CHAPTER 9

Semiconductors for water splitting: Material design principles

Sustainable energy through catalysis

The field of catalysis has important roles to play in many energy- conversion processes like decomposition of water to generate hydrogen fuel, conversion of carbon dioxide to useful fuels and in the conversion of molecules into value added products. In this, the selection of suitable and efficient materials has been one of the important tasks. Traditionally this exercise has been based on trial and error method of trying some materials and generating experimental data. These data have been subsequently used to formulate empirical rules for selection of materials for a particular application. For example, in the photo decomposition of water to generate hydrogen, one of the postulates is that the cation of the semiconductor should have d^0, d^5, and d^{10} configurations. Based on such empirical rules, new formulations are proposed and tested but the success seems to be limited in these cases. These exercises have been manly to guide experimental efforts for screening candidate materials and also to build or promote the chosen material.

However, all materials proposed in this process are based on empirical basis. They have some experimental evidences as basis but their predictive capacity is not beyond doubt. When using them to make predictions, one can only say something new in regimes where the proposed model is not explicitly fitted to experimental observations. In these cases, the confidence level of the predictions is questionable. To use such empirical models as predictive tool one has to exercise caution and care.

In order to overcome this problem, most often theoretical methods are preferred but the time and accuracy of the methods are trade off. One such example is shown in the figure 1 for some quantum chemical methods that are commonly employed in these days.

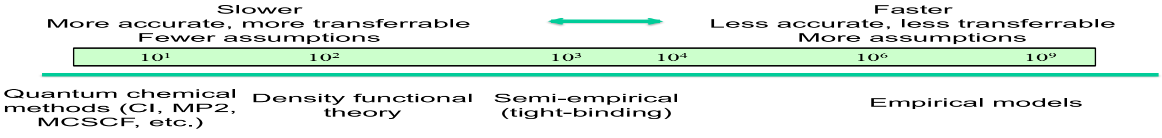


Figure 1 the relationship between time and accuracy of the empical, semiempiral and quantum chemical methods

It is seen from figure 1 that more accurate results require fewer assumptions and also most often the results are transferable.

Now turning our attention to selection of material for photo-electrochemical decomposition of water, the material of choice should have some characteristics. These include that the material chosen should be stable under the experimental conditions employed, the band gap of the semiconductor material suitable for water decomposition, the band positions should be such that hydrogen and oxygen evolution reactions take place spontaneously and the charge carrier should have suitable mobility to reach and react at the interface instead of undergoing recombination. In addition to all these, the sites on the semiconductor surface should favour hydrogen and oxygen evolution reactions efficiently. In figure 2 the band positions of oxide semiconductors and the hydrogen and oxygen evolution potentials are shown and one can deduct from this figure which semiconductor is capable of evolving hydrogen and oxygen by the decomposition of water. A similar scheme is shown for sulphide semiconductors in Figure 3.

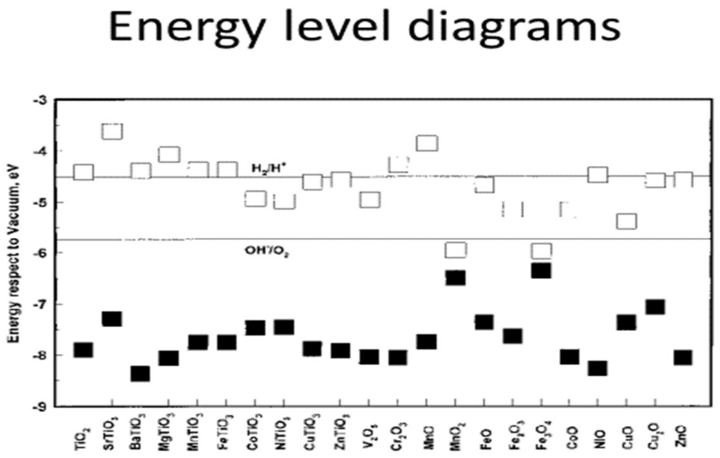


Figure 2 the position of the conduction band (open squares) and the position of the valence band (filled squares) for oxide semiconductors are shown> The hydrogen and oxygen evolution potentials are also shown.

