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# Thermodynamic Oxidation and Reduction Potentials of Photocatalytic Semiconductors in Aqueous Solution

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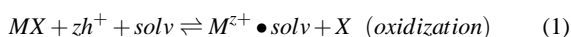
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**Abstract:** We introduce an approach to calculate the thermodynamic oxidation and reduction potentials of semiconductors in aqueous solution. By combining a newly-developed ab initio calculation for compound formation energy and band alignment with electrochemistry experimental data, this approach can be used to predict the stability of almost any compound semiconductor in aqueous solution. 30 photocatalytic semiconductors have been studied, and a graph (a simplified Pourbaix diagram) showing their valence/conduction band levels and oxidation/reduction potentials is produced. Based on this graph, we have studied the stabilities and trends against the oxidative and reductive photocorrosion for compound semiconductors. We found that, only metal oxides can be thermodynamically stable when used as the n-type photoanodes. All the non-oxides are unstable due to easy oxidation by the photo-generated holes, but they can be resistant to the reduction by electrons, thus stable as the p-type photocathodes.

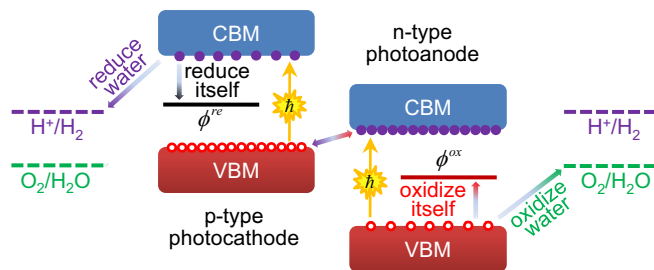
One key issue in the research of photocatalytic water splitting is to search for semiconductor photoelectrodes that can absorb the visible light and drive the hydrogen (oxygen) evolution reaction using the photo-generated electrons (holes).<sup>1-4</sup> This requires the semiconductors to have proper band alignment relative to the water redox potentials, e.g. the conduction band minimum (CBM) of the p-type photocathode should be higher (more negative in potential) than the water reduction potential  $H^+/H_2$ , and the valence band maximum (VBM) of the n-type photoanode lower (more positive in potential) than the water oxidation potential  $O_2/H_2O$ , as shown in the band alignment plot (1) for the Z-scheme water splitting system.<sup>5-9</sup> Given the importance of the band alignment, it is usually taken as a screening condition in the search and design of new photocatalytic semiconductors. However, this condition is not sufficient, and one important issue, which has attracted increasing attention but has not been well studied, is how to evaluate and enhance the stability of semiconductors in the aqueous solution.<sup>3,10,11</sup>

Resistance to the photo-induced corrosion (degradation or decomposition) under illumination is a critical condition for the photocathode and photoanode materials. It is due to this condition which makes the photocatalytic water splitting a much more challenging problem than the photovoltaic. A compound semiconductor MX (e.g. M=Zn, Ga, Ti, X=S, N, O<sub>2</sub> in ZnS, GaN, TiO<sub>2</sub> respectively) used as the n-type photoanode may have a VBM lower than the  $O_2/H_2O$  oxidation potential, but the photo-generated holes ( $h^+$ ) may oxidize the semiconductor first, rather than the water, making the compound MX decomposed through this reaction,<sup>11,12</sup>



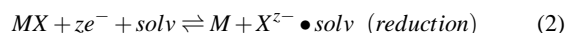
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**Figure 1.** A schematic plot of the band alignment of the p-type photocathode and n-type photoanode semiconductors relative to the water redox potentials in the Z-scheme.  $\phi^{ox}$  shows the oxidation potential of the photoanode in aqueous solution, and  $\phi^{re}$  shows the reduction potential of the photocathode.

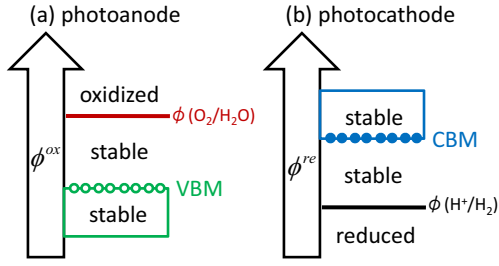
Similarly the photo-generated electrons ( $e^-$ ) in the p-type photocathode MX may reduce itself rather than the water through the following reaction,



The above reactions define two potentials for the hole and electron respectively. When the electron (hole) Fermi energy equals that potential, the reactions are in equilibrium, i.e. the Gibbs free energy change equals zero, and when the photo generated electron (hole) quasi Fermi energy is higher (lower) than that potential, the reaction will occur, hence the semiconductor will be corroded. These potentials are called the thermodynamic reduction potential  $\phi^{re}$  and oxidation potential  $\phi^{ox}$  of the semiconductor.

