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## CHAPTER 12

# Hydrogen from photo-electrocatalytic water splitting

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### 12.1 Introduction

The development of an enduring, long-term sustainable energy economy is one of the critical challenges that we face today [1]. Although we have enough oil, coal, and gas reserves to meet the energy demand for the future generations as well, the increased consumption due to the population growth and the consequent increase in carbon dioxide emission, could lead to environmental issues of catastrophic dimensions. In this scenario, the development of an environmentally sound, cost-effective alternative technology, with zero carbon footprint, to meet the Terawatt Challenge, is vital [2, 3]. Hydrogen is regarded as the clean, efficient, and viable alternative source of energy, provided it

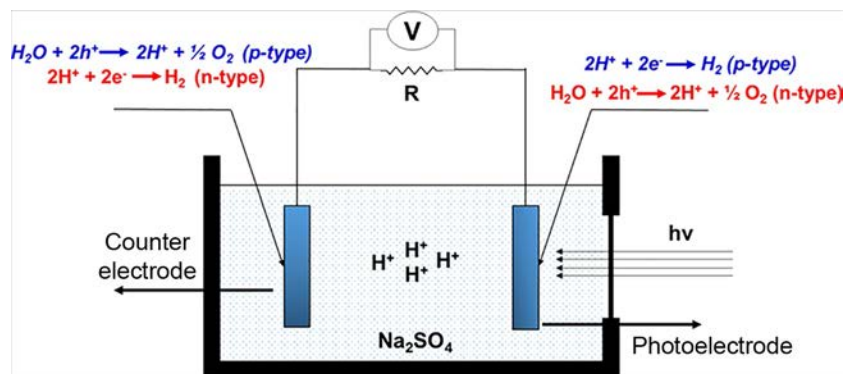
is sourced via sustainable processes. In this respect, photoelectrochemical (PEC) production of hydrogen by splitting of water is a promising technology that could offer clean and cost-effective means of utilizing 36,000 TW of solar power that is available for us to exploit [4]. Conversion of 1% of the available solar energy, using PEC cell with 10% efficiency, could produce 36 TW power, the predicted global energy consumption in the year 2050 [5].

Artificial photosynthesis enables to store the solar energy in energy-rich chemical bonds and offers an opportunity to harness the sunlight when needed so that one would get access to sunlight even at dinner time [6]. The high mass-to-energy density of hydrogen makes it as advantageous over other solar fuels. Also, hydrogen can be directly used in a fuel cell to convert back the solar energy stored in chemical bonds to electricity. However, the construction and effective utilization of a PEC cell with stable and high solar-to-hydrogen efficiency is a challenging proposition and remains a holy grail [7].

In principle, PEC water splitting integrates three fundamental steps in a solar energy conversion process; energy capture, conversion, and storage together in a single system. A PEC device is utilizing the photovoltaic effect of the semiconductor/electrolyte interface. Three fundamental processes, namely, photophysical, photochemical, and electrochemical processes, are responsible for the photovoltaic effects in a PEC system. The photophysical process involves the generation and separation of charge carriers, and the reactions of excited state molecules represent the photochemical reaction. The electrochemical process consists of the transfer of charges to a suitable redox moiety across the electrode-electrolyte interface in the presence of an electric field [8].

In a conventional PEC system (Fig. 12.1), photoelectrode immersed in an aqueous electrolyte absorbs the solar energy, produces photogenerated charge carriers, which are directed toward the interfaces to help in the evolution of hydrogen or oxygen depending on the nature of semiconductor employed. The other photoproduct will evolve at the counter electrode composed of a metal or an illuminated semiconductor [9].

The idea of PEC cells to produce hydrogen seems to be simple, but in reality, it is not. Several critical criteria should be met simultaneously to split the water into its constituents. The semiconductor system must be stable, durable, low cost, and capable of absorbing the sunlight to generate appropriate photovoltage and must have the ability to transfer the charge carriers toward the interfaces in a facile manner, to reduce the kinetic overpotential losses. Moreover, the band potentials should straddle beyond the redox potentials corresponding to oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). The photoelectrode must be stable, when in contact with the electrolyte, under electrochemical reaction conditions for several years. The total efficiency of the system depends on the absorption power of photoelectrode and kinetics of interface reactions, but materials that enhance the kinetics of the reactions (especially the kinetics of OER) are more expensive and less abundant [10]. To date, the highest reported water splitting system having at least one semiconductor-electrolyte junction is 12.4% [11, 12],



**Fig. 12.1** A schematic diagram of a photoelectrochemical cell. Usage of the n-type semiconductor as a photoelectrode evolves oxygen at the photoelectrode and hydrogen at the counter electrode (marked in red—gray in print version), and in the p-type semiconductor, hydrogen evolves at the photoelectrode and oxygen at the counter electrode (marked in blue—dark gray in print version). In n-type semiconductor photoelectrode, the ohmic contact drives the electrons to the counter electrode through an external electrical connection. In p-type systems, the hole drives to the counter electrode via the Schottky barrier formed at the semiconductor/electrode junction. (Modified with permission from B. Viswanathan, *Hydrogen as an energy carrier*, in: *Fundamentals of Chemical Conversion Processes and Applications*, Elsevier, Amsterdam, 2017, p. 170. ©2017 Elsevier B.V.)

and theoretical investigations show that maximum achievable efficiency of a tandem PEC device is 23%–32% [13–17]. Moreover, the highest achieved efficiency of a PEC cell composed of earth-abundant material is 10% [18, 19]. All these efficiencies reported in the literature are in the time scale of some days. The system should reach an efficiency of at least 15%, with an extended lifetime of the photoelectrode running into several years, to transform PEC technology into a reality. It is a challenging task to achieve the theoretical efficiency scale by satisfying all the necessary criteria in a single device. Besides, the materials used for PEC applications must be cheap, safe, robust, and efficient. Unfortunately, to date, the researchers have only succeeded to make devices with no more than three out of four critical characteristics [20] required for gainful application of PEC technology for the splitting of water.

To construct a highly efficient PEC cell, one needs to design a suitable material that satisfies all the necessary criteria mentioned. Currently, the choice of the materials is based on the intrinsic semiconductor properties (a semiconductor in the dark/vacuum) without considering the interfacial band energetics that would play a crucial role. There is a famous statement from G.N Lewis written in his fabulous book that “it is not the coal but the combustion of coal, which causes a steam engine to operate” [21]. The statement can be reframed here and say that “it is not the semiconductor but the semiconductor in the excited state causes a PEC cell to operate”! Hence, the interfacial characteristics under illumination conditions are to be taken into account, for designing appropriate material

for water splitting. In this chapter, we are mainly concentrating on the aspects of materials' design and its consequences as well as the interfacial band energetics in a PEC cell. The readers are recommended to go through various excellent state-of-the-art literature, compiled in [Table 12.1](#) in the following section, for further in-depth information on various aspects of the PEC cell.