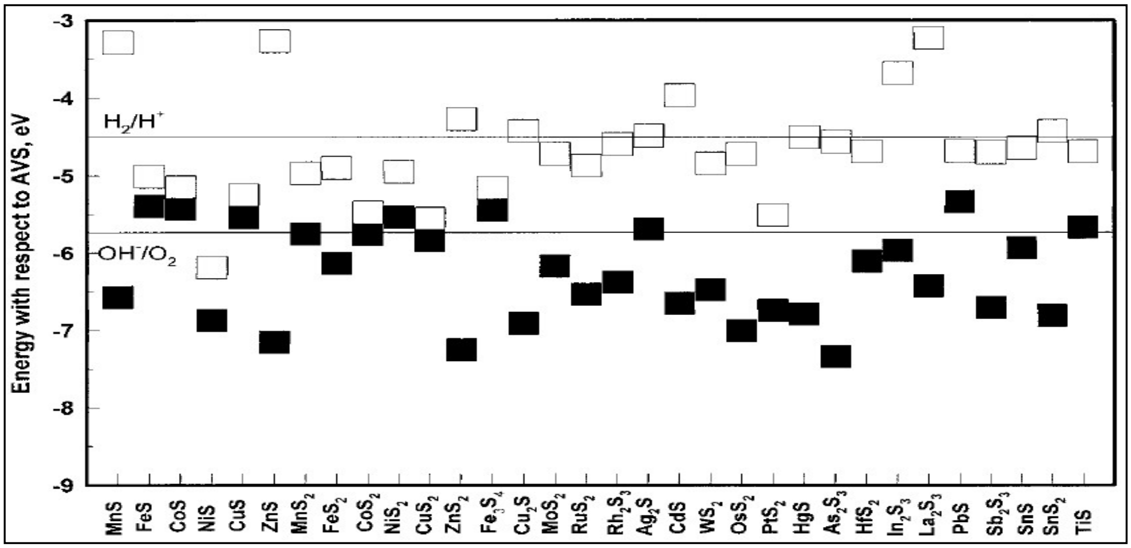


Figure 3. The position of the conduction band (open squares) and the position of the valence band (filled squares) for sulphide semiconductors are shown. The hydrogen and oxygen evolution potentials are also shown.

The positions of the conduction band minimum and valence band maximum can be deduced in a number of ways. These methods are based on the electronegativity values of the species concerned. The Mulliken electronegativity scale which is the average of the electron affinity and ionization energy has been used in these calculations. The Butler Ginley scheme makes use of the following two equations namely

$$E_{VB} = -X_{GM} – E_g/2$$

$$E_{CB} = X_{Gm} + Eg/2$$

Where X_{GM} is the geometric mean of the electronegativity values and E_g is the band gap value.

Let us illustrate these calculations with a typical example of TiO_2, ZnO and $SrTiO_3$.

The electronegativity values of Ti, O, Zn and Sr are 3.45, 7.43, 4.45 and 2.0 respectively. The band gaps of TiO_2, ZnO and $SrTiO_3$ are 3.2, 3.2 and 3.4 respectively. If one were to use these values one gets for the conduction band minimum and valence band maximum for these three semiconductors as follows

- TiO_2 : VB -7.4 eV; CB -4.2 eV
- ZnO: VB -7.38; CB -4.18

$SrTiO_3$ is left out as an exercise.

Similarly, one can calculate for sulphide semiconductors and a compilation is given Table 9.1.

An alternate method of calculating the band edge positions is available in the following reference Gritsenko *et al.*, *Phys. Rev. A* **51**, 1944 (1995).

Table.9. 1 Data of Band edges and band gaps of common sulphide semiconductors

Material	Electronegativity	Band gap (eV)	Conduction band	Valence band
Ag_2S	4.96	0.92	-4.50	-5.42
As_2S_3	5.83	2.50	-4.58	-7.08
CdS	5.18	2.40	-3.98	-6.38
$CuFeS_2$	5.15	0.35	-4.87	-5.32
FeS	5.02	0.10	-4.97	-5.07
FeS_2	5.39	0.95	-4.92	-5.87
In_2S_3	4.70	2.00	-3.70	5.70
MnS	4.81	3.00	-3.31	-6.31
MnS_2	5.24	0.50	-4.99	-5.49
MoS_2	5.32	1.17	-4.73	-5.90
NiS	5.23	0.40	-5.03	-5.43
NiS_2	5.54	0.30	-5.39	-5.69
PbS	4.92	0.37	-4.74	-5.11
$PbCuSbS_3$	5.22	1.23	-4.61	-6.11
PtS_2	6.00	0.95	-5.53	-6.48
Rh_2S_3	5.36	1.50	-4.61	-6.11
RuS_2	5.58	1.38	-4.89	-6.27
Sb_2S_3	5.63	1.72	-4.72	-6.44
SnS	5.17	1.01	-4.66	-5.67
SnS_2	5.49	2.10	-4.44	6.54
TiS_2	5.11	0.70	-4.76	-5.46
WS_2	5.54	1.35	-4.86	-6.21
ZnS	5.25	3.60	-3.46	-7.06
ZnS_2	5.56	2.70	-4.21	-6.91
$Zn_3In_2S_6$	5.00	2.81	-3.59	-6.40
ZrS_2	5.20	1.82	-4.29	6.11