Since the photoanode (photocathode) is in contact with the aqueous solution, the photo-generated holes in the valence band (electrons in the conduction band) can oxidize (reduce) either the water or itself, as shown in 2. Whether the semiconductor is resistant to the photocorrosion depends on the alignment of  $\phi^{ox}$  relative to  $\phi(O_2/H_2O)$  for the photoanode, and  $\phi^{re}$  relative to  $\phi(H^+/H_2)$  for the photocathode, as shown in 2. Generally speaking, a semiconductor is stable with respect to the hole oxidation if its  $\phi^{ox}$  is lower than either  $\phi(O_2/H_2O)$  or its VBM, and is stable with respect to the electron reduction if its  $\phi^{re}$  is higher than either  $\phi(H^+/H_2)$  or its CBM.

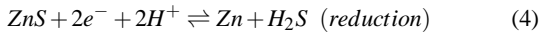
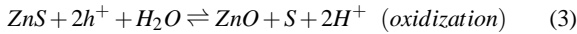
Experimentally,  $\phi^{ox}$  and  $\phi^{re}$  can be derived from the Pourbaix diagram,<sup>13,14</sup> but the diagram is not available for many novel photoelectrode semiconductors, and it is not easy to measure it. Thirty years ago,  $\phi^{ox}$  and  $\phi^{re}$  of several binary semiconductors had been calculated by Gerischer<sup>12,15</sup> (where the labels  $pE_{decomp}$  and  $nE_{decomp}$  correspond to  $\phi^{ox}$  and  $\phi^{re}$  respectively) and Bard and Wrighton.<sup>16</sup> Park and Barber have also calculated the full Pourbaix diagram for a few simple semiconductor compounds.<sup>14</sup> These calculated  $\phi^{ox}$  and  $\phi^{re}$  are widely cited in literatures to explain the corrosion of semiconductors in aqueous solution.<sup>11,17,18</sup> As proposed by Lewis and coauthors in their review paper,<sup>1</sup> the  $\phi^{ox}$  and



**Figure 2.** The stability change of the photoanode (a) as its oxidation potential  $\phi^{ox}$  shifts up from below the VBM to above  $\phi(\text{O}_2/\text{H}_2\text{O})$ , and of the photocathode (b) as its reduction potential  $\phi^{re}$  shifts down from above the CBM to below  $\phi(\text{H}^+/\text{H}_2)$ .

$\phi^{re}$  should be taken into account when choosing the candidate photoelectrodes, in addition to the optimal band gap and band edge alignment. Because the calculation of  $\phi^{ox}$  and  $\phi^{re}$  requires the Gibbs free energy of all the reactants and products in the related reactions, which are not available for some semiconductors (especially for multinary ones),  $\phi^{ox}$  and  $\phi^{re}$  of only a few simple semiconductors had been reported, and no general trend had been studied systematically. Recently new ab initio methods based on the density functional theory have been developed to calculate the formation energies of semiconductors with high accuracy,<sup>19</sup> and also more experimental electrochemistry data can be found in the latest handbooks,<sup>20,21</sup> thus a more extended study of  $\phi^{ox}$  and  $\phi^{re}$  for almost all semiconductors becomes possible. To facilitate the future choice of candidate photocatalytic materials, we here report the  $\phi^{ox}$  and  $\phi^{re}$  for more than 30 semiconductors as well as their band alignment relative to the normal hydrogen electrode (NHE) potential. Based on these results, we will discuss the trend in the oxidative/reductive stabilities of a series of metal oxides, II-VI and III-V related semiconductors.