**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90

Serial No.	Title of the article	Comments	Year	Reference
1	Electrochemical photolysis of water at a semiconductor electrode	A benchmark study in the area of photon-assisted electrolysis of water	1972	[22]
2	Photocatalytic hydrogen production: a solar energy conversion alternative?	Three methods of photolysis of water described and assessed.	1974	[23]
3	Photovoltaic effect on the surface of rutile single crystal	The barrier height that corresponds to the positive electrode increases linearly with applied voltage	1974	[24]
4	Solid electrolytes and photo-electrolysis	Semi-annual technical report summary from Lincoln Laboratory, MIT	1974	[25]
5	The use of hydrogen as an energy carrier	Book chapter	1974	[26]
6	Photo-electrolysis of water in cells with TiO <sub>2</sub> anodes	First hypothetical report on the simultaneous use of semiconductor as photoanode (n) and photocathode (p)	1975	[27]
7	Photo-assisted electrolysis of water by irradiation of a titanium dioxide electrode	The wavelength response (351 and 364 nm) of the TiO <sub>2</sub> and the correlation of product yield and current are reported.	1975	[28]
8	Electrochemical photo and solar cells: Principles and some experiments	Gerischer's work. The description of the theory of PEC	1975	[29]
9	Future hydrogen production methods		1975	[30]
10	Effects of electronic excitation on reaction rates at the solid-electrolyte interface	An in-depth description of the mechanistic aspects of PEC	1975	[31]

**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
11	Application of sintered bodies of TiO <sub>2</sub> doped with Nb <sub>2</sub> O <sub>5</sub> to anodic photooxidation of water	The initial report on the aspect doping	1975	[32]
12	Electricity from photosensitisation of titanium		1975	[33]
13	Formation of hydrogen gas with an electrochemical photo-cell	A continuation study of 1972 article [22]	1975	[34]
14	Photoelectrochemical behaviour of semiconductor electrodes coated with thin metal films	The first use of thin metal-coated semiconductor photoelectrode	1975	[35]
15	Hydrogen energy	Proceedings of the hydrogen economy Miami energy conference	1975	[36]
16	Electrochemical aspects of solar energy conversion		1975	[37]
17	Photo-effects at polycrystalline tin oxide electrodes	Proposed a superficial hydrogen bonding interaction between water and SnO <sub>2</sub> molecule.	1975	[38]
18	The quantum yield of photolysis of water on TiO <sub>2</sub> electrodes	One of the early report on the quantum yield of a PEC cell	1975	[39]
19	Aspects of electrochemistry, chemistry, physics, and applications of “less-common metals.”		1975	[40]
20	Photo-electrolysis of water using semiconducting TiO <sub>2</sub> crystals	Proved for the first time the additional requirement of 0.3 V external bias for the water splitting	1975	[41]
21	On hydrogen and energy systems		1976	[42]
22	Photo-assisted electrolysis of water by ultraviolet irradiation of an antimony-doped stannic oxide electrode	One of the early report on the metal-doped photoelectrode	1976	[43]

*Continued*

**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
23	Photo-effects on semiconductor ceramics electrodes	Initial report on BaTiO <sub>3</sub> , SrTiO <sub>3-x</sub> photoelectrode	1976	[44]
24	Photoelectrochemical energy conversion and storage using polycrystalline chalcogenide electrodes	Primary report on the chalcogenide photoelectrode	1976	[45]
25	Visible light to electrical energy conversion stable cadmium sulfide and cadmium selenide photoelectrodes in aqueous electrolytes	One of the early studies on the stabilization of photoelectrodes	1976	[46]
26	A new photovoltaic effect observed on metal-coated semiconductor electrodes and its utilization for the photolysis of water	First report on the surface passivation and catalytic action of metal layers	1976	[47]
27	Photoelectrochemical processes: The prevention of competitive anodic dissolution of the photon absorber in hydrogen production	Studies of J. O'M Bockris	1976	[48]
28	Photo-electrolysis of water: Si in salt water		1976	[49]
29	Semiconducting potassium tantalate electrodes. Photoassistance agents for the efficient electrolysis of water	Perovskite oxide as photoelectrode KTaO <sub>3</sub> , KTa <sub>0.77</sub> Nb <sub>0.23</sub> O <sub>3</sub>	1976	[50]
30	Photoelectrochemical reactions at SrTiO <sub>3</sub> single crystal electrode	Perovskite oxide as photoelectrode	1976	[51]
31	Photoassisted electrolysis of water using a BaTiO <sub>3</sub> electrode		1976	[52]
32	Photo-assisted electrolysis of water using single crystal alpha-Fe <sub>2</sub> O <sub>3</sub> anodes	Comparison between TiO <sub>2</sub> , WO <sub>3</sub> , SrTiO <sub>3</sub> , and BaTiO <sub>3</sub>	1976	[53]
33	Photo-electrolysis using chlorophyll electrodes	The first use of dye sensitized photoelectrode	1976	[54]

**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
34	Dye sensitised zinc oxide: aqueous electrolyte: platinum photocell	Early report on dye sensitized PEC cell	1976	[55]
35	Photocell using covalently-bound dyes on semiconductor surfaces	Early report on dye sensitized PEC cell	1976	[56]
36	The development of photo-electrochemical cells from systems with photocatalytic reactions		1976	[57]
37	Tungsten trioxide as a photo-anode for a photoelectrochemical cell (PEC)	One of the independent study on the $WO_3$ photoelectrode	1976	[58]
38	Improved solar energy conversion efficiency for the photocatalytic production of hydrogen via $TiO_2$ semiconductor electrodes		1976	[59]
39	Electrochemical properties of the semiconducting $TiO_2$ (Rutile) single crystal electrode		1976	[60]
40	Conversion of laser energy to chemical energy by the photoassisted electrolysis of water		1976	[61]
41	In vitro photosynthesis	Review of the direct devices for the solar energy utilization	1976	[62]
42	Tungsten trioxide as an electrode for photo-electrolysis of water		1976	[63]
43	p-n photo-electrolysis cells	First experimental report on the p-n junction photoelectrode	1976	[64]
44	Electrochemical reactions involving holes at the illuminated $TiO_2$ (rutile) single crystal electrode	Comparison of rate of oxidation of inorganic and organic moieties with that of the water	1976	[65]

*Continued*



**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
45	Hydrogen energy technology-Update 1976		1976	[66]
46	Electrochemical, solid state, photochemical and technological aspects of photoelectrochemical energy converters	Review article	1976	[67]
47	Photo-electrolysis of water with TiO <sub>2</sub> covered solar cell electrodes	Use of solar cell for water splitting	1976	[68]
48	Intensity effects in the electrochemical photolysis of water at the TiO <sub>2</sub> electrode		1976	[69]
49	Aging effects in single crystal reduced rutile anodes		1976	[70]
50	Decomposition of water exposed to UV light in the presence of platinised titanium dioxide	Metal deposited photoelectrodes	1976	[71]
51	Photo-electrolysis of water in cells with SrTiO <sub>3</sub> anodes	Perovskite oxide photoelectrode	1976	[72]
52	Correlation of photosensitive electrode properties with electronegativity	The first article correlating the ability of photoelectrode to split water to the electronegativity of the constituent atoms	1977	[73]
53	Photo-electrolysis of water in sunlight with sensitized semiconductor electrodes	Cr- and Al-doped TiO <sub>2</sub> photoelectrodes	1977	[74]
54	A model for the current-voltage curve of photoexcited semiconductor electrodes	A mathematical model describing the behavior of photoelectrode in PEC system	1977	[75]
55	Photo-electrolysis of water by solar radiation	First US Patent on the design of a PEC cell by Arthur Nozik from Allied Chemical Corporation	1977	[76]
56	Prospects for hydrogen production by water electrolysis to be competitive with conventional methods	Perspective on photoelectrochemical effects described	1977	[77]