The values are calculated using the two following equations:

E_{CB} = -A = -X+0.5 E_g

E_{VB} = -I = -X+ 0.5E_g

X is the electronegativity, E_g is the value of the band gap, A is the electron affinity and I is the ionization potential

It is necessary to compare these computed band gap values with the experimental values and one such test is shown in Figure 3

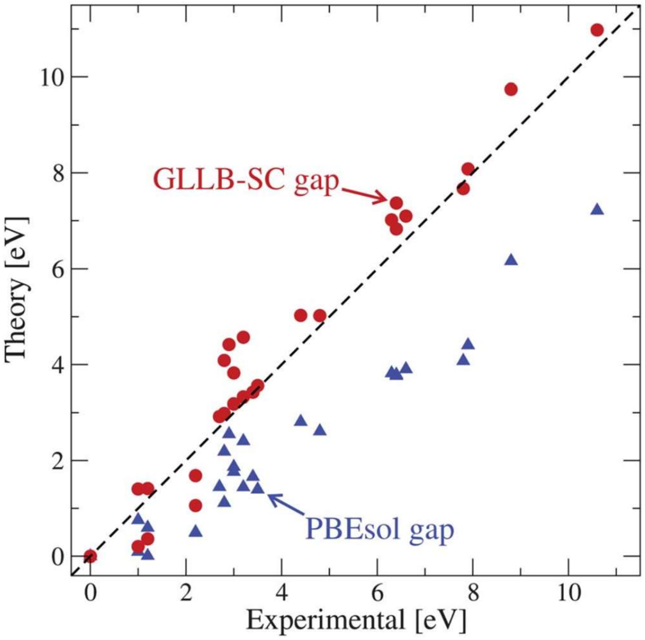
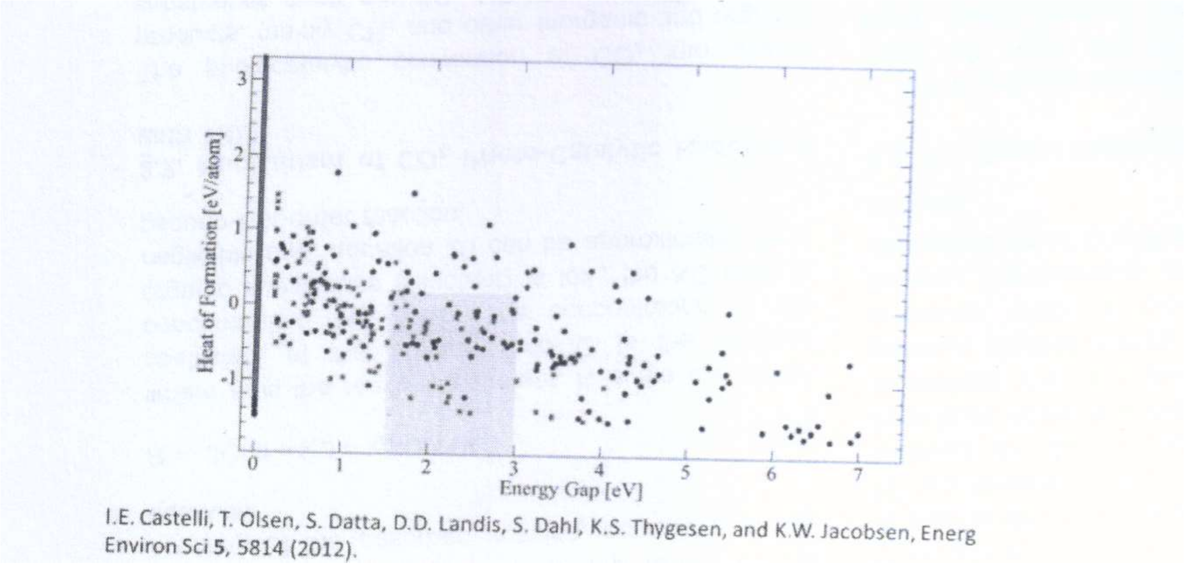