To start with, we will take ZnS as an example and introduce how we calculate its  $\phi^{ox}$  and  $\phi^{re}$ . The specific exemplification of Eqs.(1-2) for ZnS are,



which define the  $\phi^{ox}$  and  $\phi^{re}$  of ZnS respectively, *i.e.* when the chemical potentials (Fermi energies) of the holes and electrons are equal to  $\phi^{ox}$  and  $\phi^{re}$  respectively, the Gibbs free energy changes of Eq.(3) and (4) are zero, thus,

$$\phi^{ox} = [G(\text{ZnO}) + G(\text{S}) + 2G(\text{H}^+) - G(\text{ZnS}) - G(\text{H}_2\text{O})]/2eF \quad (5)$$

$$\phi^{re} = -[G(\text{Zn}) + G(\text{H}_2\text{S}) - G(\text{ZnS}) - 2G(\text{H}^+)]/2eF \quad (6)$$

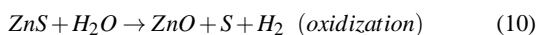
where  $G(\text{X})$  stands for the Gibbs free energy of X at the standard state,  $e$  is the elementary charge and  $F$  is the Faraday constant. To reference the potentials to the hydrogen reduction potential  $\phi(\text{H}^+/\text{H}_2)$ , the following half reactions can be used:



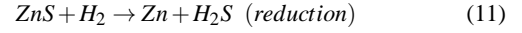
Here the chemical potentials of both the electron and hole are equal to  $\phi(\text{H}^+/\text{H}_2)$ , thus  $h^+$  is equivalent to  $-e^-$ , and the above two equations are equivalent.  $\phi(\text{H}^+/\text{H}_2)$  can be written as

$$\phi(\text{H}^+/\text{H}_2) = [2G(\text{H}^+) - G(\text{H}_2)]/2eF \quad (9)$$

Now, we can add the reverse of Eq.(7) [exchange the left and right hand side] to Eq.(3), then get the sum reaction,



and add the reverse of Eq.(8) to Eq.(4), then get



Note, to make  $h^+$  in Eq. (3) and (7) and  $e^-$  in (4) and (8) equivalent, it is assumed that their chemical potentials are the same as  $\phi(\text{H}^+/\text{H}_2)$ , so now the Gibbs free energy changes ( $\Delta G$ ) of Eq. (3) and (4) are not zero, and they are equal to  $\Delta G$  of the reactions (10) and (11) respectively, thus the sign  $\rightarrow$  is used rather than  $\rightleftharpoons$ .  $\Delta G$  of the reactions (10) and (11) can be calculated directly,

$$\Delta G(10) = G(\text{ZnO}) + G(\text{S}) + G(\text{H}_2) - G(\text{ZnS}) - G(\text{H}_2\text{O}) \quad (12)$$

$$\Delta G(11) = G(\text{Zn}) + G(\text{H}_2\text{S}) - G(\text{ZnS}) - G(\text{H}_2) \quad (13)$$