**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
57	State of development in the area of water electrolysis	Proceedings Miami international conference on alternative energy sources	1977	[78]
58	Hydrogen photo production from water	Water splitting using hydroquinone–quinone redox system	1977	[79]
59	Semiconducting oxide anodes in photoassisted electrolysis of water	Comparative study of 11 photoelectrodes including Fe <sub>2</sub> O <sub>3</sub> and other perovskite oxides	1977	[80]
60	The role of metal overlayers on gallium phosphide photoelectrodes	Photoprotection of GaP with a gold overlayer	1977	[81]
61	Photo–electrolysis semi–conducting of water by irradiation metal oxides of platinized n–type	Platinized photoelectrode and their ability to split water explained concerning the semiconductor–electrolyte interface	1977	[82]
62	Photochemical diodes	Photoelectrodes sandwiched together using an ohmic contact	1977	[83]
63	Photo–electrolysis of water with semiconductor materials	TiO <sub>2</sub> , SnO <sub>2</sub> , Nb <sub>2</sub> O <sub>3</sub> , Si <sub>3</sub> N <sub>4</sub> , Al <sub>2</sub> O <sub>3</sub> , GaAs, GaAlAs	1977	[84]
64	On the stability of semiconductor electrodes against photodecomposition	A classic article on photo–corrosion aspects by Gerischer	1977	[85]
65	Nonbiological photochemical energy conversion—can it compete?	Review	1977	[86]
66	Electrode materials for photoelectrochemical devices	Review	1977	[87]
67	Photoelectrochemical production of hydrogen	State-of-the-art review from Bockris	1977	[88]
68	Stable photoelectrochemical cells for the splitting of water	p–n photoelectrodes	1977	[89]
69	The photo–electrolysis of water using iron titanate anodes	FeTiO <sub>3</sub> , Fe <sub>2</sub> TiO <sub>4</sub> , Fe <sub>2</sub> TiO <sub>5</sub>	1977	[90]

*Continued*

**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
70	Water photolysis apparatus	US Patent	1977	[91]
71	Suppression of surface dissolution of CdS photoanode by reducing agents	Article from Fujishima group	1977	[92]
72	Semiconductor/electrolyte photoelectric energy conversion: the use of a molybdenum oxide coating to avoid corrosion	n-type GaAs coated with thin layer MoO <sub>2</sub>	1977	[93]
73	Hydrogen and electricity from water and light	Comparative study of various p-/n-photoelectrodes	1977	[94]
74	Photocell using covalently-bound dyes on semiconductor surfaces	A sequel article of [56]	1977	[95]
75	Irreversibilities in the mechanism of photo-electrolysis	Deals with the irreversible aspects of charge transfer across the interface	1978	[96]
76	Doped polycrystalline TiO <sub>2</sub> electrodes for the photo-assisted electrolysis of water	M/TiO <sub>2</sub> photoelectrode (M = Al, V, Cu, Ta, Y, Nb, Mo, Ni, Pd)	1978	[97]
77	Trends in Electrochemistry	Based on a theme "electrochemistry for future society."	1978	[98]
78	Sun: Mankind's Future Source	Proceedings of the International Solar Energy Society Congress	1978	[99]
79	Energy conversion in photoelectrochemical systems—a review	Review	1978	[100]
80	Semiconductors for photo-electrolysis	Review	1978	[101]
81	Light energy conversion with chlorophyll monolayer electrodes. In vitro electrochemical simulation of photosynthetic primary processes	SnO <sub>2</sub> modified with chlorophyll (Chl) a and b monolayers	1978	[102]
82	Electrolytic decomposition and photodecomposition of compound semiconductors in contact with electrolytes	Classic write-up from Gerischer on the photodecomposition of photoelectrodes	1978	[103]

**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
83	Prediction of flatband potentials at semiconductor-electrolyte interfaces from atomic electronegativities	Arrived at a quantitative relation between electron affinity of the photoelectrode and flat band potential	1978	[104]
84	Solar Fuels	A brief on the solar energy conversion process	1978	[105]
85	Photo-electrolysis of water with semiconductors	An exhaustive review of photoelectrode materials, preparation and its stability	1979	[106]
86	Solar photo-electrolysis with semiconductor electrodes	Book chapter from Gerischer deals with the photochemistry, photophysics and photo-electrochemistry	1979	[107]
87	Thermodynamic stabilities of semiconductor electrodes	Pourbiax diagram of CdS, CdTe, CdSe, and GaP, used to predict the thermodynamic stability	1979	[108]
89	Competitive photoelectrochemical oxidation of reducing agents at the TiO <sub>2</sub> photoanode		1979	[109]
90	Photo-electrochemistry and heterogeneous photocatalysis at semiconductors	Review	1979	[110]
91	Photoelectrochemical conversion of optical energy to electricity and fuels	A brief account	1979	[111]
92	Conversion and storage of light energy. Evolution of hydrogen in neutral aqueous solution by a catalytic electrode process	Reduction of water using zinc-tetraphenyl porphine as a photoelectrode	1979	[112]
93	Surfaces for photoelectrochemical cells	Review on the surface barriers in semiconductors and electrolyte energy levels	1979	[113]
94	Photolysis of water using rhodate semiconductive electrodes	US patent	1979	[114]
95	Photolysis of water on illuminated strontium titanium trioxide		1979	[115]

*Continued*

**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
96	Hydrogen production by photo-electrolytic decomposition of H <sub>2</sub> O using solar energy	Report submitted to Jet Propulsion Laboratory, California Institute of Technology	1979	[116]
97	Materials for solar energy conversion	Book chapter	1979	[117]
98	Photo-electrolysis of aqueous solutions to hydrogen—an approach to solar energy storage	Review	1979	[118]
99	Photochemical aspects of solar energy conversion and storage	Book chapter	1979	[119]
100	Solar energy: Chemical Conversion and Storage	Up to date book on the solar energy conversion	1979	[120]
101	Electrochemically codeposited large-area photoelectrodes for converting sunlight to electrical energy	A brief book chapter on the photoelectrode fabrication	1979	[121]
102	Charge transfer by surface states in the photo-electrolysis of water using a semiconductor electrode		1979	[122]
103	Temperature effects in photoelectrochemical cells		1979	[123]
104	Possibilities of solar energy utilization	Review	1979	[124]
105	Solar Energy Conversion: An Introductory Course	Book	1979	[125]
106	Electrochemical solar cells: Principles and recent results	Review	1980	[126]
107	Determination of intrinsic quantum efficiencies of photoelectrochemical reactions on semiconductor electrodes by temperature measurement		1980	[127]
108	Solar energy conversion by photoelectrochemical processes	Memming's review	1980	[128]
109	The applicability of semiconducting layered materials for electrochemical solar energy conversion	Gerischer's review	1980	[129]