Fig. 3 DFT calculated bandgaps of selected oxides. Comparison between the theoretical and experimental bandgap of non-magnetic metal oxides in their most stable structure. The gaps are calculated using both the standard PBEsol (blue triangles) and the GLLB-SC functional (red circles). The dashed line represents the perfect matching between experiments and theory. (Details of the calculations with a list of the calculated oxides can be found in Table 1 of the ESI†). Plot of computed band gap values against the experimental values.[Reproduced from Ivano E. Castelli, Thomas Olsen, Soumendu Datta, David D. Landis, Søren Dahl, Kristian S. Thygesen and Karsten W. Jacobsen, Energy Environment Sci., 5,5814 (2012).]

One can assume the agreement is good enough and the values of band gap estimated by using these two equations can be good estimates for all practical purposes.

The next issue to be considered is the stability of the semiconductors in relation to the band gap values.



I.E. Castelli, T. Olsen, S. Datta, D.D. Landis, S. Dahl, K.S. Thygesen, and K.W. Jacobsen, Energ Environ Sci 5, 5814 (2012).

Fig. 3 Correlation between the heat of formation per atom and the bandgap for the oxide (black circles) and oxynitride (red squares) compounds. The region for candidates for solar light harvesting corresponds to the orange area. [reproduced from I.E.Castelli et al., Energy Environment Sci., 5,5814 (2012)].

The possible candidates for this reaction are shown in Fig.4.

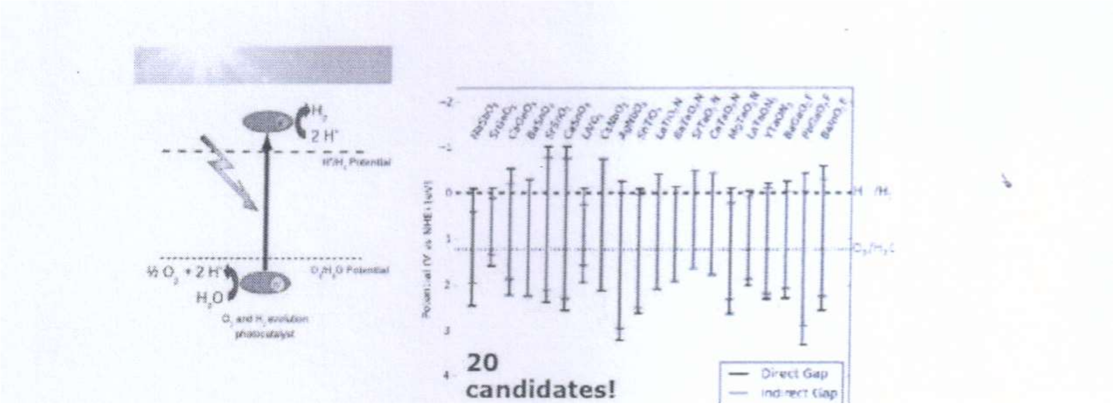


Fig. 4 The identified oxides and oxynitrides in the cubic perovskite structure with potential for splitting water in visible light. The figure shows the calculated band edges for both the direct (red) and indirect (black) gaps. The levels for hydrogen and oxygen evolution are also indicated. Among these the known and successful materials are $AbNbO_3$, $LaTiO_2N$, $BaTaO_2N$, $SrTaO_2N$, $CaTaO_2N$ and $LaTaON_2$.

The essential steps involved in electrolytic water splitting reaction is listed below

$H_2O(l0 + * \rightarrow OH* + H^+ + e$

$OH* \rightarrow O* + H^+{}_+ e$

$O* + H\ {}_2O(l) \rightarrow OOH* + H^+ + e$

$OOH* \rightarrow * + O_2 (g) + H^+ + e$

$*+ 2H^+{}_+ 2e \rightarrow H* + H^+ + e$

$H* + H^+ + e \rightarrow * + H_2(g)$

It is essential that one takes into account the elementary steps indicated for selecting suitable semiconductor for water decomposition by photoelectrolysis or photocatalytically.