From Eq. (5), (6), (9), (11) and (12), we have

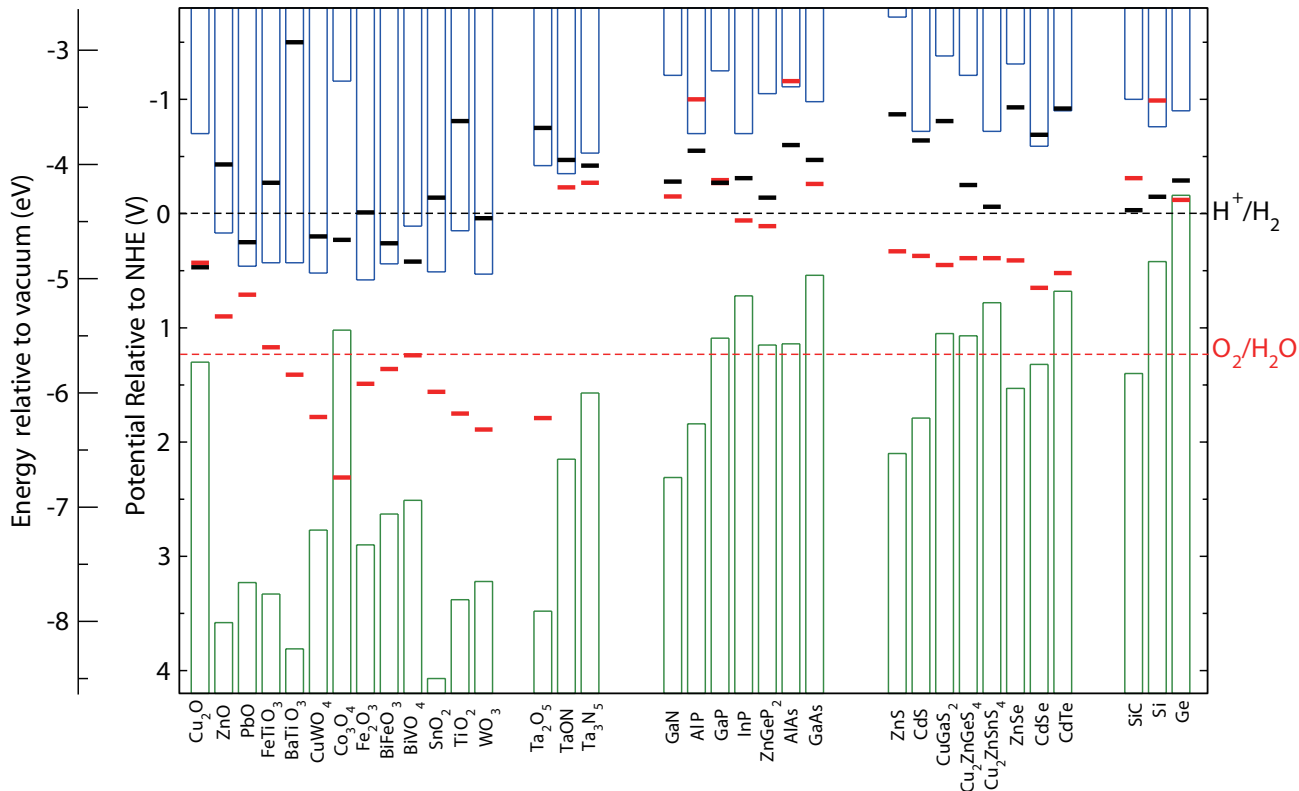
$$\phi^{ox} = \Delta G(10)/2eF + \phi(\text{H}^+/\text{H}_2) \quad (14)$$

$$\phi^{re} = -\Delta G(11)/2eF + \phi(\text{H}^+/\text{H}_2) \quad (15)$$

Since the NHE potential is  $\phi(\text{H}^+/\text{H}_2)$  at pH=0,  $\phi^{ox}$  and  $\phi^{re}$  relative to NHE can be calculated using Eq. (14) and (15). The key of the procedure is to find the plausible oxidation and reduction reactions, such as (10) and (11), and get their  $\Delta G$ , then the relevant  $\phi^{ox}$  and  $\phi^{re}$  can be calculated. Several plausible reactions can be tried, then the lowest  $\phi^{re}$  and highest  $\phi^{ox}$  should be used as the true reduction and oxidization potentials. Thus, in a sense, what we get is a simplified Pourbaix diagram, only the potentials limiting the photo-corrosions are reported here. In the supplement materials, we listed the reactions we considered in determining  $\phi^{ox}$  and  $\phi^{re}$  for different semiconductors. It should be mentioned that there is no guarantee that we have enumerated all the possible reactions, thus strictly speaking, the potentials reported here should be considered as a higher limit for  $\phi^{re}$  and a lower limit for  $\phi^{ox}$ . Nevertheless, in practice, we believe the results we obtained are very close to the true oxidation/reduction potentials.

3 shows our calculated  $\phi^{ox}$  and  $\phi^{re}$  relative to NHE, the water redox potentials  $\phi(\text{O}_2/\text{H}_2\text{O})$  and  $\phi(\text{H}^+/\text{H}_2)$ , and the valence and conduction band edges for five selected classes of semiconductors at pH=0. It is well-known that  $\phi(\text{O}_2/\text{H}_2\text{O})$  and  $\phi(\text{H}^+/\text{H}_2)$  depend on the pH value according to Nernstian relation,<sup>22</sup> *i.e.* shifting up by -0.059 V as the pH increases by 1. The dependence of  $\phi^{ox}$  and  $\phi^{re}$  on the pH value is determined by the specific reactions: when the sum reactions such as Eq. (10) and (11) are irrelevant to  $\text{H}^+$  or  $\text{OH}^-$ , their  $\Delta G$  is fixed, then  $\phi^{ox}$  and  $\phi^{re}$  shift together with  $\phi(\text{H}^+/\text{H}_2)$  as described by Eq. (14) and (15) and also follow the Nernstian relation; when the reactions are relevant to  $\text{H}^+$  or  $\text{OH}^-$ , the dependence is different, at variance to the Nernstian relation. Most of  $\phi^{ox}$  and  $\phi^{re}$  plotted in 3 follow the Nernstian relation, similar as  $\phi(\text{H}^+/\text{H}_2)$ , and the exceptions include: (i) all oxides have fixed  $\phi^{ox}$  with respect to pH change. (ii)  $\phi^{ox}$  of  $\text{CuGaS}_2$ ,  $\text{Cu}_2\text{ZnGeS}_4$  and  $\text{Cu}_2\text{ZnSnS}_4$  shift up by -0.044 V (instead of -0.059 V) as pH increases by 1. With these relations clear, the  $\phi^{ox}$  and  $\phi^{re}$  relative to NHE or  $\phi(\text{O}_2/\text{H}_2\text{O})$  and  $\phi(\text{H}^+/\text{H}_2)$  at different pH can be plotted (as a simplified Pourbaix diagram).