**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
110	Heterogeneous electrochemical systems for solar energy conversion	Gerischer's review	1980	[130]
111	Energy storage: A vital element in mankind's quest for survival and progress	Transactions of the First International Assembly held at Dubrovnik, Yugoslavia, May 27–June 1, 1979	1980	[131]
112	Oxide semiconductors in photoelectrochemical conversion of solar energy	Scaife's Review	1980	[132]
113	Principles of photoelectrochemical solar energy conversion	Review	1980	[133]
114	A theoretical treatment of charge transfer via surface states at a semiconductor-electrolyte interface: Analysis of the water photo-electrolysis process		1980	[134]
115	Photoelectrochemical and solid-state properties of LuRhO <sub>3</sub>		1980	[135]
116	Simultaneous determination of quantum efficiency and energy efficiency of semiconductor photoelectrochemical cells by photothermal spectroscopy	Sequel study of [127]	1980	[136]
117	Charge Transfer at Illuminated Semiconductor-Electrolyte Interfaces	Book chapter	1980	[137]
118	Photoelectrochemical cell for solar energy conversion using electro co-deposited CdSe films		1980	[138]
119	Electrolytic Production of Hydrogen	Book chapter	1981	[139]
120	Efficient solar to chemical conversion: 12% efficient photo-assisted electrolysis in the [p-type InP(Ru)]/HCl-KCl/Pt(Rh) cell	Photodecomposition of hydrochloric acid and production of hydrogen out of that.	1981	[140]

*Continued*

**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
121	Mechanistic studies on semiconductor electrodes	Thesis	1981	[141]
122	Ceramic electrodes for photo-electrolytic decomposition of water	Review	1981	[142]
123	Photocurrent conversion efficiency in a Schottky barrier		1981	[143]
124	The principles of photoelectrochemical energy conversion	Gerischer's book chapter	1981	[144]
125	Artificial photosynthesis: water cleavage into hydrogen and oxygen by visible light	Account	1981	[145]
126	Conversion of sunlight into electrical power and photoassisted electrolysis of water in photoelectrochemical cells	Account	1981	[146]
127	Interface energetics for n-type semiconducting strontium titanate and titanium dioxide contacting liquid electrolyte solutions and competitive photoanodic decomposition in non-aqueous solutions	Excellent article on the photo-corrosion aspects of $\text{TiO}_2$ and $\text{SrTiO}_3$	1982	[147]
128	Photo-assisted electrolysis of water by Si photoelectrodes	Si/ $\text{SnO}_2$	1982	[148]
129	Comparative measurements of photocurrent quantum efficiency: fluorometric, thermometric and actinometric methods applied to a fluorescent polycrystalline ZnO electrodes	$\text{Cu}^{2+}/\text{ZnO}$	1982	[149]
130	Photoelectrochemical kinetics and related devices	Book chapter by Bockris	1982	[150]
131	The electrochemical and n-photoelectrochemical characteristics of n-type sodium niobate		1982	[151]

**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
132	Interfacial oxide layer mechanisms in the generation of electricity and hydrogen by solar photoelectrochemical cells	The excellent article dealing with the interfacial oxide layer mechanisms	1982	[152]
133	Design of semiconductor photoelectrochemical systems for solar energy conversion	Featured article from A J Bard	1982	[153]
134	Studies on ferric oxide electrodes for the photo-assisted electrolysis of water	Ferric oxide and doped ferric oxide photoelectrodes	1982	[154]
135	Device for the photoelectrochemical generation of hydrogen at p-type semiconductor electrodes	US patent	1982	[155]
136	Photo-electrolysis at Fe <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub> heterojunction electrode	Fe <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	1982	[156]
137	Electrochemical solar cells	Book chapter	1982	[157]
138	Semiconductor photoelectrochemical solar cells	Review article	1982	[158]
139	Light-induced electron transport across semiconductor electrode/reaction-center film electrolyte interfaces		1982	[159]
140	TiO <sub>2</sub> -VO <sub>2</sub> alloys reduced bandgap effects in the photo-electrolysis of water		1982	[160]
141	Photo-assisted decomposition of water over modified rutile electrodes		1982	[161]
142	Photo-assisted heterogeneous catalysis with optical fibres	Photoelectrodes semiconductor-coated with optical fibers	1982	[162]
143	Photoelectrochemical electrodes	US patent	1982	[163]
144	Chemically derivatised semiconductor photoelectrodes	Highlights the essential results from semiconductor modification	1983	[164]

*Continued*



**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
145	Photoelectrochemical characteristics of semiconductor-metal/SPE/metal cells		1983	[165]
146	Photoelectrochemical catalysis with polymer electrodes		1983	[166]
147	Photo- and electroluminescence spectra from an n-TiO <sub>2</sub> semiconductor electrode as related to the intermediates of the photooxidation reaction of water		1983	[167]
148	Hydrogen pathways for massive solar energy utilization	Discusses the merits of hydrogen pathways and durable long-term methods of hydrogen production	1983	[168]
149	New problems and prospects in the electrochemistry of semiconductors	Pleskov's review		[169]
150	Interfacial studies of molybdenum disulfide semiconductor/electrolyte systems	PhD thesis	1983	[170]
151	Thin layer photo-electrochemistry of dye-modified electrodes	PhD thesis	1983	[171]
152	Thin film solar cells	Book discusses the solar cell materials including PEC materials	1983	[172]
153	Photo-electrochemistry of semiconductors	Book chapter by Pleskov	1983	[173]
154	The nature of transition-metal-oxide surfaces	The classic paper on the surface of metal oxide materials	1983	[174]
155	Theory of electronic structure of oxide surfaces	Review	1983	[175]
156	Interfacial charge transfer reactions in colloidal dispersions and their application to water cleavage by visible light	Book chapter	1983	[176]

**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
157	Semiconductor photo-electrochemistry	NASA technical report	1983	[177]
158	A review of photoelectrochemical methods for the utilisation of solar energy	Review	1983	[178]
159	In situ in situ characterisation and non-solar applications of semiconductor liquid junctions	A brief review of the in-situ characterization techniques	1983	[179]
160	Photo-electrochemistry and solar energy: progress, promise and problem	Review from AJ Bard	1984	[180]
161	Photoelectrochemical cells including chalcogenophosphate photoelectrode	US patent	1984	[181]
163	Electrochemical solar energy conversion	Perspective	1984	[182]
164	Effective threshold energy of photoelectrochemical process on semiconductor electrodes		1984	[183]
165	Chalcogenide glasses as photoelectrodes for solar energy conversion	Review	1984	[184]
166	The catalysed photodissociation of water	Review	1984	[185]
167	Photoelectrochemical energy conversion	Gerischer's book chapter	1984	[186]
168	Photoelectrochemical properties of single-crystalline n-SiC in aqueous electrolytes		1984	[187]
169	Hydrogen-evolving solar cells	Review	1984	[188]
170	Basic problems of photochemical and photoelectrochemical hydrogen production from water	Review of hybrid water splitting systems	1984	[189]

