathodic catalysts or electrodes; however, their heterojunctions with proper partner materials are an encouraging approach. Distinction between the role of numerous factors is required, protection from photocorrosion vs. CO<sub>2</sub>-reduction pathways, band-gap engineering, nano-facet engineering.

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