The valence and conduction band edges in 3 are collected from Ref. [11] for most metal oxides and from Ref. [23,24] for non-oxides. For the metal oxides, the band edge position relative to NHE is reported to depend on the pH value of the solution through the same Nernstian relation as for the water redox potentials.<sup>22</sup> For the non-oxides, the relation between the band edge position and the pH value is so far not clear.<sup>22</sup> Ref. [23] derived the band edge positions of the group IV, III-V and II-VI semiconductors relative to NHE based on the calculated band offsets among semiconductors, assuming that the conduction band edge of Si corresponds to its electron affinity (about -3.7 eV relative to vacuum level) and NHE is -4.44 eV relative to vacuum level. This implicitly assumes that the band edge positions for these materials do not depend on the



**Figure 3.** The calculated oxidation potential  $\phi^{ox}$  (red bars) and reduction potential  $\phi^{re}$  (black bars) relative to the NHE and vacuum level for a series of semiconductors in solution at pH=0. The water redox potentials  $\phi(\text{O}_2/\text{H}_2\text{O})$  and  $\phi(\text{H}^+/\text{H}_2)$  (dashed lines), and the valence (green columns) and conduction (blue columns) band edge positions at pH=0 are also plotted. The alignment for these potentials at different pH values (a simplified Pourbaix diagram) can be derived according to the relations described in the text, such as the Nernstian relation.

pH value. The band offsets of almost all group IV, III-V and II-VI related semiconductors had been calculated using the ab initio methods with reasonable consistence compared to experiments,<sup>25</sup> and the similar calculation procedures can be used to estimate the band edge positions of other semiconductor whose experimental values are unavailable.<sup>26</sup>

Compared to the calculation performed by Gerischer *et al.*,<sup>12,15</sup> Bard and Wrighton,<sup>16</sup> and Park and Barber<sup>14</sup> 30 years ago, our current work benefits from the progresses in both experiment and ab initio calculations. It is the combination of these two progresses which allow us to calculate  $\phi^{ox}$  and  $\phi^{re}$  for almost any given semiconductors, no matter binary or multinary compounds, as shown in 3. (i) Experimentally, the Gibbs free energy data in handbooks like Ref. [20,21] covers much more chemical compounds with higher accuracy compared to those published 30 years ago. (ii) If the experimental Gibbs free energy (formation enthalpy plus entropy contribution) for a compound in the proposed reaction is not reported in those handbooks, mostly for some novel compound semiconductors, its formation energy can be calculated using modern ab initio methods. The Gibbs free energy of that compound is then calculated from the formation energy plus the Gibbs free energies of the elementary compounds which are all known experimentally. For example, in this work, we have calculated the formation energies of  $\text{Ta}_2\text{N}_5$ ,  $\text{TaON}$ ,  $\text{ZnGeP}_2$ ,  $\text{Cu}_2\text{ZnGeS}_4$ ,  $\text{Cu}_2\text{ZnSnS}_4$ , etc. using a newly developed approach<sup>19</sup> based on the density functional theory. This approach reduces the formation energy error from 0.25 eV/atom to less than 0.05 eV/atom for the compound semiconductors.<sup>19</sup> As a result, if a compound in the reactions has 4 atoms per formula unit, the errors of the calculated  $\phi^{ox}$  and  $\phi^{re}$  are reduced from 1 V to 0.2 V (assuming one electron is transferred in the reaction). Note that the entropy contribution in the formation energy is neglected for those semiconductors with no experimental data, but

for crystals this contribution is small and we estimate it causes errors less than 0.2 V in  $\phi^{ox}$  and  $\phi^{re}$ . In the supplement materials, we listed how we get the Gibbs free energy of all the solid compounds which are not available in Ref. [20,21].