*Continued*

**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
171	Polymer modification of electrodes	Review	1984	[190]
172	Photoelectrochemical studies of BaTiO <sub>3</sub> electrolyte redox systems	La-doped BaTiO <sub>3</sub>	1984	[191]
173	The efficiency of splitting water with semiconducting photoelectrodes		1984	[192]
174	Synergic electrocatalyst for efficient photoelectrochemical generation of hydrogen at p-InP		1984	[193]
175	Catalyzed photodissociation of water—the first step in inorganic photosynthesis?	Review	1984	[194]
176	Solar energy conversion by functional polymers	Review	1984	[195]
177	The characterisation of doped iron oxide electrodes for the photodissociation of water		1984	[196]
178	Solar energy conversion in photoelectrochemical cells with semiconductor electrodes	Review by Pleskov	1984	[197]
179	Solar energy conversion through photo-electrochemistry	Proceedings of the UNESCO forum on electrochemistry in research and development	1985	[198]
180	Kinetic investigation on the mechanism of the photoelectrochemical oxidation of water and of competing hole processes at the TiO <sub>2</sub> (Rutile) semiconductor electrode		1985	[199]
181	Observation of a long-life photoelectrochemical conversion with n-type porous Si photoelectrodes		1985	[200]

**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
182	Photoelectrochemical behaviour of p-type boron phosphide photoelectrode in acidic solution		1985	[201]
183	Solar photochemical process engineering for production of fuels and chemicals	Review	1985	[202]
184	Semiconductor electrodes LVI. Principles of multijunction electrodes and photo-electrosynthesis at Texas instruments p/n-Si solar arrays		1985	[203]
185	Problems and potential in the semiconductor/electrolyte approach to solar conversion	Review	1985	[204]
186	On the splitting of water	Review	1985	[205]
187	Photoelectrochemical properties of polycrystalline TiO <sub>2</sub> electrodes: anomalous photoeffects		1985	[206]
188	Photoelectrochemistry, Photocatalysis and Photoreactors: Fundamentals and Developments	Exclusive book on various aspects of PEC and reactor configurations	1985	[207]
189	Photoeffects of semiconductor electrolyte	Report	1985	[208]
190	Limiting and realizable efficiencies of solar photolysis of water	Review	1985	[14]
191	The surfaces of metal oxides	Review deals with electronic, geometric and chemisorption properties of metal oxide surfaces	1985	[209]
192	Interfacial processes involving strong electronic interactions in solar energy conversion and storage	A review comparing the performance of various ruthenium dichalcogenides	1985	[210]
193	Theoretical aspects of semiconductor electrochemistry	Book chapter	1986	[211]
194	Photoelectrochemical devices for solar energy conversion	Book chapter	1986	[212]

*Continued*

**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
195	Perspectives in electrochemical physics	Book chapter	1986	[213]
196	Photo-electrolysis and photoelectrochemical catalysis	Book chapter	1986	[214]
197	Photoelectrochemical methods for the utilization of solar energy	Review	1986	[215]
198	Catalysis of electrochemical and photoelectrochemical reactions at semiconductor electrodes	Review	1987	[216]
199	The interaction of water with solid surfaces: Fundamental aspects	Review of water/solid interaction	1987	[217]
200	Scientific contributions from the hydrogen research center at Texas A&M, 1982–1987	Report	1988	[218]
201	Photoelectrochemical water splitting by tandem type and heterojunction amorphous silicon electrodes		1988	[219]
202	Photoelectrochemical solar energy conversion	Memming's review	1988	[220]
203	On the photoelectrodes $\text{TiO}_2$ and $\text{WSe}_2$ for hydrogen production through photo-electrolysis		1988	[221]
204	Photochemical and photoelectrochemical hydrogen production from water	Short Review	1988	[222]
205	India's hydrogen energy program—a status report	Report	1989	[223]
206	Physical properties of the semiconductor-electrolyte interface	Review	1989	[224]
207	Structural and photoelectrochemical studies of $\text{In}_2\text{O}_3$ modified $\text{TiO}_2$ in regard to hydrogen production through photo-electrolysis		1989	[225]

**Table 12.1** The development in the area of photoelectrochemical decomposition of water during 1972–90—cont'd

Serial No.	Title of the article	Comments	Year	Reference
208	Surface investigation of NiNb <sub>2</sub> O <sub>6</sub> electrodes for water photo-electrolysis		1989	[226]
209	Photo-electrolysis and In Situ Storage of Solar Energy		1989	[227]
210	Photoelectrochemical and photocatalytic methods of hydrogen production: a short review		1990	[228]
211	Mechanistic studies of light-induced charge separation at semiconductor/liquid interfaces	An account	1990	[229]
212	A solar hydrogen energy system	A detailed review by Bockris	1990	[230]
213	Photoelectrochemical cells—a review		1990	[231]
214	Photoeffects at semiconductor surfaces	Book chapter	1990	[232]

## 12.2 Early breakthroughs in PEC hydrogen production

Photoeffects in the electrochemical systems were first discovered in 1839 by Becquerel in his famous study “Research on the effects of chemical radiation from sunlight, using electric currents” [233]. The first idea to use of water as fuel, instead of coal, also dates back to the 19th century, and it belongs to a novel of Jules Verne’s *The Mysterious Island* published in 1874 [234]. The relevant part of the book is reproduced below:

*“And what will they burn instead of coal?”*

*“Water,” replied Harding.*

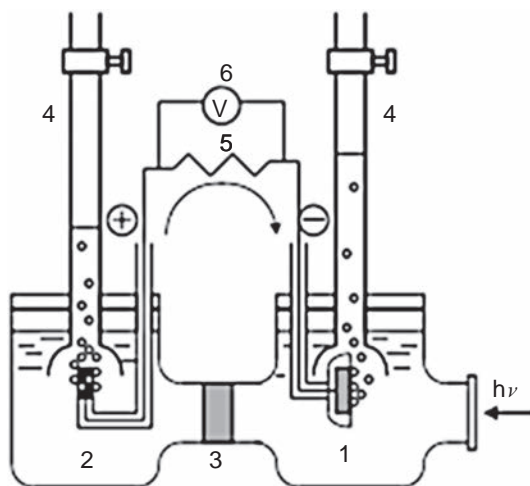
*“Water!” cried Pencroft, “water as fuel for steamers and engines! Water to heat water!”*

*“Yes, but water decomposed into its primitive elements,” replied Cyrus Harding, “and decomposed doubtless, by electricity, which will then have become a powerful and manageable force, for all great discoveries, by some inexplicable laws, appear to agree and become complete at the same time. Yes, my friends, I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable.”*

The first report on the decomposition of water by light was reported in 1959 by Kallmann and Pope [235]. In this work, an anthracene crystal sandwiched between the 1-M NaCl

solution acting as a transparent electrical contact with each face of the crystal and connected by an external wire between them. The irradiation of one side of the single crystal produced a photocurrent and released some gases from the system. Initially, the authors did not recognize the evolved gas and reported at the end of the article as “The fate of the gases evolved is not yet known.” A year after, in 1960, the same group identified that the evolved gases are hydrogen and oxygen [236]. Before and after this, several studies reported on the electrochemical response of semiconductor/electrolyte interface on light illumination by veterans, Brattain and Garratt [237, 238], Heinz Gerischer [239–246], Yurii Pleskov [247], and Rudiger Memming [248–252].