In the following we will discuss the trends in 3 and their influence on the design of photocatalytic system.

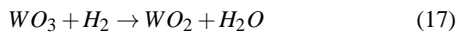
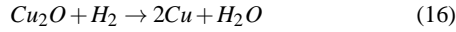
(i) For the oxidation potential, most metal oxides have  $\phi^{ox}$  lower than  $\phi(\text{O}_2/\text{H}_2\text{O})$  at pH=0, indicating they are resistant to the hole oxidation and stable in the solution, but four exceptions are also found,  $\text{Cu}_2\text{O}$ ,  $\text{ZnO}$ ,  $\text{PbO}$  and  $\text{FeTiO}_3$ . The reasons for the easier oxidation of  $\text{Cu}_2\text{O}$ ,  $\text{PbO}$  and  $\text{FeTiO}_3$  are obvious, since the cations in these compounds are not at their highest valences and can be further oxidized to higher valences ( $\text{Cu}^+$  to  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  to  $\text{Pb}^{4+}$  and  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ ).<sup>27</sup> Comparing  $\text{Cu}_2\text{O}$  with  $\text{Cu}^+$  and  $\text{CuWO}_4$  with  $\text{Cu}^{2+}$ , we can find that  $\text{CuWO}_4$  has a much lower  $\phi^{ox}$  than  $\text{Cu}_2\text{O}$ , since both cations in  $\text{CuWO}_4$  are in the highest valence state. According to this simple trend, all the metal oxide semiconductors at a not-highest valence state of cations are likely susceptible to oxidation in water, and tend to be unstable (Note  $\text{Co}_3\text{O}_4$  is an exception, Co has higher valence in  $\text{Co}_2\text{O}_3$ , but  $\text{Co}_2\text{O}_3$  is not as stable as  $\text{Co}_3\text{O}_4$ , thus its  $\phi^{ox}$  is quite low). The easy oxidation of  $\text{ZnO}$  is also unique considering that Zn is at its highest valence state and its band gap is quite large with a very low valence band. Thus the stability of  $\text{ZnO}$  cannot be predicted according to its valence state of elements, or its valence band position. This is related more to its formation energy relative to other phases or compounds. Since  $\phi^{ox}$  of the listed oxides does not shift with pH value, when pH=7, the  $\phi^{ox}$  of  $\text{ZnO}$  and  $\text{FeTiO}_3$  fall below  $\phi(\text{O}_2/\text{H}_2\text{O})$ , indicating that these compounds are stable under illumination in the neutral or alkaline solution, which is consistent with the observation of  $\text{ZnO}$  in solution: no photocorrosion at pH=10 while complete decomposition at acid pH=4.5.<sup>28</sup>

(ii)  $\phi^{ox}$  of all non-oxide semiconductors are higher than

$\phi(\text{O}_2/\text{H}_2\text{O})$ , at least 0.5 V more at pH=0, and the alignment of  $\phi^{ox}$  relative to  $\phi(\text{O}_2/\text{H}_2\text{O})$  is not changed by pH value. This indicates these non-oxide semiconductors are thermodynamically unstable in aqueous solution and will be oxidized by the holes under illumination. The reason is also simple: the anions such as  $\text{N}^{3-}$ ,  $\text{P}^{3-}$ ,  $\text{As}^{3-}$ ,  $\text{S}^{2-}$ ,  $\text{Se}^{2-}$ ,  $\text{Te}^{2-}$  can all be oxidized to neutral or positive valence states, *e.g.*  $\text{N}^{3-}$  to  $\text{N}_2$  or  $\text{NO}_3^-$ , and  $\text{S}^{2-}$  to  $\text{S}$  or  $\text{SO}_4^{2-}$ . It is interesting to note that the oxynitride TaON, which is between the oxide and nitride and naively expected to combine the better stability of the oxides and higher valence band (hence smaller band gap) of the nitrides,<sup>9,29,30</sup> has the oxidation potential close to the nitride  $\text{Ta}_2\text{N}_5$ , therefore it does not inherit the good oxidative stability of the oxides. This further indicates that although doping or alloying the oxide semiconductors with weaker electron-negative anions can decrease the band gap, they become less stable with respect to oxidation in water.

(iii) For the reduction potential  $\phi^{re}$ , all the non-oxide semiconductors have higher  $\phi^{re}$  than  $\phi(\text{H}^+/\text{H}_2)$  at pH=0, and thus are resistant to the electron reduction under illumination, corresponding to the situation in 2(b) with  $\phi^{re}$  above  $\phi(\text{H}^+/\text{H}_2)$ . Since  $\phi^{re}$  and  $\phi(\text{H}^+/\text{H}_2)$  change at the same rate with pH value, this situation is not influenced by the pH change. Our results are consistent with the reported Pourbaix diagrams for CdS, CdSe, CdTe, GaP and GaAs,<sup>14</sup> which clearly show that their reduction and oxidation potentials are negative (higher in Fig.3) relative to  $\phi(\text{H}^+/\text{H}_2)$  and  $\phi(\text{O}_2/\text{H}_2\text{O})$  respectively at  $0 < \text{pH} < 14$ .

(iv) For  $\phi^{re}$  of the metal oxides, a few metal oxides have lower  $\phi^{re}$  than  $\phi(\text{H}^+/\text{H}_2)$  at pH=0, such as  $\text{Cu}_2\text{O}$ ,  $\text{PbO}$ ,  $\text{CuWO}_4$ ,  $\text{BiFeO}_3$ ,  $\text{BiVO}_4$ ,  $\text{WO}_3$  and  $\text{Co}_3\text{O}_4$ , caused by the ease of reactions such as,



In these compounds, the bonding between the metal cations and oxygen anions are weaker than the H-O bonding in  $\text{H}_2\text{O}$ , so the above reactions are energetically favorable. According to the experimental Pourbaix diagrams,<sup>13</sup> the  $\text{WO}_3/\text{WO}_2$  and  $\text{Cu}_2\text{O}/\text{Cu}$  reduction potentials are 0 V and 0.45 V relative to  $\phi(\text{H}^+/\text{H}_2)$  respectively, in good agreement with our calculated  $\phi^{re}$ . Although  $\text{PbO}$ ,  $\text{CuWO}_4$ ,  $\text{BiFeO}_3$  and  $\text{WO}_3$  have lower  $\phi^{re}$  than  $\phi(\text{H}^+/\text{H}_2)$ , they are still stable because their  $\phi^{re}$  is above their CBM, and thus the conduction band electrons can reduce neither the water nor the semiconductors (Note  $\phi^{re}$ , CBM and  $\phi(\text{H}^+/\text{H}_2)$  change at the same rate with pH, so the stability analysis of these metal oxides is not changed by pH). However,  $\text{Cu}_2\text{O}$ ,  $\text{BiVO}_4$  and  $\text{Co}_3\text{O}_4$ , have  $\phi^{re}$  lower than both  $\phi(\text{H}^+/\text{H}_2)$  and CBM, corresponding to the alignment in 2(b) with  $\phi^{re}$  below  $\phi(\text{H}^+/\text{H}_2)$ , thus they will be reduced in the solution under illumination. Actually the reduction of photocatalytic p-type  $\text{Co}_3\text{O}_4$  to inactive  $\text{CoO}$  had been observed experimentally.<sup>31</sup> All the other oxides listed in 3 have  $\phi^{re}$  higher than  $\phi(\text{H}^+/\text{H}_2)$ , and thus are stable against reduction.

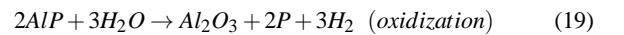
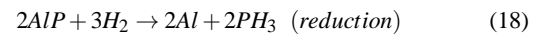
According to the above trends, one can find a series of metal oxides which are both resistant to the hole oxidation and the electron reduction and thus stable in the solution. Due to the lower CBM than  $\phi(\text{H}^+/\text{H}_2)$ , most oxides except  $\text{Cu}_2\text{O}$ ,  $\text{BiVO}_4$  and  $\text{Co}_3\text{O}_4$  can not be used as the photocathode, but can be used as the photoanode given their low VBM. Furthermore, the low VBM also makes the p-type doping difficult and most metal oxides are intrinsically n-type according to the doping-limit rule,<sup>32</sup> which states that a semiconductor is difficult to be doped p-type if its valence band is too low and is difficult to be doped n-type if its conduction band is too high. Therefore the metal oxides with low valence band should be better used as the n-type photoanodes.