The first report on PEC water splitting was published in 1969 in the Journal of Chemical Society of Japan [253], and the article was then republished in Nature in 1972 by Akira Fujishima and Kenichi Honda. The reaction setup is now known as the Honda-Fujishima cell [22]. In this work, photoanode (rutile  $\text{TiO}_2$ ) and photocathode (Pt) immersed in an aqueous electrolyte were connected externally (Fig. 12.2) [254]. They have shown for the first time that water can be split to its constituents when the photoanode irradiated with near UV light using the cell and the process was termed as PEC energy conversion or photoelectrolysis, based on the semiconductor–electrolyte interface. Even though the work is regarded as the starting point of photoelectrocatalysis, this work could have been termed more appropriately as photon-assisted electrolysis because of the inherent electrochemical bias (0.82 V) that exists between the two electrodes immersed in two different electrolytes, namely in NaOH and  $\text{H}_2\text{SO}_4$ . This article initially did not get sufficient attention until the 1973 oil crisis [255]. From



**Fig. 12.2** Reaction setup for photolysis of water or Honda-Fujishima cell. (Reproduced with permission from K. Hashimoto, H. Irie, A. Fujishima, *TiO<sub>2</sub> photocatalysis: a historical overview and future prospects*, *Jpn. J. Appl. Phys.* 44 (2005) 8269–8285. ©2005 The Japan Society of Applied Physics.)

1974 onwards, the article became viral in the photo-electrocatalysis as well as the photocatalysis scientific community.

In 1975, Arthur Nozik proved the additional requirement of 0.3 V external bias for the splitting of water [41]. In the following year, Nozik showed that the irradiation of the two photoelectrodes made up of an n-type TiO<sub>2</sub> photoanode and p-type GaP photocathode is capable of eliminating the external bias, and thus the first real water photoelectrolysis was reported [64, 76, 83, 87]. The year 1979 witnessed the release of the book on Solar Hydrogen Energy Systems from Japan, containing a collection of contributions from various leading scientists in the field [256]. In one of the chapters in this book, Akira Fujishima reviewed the state-of-the-art PEC hydrogen production up to 1979 [257]. Because of the difficulty to cover all the early developments in this field of water splitting in detail: the readers may refer to the collection of the relevant articles/reviews/book chapters/books includes both essential as well as applied aspects of PEC and published between 1972 and 1990. The period of 1972–85 considered the boom years [258] of PEC water splitting presented in chronological order as you can see in Table 12.1.

## 12.3 Basic postulates and principles

The design of the photoelectrode depends on various factors, and each is having a specific role in the totality of the process. These factors include the nature of light irradiation, penetration of the light into the semiconductor, absorption of photons, generation, separation, and transportation of the charge carriers to the interface, thermodynamic and kinetic factors of the interface reactions, competing reactions, and overall the stability of the photoelectrode. The characteristics of the materials, like, particle size, surface area, pore size, active sites on the surface, and morphology would have a pronounced impact on the water splitting process. Since these factors are interrelated in some way makes the correlations more complicated. Concentrating only on the inherent properties of the material does not lead the process on a viable scale, and therefore, the optimization of all the physical, chemical, and electrochemical parameters in an efficient way is required for the selection and the design of new materials for overall water splitting.

### 12.3.1 Photon management

The primary process in the PEC cell is the excitation of charge carriers under the irradiation of light of appropriate wavelength with constant intensity. Any variation in the light intensity would have a pronounced impact on the subsequent processes. For better absorption of the light, the surface morphology of the photoelectrode is to be controlled, to get the benefit of maximum absorption of light. It is to be noted that the absorption coefficient depends on both intrinsic material properties as well as the nature of incident light [259].

$$\text{Photon intensity} \propto e^{-\alpha x} \quad (12.1)$$



The semiconductor does not absorb photons with energy less than the bandgap energy  $E_g$ . Photons with energy larger than  $E_g$  are absorbed but, some photons may travel a considerable distance before being absorbed. The light intensity decreases exponentially with the distance traveled ( $x$ ) inside a semiconductor.  $\alpha$  is called the absorption coefficient or absorptivity and is proportional to the extinction coefficient ( $\kappa$ ), the square root of the complex part of the dielectric constant. The inverse of the absorption coefficient, usually referred to as the penetration depth or skin depth ( $\delta$ ), is the distance over which the incident light intensity falls to  $1/e$  of its original value in a semiconductor, roughly proportional to the inverse of the square root of the dielectric constant [260, 261].

$$\text{Penetration depth, } \delta = \frac{1}{\alpha} \text{ or } \alpha^{-1} \quad (12.2)$$

The skin depth value enables prediction of the distance to which the light penetrates a semiconductor, and the value of  $\delta$  depends on the frequency (inverse of wavelength) as well as the semiconductor properties. For example, in the case of  $\text{Fe}_2\text{O}_3$ ,  $\delta = 118 \text{ nm@}550 \text{ nm}$ , for Si,  $\delta = 680 \text{ nm@}510 \text{ nm}$ , and CdTe,  $\delta = 106 \text{ nm@}550 \text{ nm}$  [262]. The penetration depth of the incident light in a photoelectrode should be in the range of the thickness of the space charge layer so that excitation in that region would be uniform. If the bulk diffusion length is higher than the width of the space charge layer, the recombination via surface states is negligible, and no diffusion current flows toward the interface [263]. Controlling the penetration depth up to the space charge layer has a high significance because it reduces the charge carrier recombination and better migration of the same into the interface. Because of the direct dependence of wavelength on the penetration depth [260], use of monochromatic radiation is encouraged for water splitting so that one has precise control over the penetration depth. This indicates, the selection of incident radiation is not random, and penetration depth has to be factored in, before choosing the appropriate wavelength of incident radiation for PEC water splitting.

### 12.3.2 Bandgap, photovoltage, and band edge positions

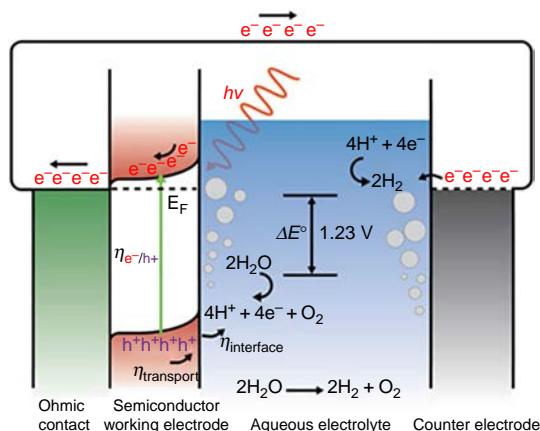
The photoelectrode must have enough bandgap to generate sufficient photovoltage, the real driving force for water splitting, across the interface. For efficient water splitting, the photovoltage generated should address the overvoltage associated with the water splitting process. The thermodynamic voltage required to split water is 1.23 V, and the additional overpotential enhances this value to 1.8 V depending on the photoelectrode employed. So, the generation of 1.8–2 V of photovoltage requires a photoelectrode with a band gap of more than 2.2–2.4 eV because the quasi-Fermi level lies above and below the respective bands due to the non-radiative recombination, incomplete light trapping, and spontaneous emission [10]. The nonideal alignment of band structure can further reduce the photovoltage. The photophysical processes happening under the illumination conditions

are also affecting the stable photovoltage. In addition to the photovoltage and bandgap, the photoelectrode must have enough band potential compared to water redox potential or the water redox potential should be in the bandgap of the material in any pH value (Fig. 12.3). The selection of materials with significant band gap and band edge position does not guarantee the full-fledged water splitting. For efficient water splitting, photovoltage generated under illumination has to be uniform throughout the reaction. Sustaining the photovoltage throughout the reaction is a bottleneck, and a stable photovoltage generation depends on many factors, such as some additional states present between the bandgap and the morphology of the photoelectrode surface. These aspects are covered in the upcoming sections.