For the p-type photocathode, one can easily find metal non-oxides which have higher CBM than  $\phi(\text{H}^+/\text{H}_2)$  and are also re-

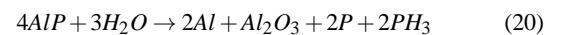
sistant to the electron reduction, thus can be used the photocathode if doped to p-type. According to the doping limit rule, the p-type doping in the non-oxides are easier than in the oxides due to the higher VBM. One may worry about the bad stability of the non-oxides with respect to the hole oxidation. However, we should note that, for the p-type photocathode, (i) the downward band bending at the semiconductor/water interface prevent the majority holes from reacting with water; (ii) the photo generated hole is expected to flow to the connected anode quickly through majority carrier conduction (at least when the device is working),<sup>33</sup> thus in this sense we can ignore whether it is oxidation resistant. As a result, some of the III-V and II-V semiconductors with suitable band gaps can be used as photocathodes, despite the fact they might be prone to oxidation from the pure thermodynamic point of view. The same can be said for n-type photoanodes where we are mostly concerned about their resistance to oxidation.

Finally, we want to mention that the results represented in Fig.3 considered only the thermodynamic resistance to the reductive and oxidative decomposition, but the real decomposition also depends on the specific kinetic processes. If the material is stable thermodynamically against the decomposition process, this material is stable regardless of the kinetic process. However, if the material is unstable thermodynamically, there might still be ways to make it stable kinetically. For example, an oxide layer, which forms as a result of oxidation, but stops itself after a certain thickness, can be a good protective layer and make the material stable kinetically. For some p-type photocathodes, such protective oxide layer can also serve as a hole blocker, which prevents the recombination of the minority electron and the majority hole, and thus can be essential to the efficiency of a photochemical cell.

Note, through out our study, we have not considered the possibility of the semiconductor compound to be dissolved in the solvent in dark condition. That can correspond to a reaction where the valences of cations and anions in the compound are not changed, but their total Gibbs energy is smaller in the solvation form than as in a solid crystal structure. For example, this can happen to GaAs within some pH range.<sup>14</sup> However, we do find some interesting cases for some compounds where reactions in the dark will occur. Comparing the oxidation potential  $\phi^{ox}$  and reduction potential  $\phi^{re}$  in 3, most compounds have  $\phi^{ox}$  lower than  $\phi^{re}$ , which is easy to understand since the oxidation means the electrons are taken away from the low valence band while the reduction means the electrons are added to the high conduction band. However, several exceptions exist, *i.e.*  $\text{Cu}_2\text{O}$ , AIP, GaP, AlAs, Si and SiC have  $\phi^{re}$  lower than  $\phi^{ox}$ . As a result, the electron-hole pair needed for the reduction and oxidation reactions can be generated spontaneously (they cost negative energy), without the help of any photon. This will cause these materials to decompose even in the dark. For example, the following two reactions are used to calculate the  $\phi^{re}$  and  $\phi^{ox}$  of AIP respectively,



giving that  $\phi^{re}$  is lower than  $\phi^{ox}$ , which makes the two reactions spontaneous, corresponding to a sum reaction,



The calculated Gibbs free energy change of this reaction is negative, indicating the reaction is exothermal, and thus AIP will be decomposed in water even without any illumination. But once again, a kinetic barrier (*e.g.*, an oxide layer) can block the otherwise thermodynamically plausible reaction.

In conclusion, we studied the thermodynamic oxidation and reduction potentials for a series of photocatalytic semiconductors,

and plotted their alignment relative to the valence and conduction band edges as well as the water redox potentials. According to these potentials, we found only metal oxides can be thermodynamically stable when used as the n-type photoanodes, and all the non-oxides are unstable due to easy oxidation by photo generated holes. This indicates although the oxides doped or alloyed by less electronegative anions can have smaller band gaps, their stability is also degraded. On the other hand, many non-oxides are resistant to the electron reduction, and thus may be used as p-type photocathode provided the hole oxidation is prevented in the working devices. The method we used is universal and can be applied to evaluate the stability of any semiconductors. We believe the presented stability diagram (3) will be useful in guiding the search for stable photocathode and photoanode materials.

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