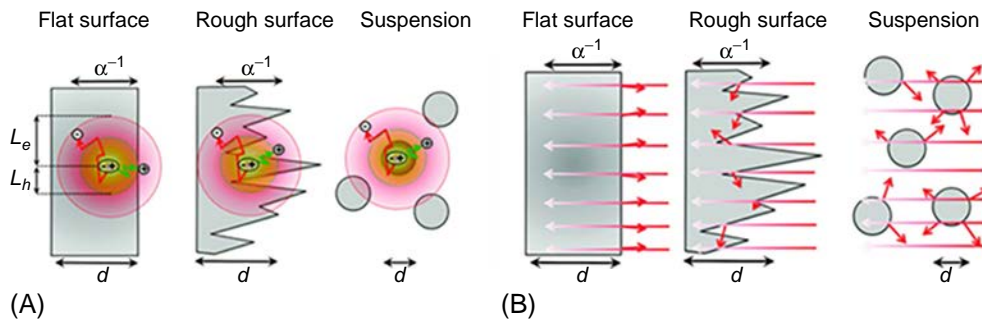
### 12.3.3 Morphology and textural parameters

The morphology of the photoelectrode is to be designed in such a way that it captures the maximum amount of the incident light. Roughening the surface of the photoelectrode allows trapping the light by increasing the degree of horizontal light distribution through light scattering (Fig. 12.4). The flat surface is usually not preferred because of the increase in the direct reflection [264].

The size of the particle has a significant role in the solar fuel generation process. Materials with smaller particle size have a high surface to volume ratio. The higher surface area containing suitable active sites is a prerequisite of any surface reaction, and it promotes the reaction far better than the same particle with the larger size. In nanoscale particles, the



**Fig. 12.3** The illustration of the various processes involved in a photoelectrochemical water splitting process. (Reproduced with permission from Z. Chen, T.G. Deutsch, H.N. Dinh, K. Domen, K. Emery, A.J. Forman, N. Gaillard, R. Garland, C. Heske, T.F. Jaramillo, A. Kleiman-Shwarstein, E. Miller, K. Takanabe, J. Turner, Introduction, in: Z. Chen, H.N. Dinh, E. Miller (Eds.), *Photoelectrochemical Water Splitting Standards, Experimental Methods, and Protocols*, Springer New York, New York, 2013, pp. 1–5. ©2013 Springer International Publishing.)

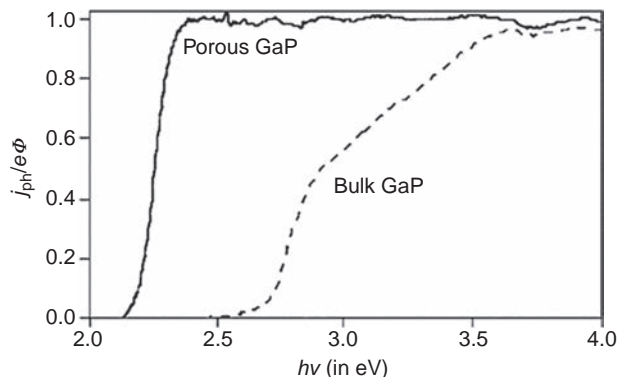


**Fig. 12.4** (A) Charge collection on a flat surface, nanostructured surface, and in a particle suspension.  $d$  is the thickness of the particle, and  $L_e$  and  $L_h$  are the electron and hole diffusion length. (B) Diffusion of light in flat and rough surfaces and suspension;  $\alpha^{-1}$  is the optical penetration depth. (Reproduced with permission from F.E. Osterloh, *Inorganic nanostructures for photoelectrochemical and photocatalytic water splitting*, *Chem. Soc. Rev.* 42 (2013) 2294–2320. ©2013 The Royal Society of Chemistry.)

potential drop as well as the electric field across space charge region, are considerably low, thus hindering the carrier transportation to the surface interface due to the rapid recombination of excitons [263]. Increase in electron-hole recombination in nanoscale particle retards the advantage gained from the higher interfacial surface area. The surface and interfacial electron-hole recombination in smaller particles can be reduced by appropriate surface treatments to remove any surface defects. The decrease in particle size also increases the band gap of the material because of the modification in the band edge positions due to quantum confinement [262, 265]. In another way, one can say that the nanoscale particles are a better reducing/oxidizing agent than that of the bulk semiconductor. Again, the increased bandgap shifts the absorption properties into the blue region of the spectrum, decreasing the absorption of visible light.

Increasing the surface area of the photoelectrode or cocatalyst has pronounced effect on the rate of the reaction because it promotes the charge transfer across the interfaces, allowing water splitting reactions to occur at significantly lower current densities. Besides, the photoelectrode or cocatalyst should possess active sites responsible for capturing water in their surface lattices.

The scattering and internal reflection within the porous layer of a photoelectrode enhance the light absorption cross section. As a consequence, the penetration depth in a porous photoelectrode becomes smaller and therefore, produces minority charge carriers near the semiconductor-electrolyte interface, thus reducing the light-induced recombination of excitons. For example, the penetration depth of the polished n-type GaP is around 10  $\mu\text{m}$  at 2.4 eV, which is considerably larger than the diffusion length of the hole; hence, the recombination over charge transfer across the interface. However, the usage of porous GaP (Fig. 12.5) enabled the absorption of light within the porous layer that produces minority charge carriers near the interface, thus enhancing quantum efficiency to unity in the presence of bandgap photon energy [266, 267].



**Fig. 12.5** The dependence of the photocurrent quantum yield on the photon energy of a polished n-GaP electrode (*dashed curve*) and the same electrode after porous etching (*solid curve*)  $16\text{Ccm}^{-2}$ , 10V vs. SCE in 0.5 M  $\text{H}_2\text{SO}_4$  solution at 1V vs. SCE. (Reproduced with permission from J.J. Kelly, D. Vanmaekelbergh, *Charge carrier dynamics in nanoporous photoelectrodes*, *Electrochim. Acta* 43 (1998) 2773–2780. ©Springer Science+Business Media, LLC 2009.)

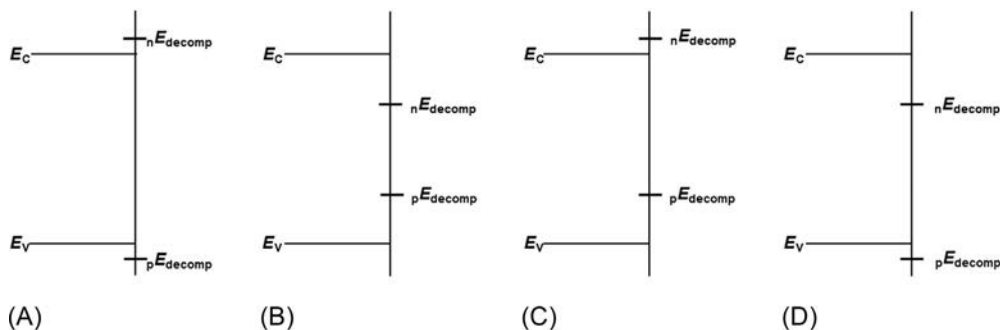
### 12.3.4 Stability

The major problem existing in the PEC cell is the susceptibility of the photoelectrode to decomposition under reaction conditions. A better understanding of the photo-corrosion mechanism helps to find out the optimal material under the reaction conditions. Therefore, the material selection deserves particular attention among others, and independent analysis is required which would throw light into the necessary actions that need to be taken to stabilize the photoelectrode [268].

The conduction band electrons and valence band holes are responsible for the PEC decomposition of photocathode and photoanode, respectively. The respective quasi-Fermi level of the photoelectrode under illumination gives the energetics of the electron and hole. Therefore, the position of the decomposition Fermi levels concerning the quasi-Fermi levels would give the thermodynamic stability of the photoelectrode. Based on this aspect, one can represent the stability of a photoelectrode in four different ways as seen in Fig. 12.6 [107].

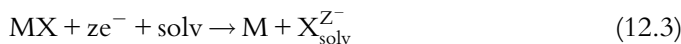
If the decomposition Fermi level lies outside the bandgap, then it is called a stable photoelectrode and if it lies inside the bandgap, then it is called an unstable photoelectrode. The free energy difference between band edges and the decomposition Fermi levels would give the extent of anodic and cathodic decomposition. The first case is ideal in reality; no semiconductor exists that is entirely stable against the photodecomposition. Most of the materials used as photoelectrode belong to the last two categories. The semiconductor represented in Fig. 12.6B would decompose entirely in the presence of light irradiation.

According to Gerischer [103], photoelectrode (MX) decomposition can be expressed as

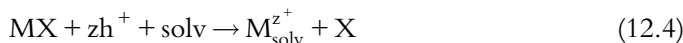


**Fig. 12.6** Possible positions of the decomposition energy levels relative to the band edges: (A) for a relatively stable semiconductor; (B) implies instability if either electrons or holes reach the surface; and (C, D) imply instability of holes and to electrons, respectively. (Reproduced with permission from H. Gerischer, *Electrolytic decomposition and photodecomposition of compound semiconductors in contact with electrolytes*, *J. Vac. Sci. Technol.* 15 (1978) 1422. ©AIP Publishing LLC1978.)

For a photocathodic reaction,



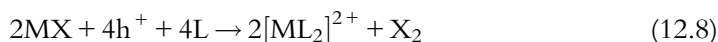
For a photoanodic reaction,



The presence of holes in the surface can also be treated as the missing of electrons from the bonding states of the valence band. This weakens the bonding between the adjacent atoms in the surface lattice and makes them more susceptible toward electrons of the nucleophilic reactants present in the electrolyte. In this situation, the extent of bond weakening depends on the localization of the wave functions. Even though all surface atoms are statistically involved; the kink sites, lattice defects, and dislocations present on the surface are predominantly responsible for the “transitorial hole capturing process.” The interaction of these sites with the electron-donating atoms or molecules from the electrolyte causes further localization of the hole by the formation of a new bond. In the case of the electrons of the conduction band, the localization of the electrons in the antibonding states weakens the bond, making it vulnerable to the electrophilic reactants present in the electrolyte. The new bond formation with the electrophiles stabilizes the reduced state, which allows the decomposition to proceed spontaneously [107].

Reaction kinetics is the primary determining factor for photodecomposition to occur. The thermodynamic aspects of photocorrosion are presented in Fig. 12.6. The photodecomposition of the photoelectrode largely depends on the surface kinetics of the particular surface redox reaction of interest. The photoelectrode may be stable in

harsh conditions where thermodynamics predicts instability. Consequently, at least to some extent, kinetics helps to prevent the photodecomposition. The kink sites present on the surface step site are responsible for the formation and decomposition of any crystals where an atom possesses nearly half of the binding energy compared to the same atom situated in the bulk of the crystal. The shielding of the kink site using some inhibitors slows down the rate of photodecomposition process. Since photodecomposition reaction constitutes a series of reactions, there will be a rate-determining step that favors the formation of the most active intermediates. The activation energy of the rate-determining step controls the overall rate of photodecomposition. The thermodynamic decomposition potential derived for the overall reaction does not give any details on the energetics of the reaction steps and generating high-energy intermediates is regarded as the rate-determining step. In such conditions, the better indicator of the photodecomposition reaction is the redox potential corresponding to the rate-determining step. From the above discussion, it is evident that the intermediate steps involved in the photodecomposition process depend on the surface composition and the nature of redox reactions at the interface and significantly vary with each photoelectrode. Consequently, how photodecomposition begins and how fast it proceeds depends on many factors and cannot be predicted using any general principles. The following equations show the generalized indication of a compound with kink sites (MX) and the successive association of the surface with the holes and ligands [103].

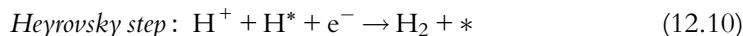
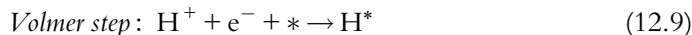


One way to prevent photodecomposition is the use of photogenerated minority scavengers. They are usually one electron reactions with no kinetic complications which proceed faster than that of the photodecomposition reactions. Unfortunately, we cannot use this one for water splitting reactions, wherein the solvent itself gets reduced or oxidized. Water splitting reaction is complex and proceeds through a series of intermediate steps just like photodecomposition reaction. The kinetics of water splitting possess some kinetic restrictions to proceed as the reaction, and therefore, it will protect the photoelectrode only under those conditions where the thermodynamic potential reaches much lower than the potential required for photodecomposition [107].

### 12.3.5 Hydrogen evolution reaction

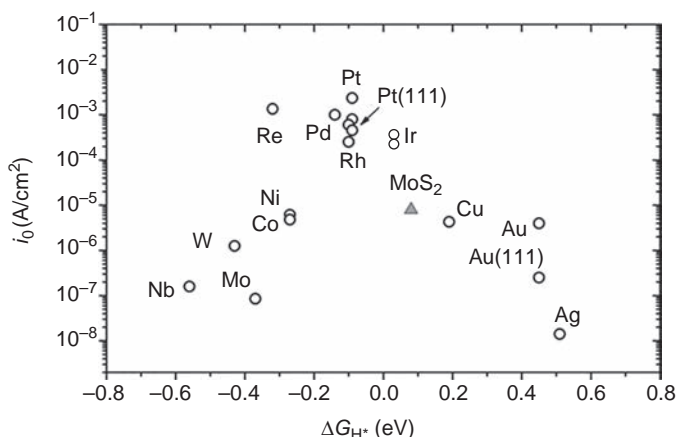
The primary dependence of hydrogen evolution from a photoelectrode is the nature of surface active sites exposed, which reduces the required overpotential significantly. That

means a photoelectrode that generates sufficient photovoltage and possesses desired band-edge positions does not evolve appreciable amount of hydrogen if the surface is inactive. The hydrogen evolution mechanism on a catalyst surface proceeds through the Volmer–Heyrovsky or the Volmer–Tafel mechanism [269–271].



A photoelectrode active toward hydrogen evolution binds the reaction intermediates to the surface neither too weakly nor too firmly, according to the Sabatier principle. The weak adsorption to the surface limits the overall reaction rate through Volmer step, and strong adsorption limits the desorption (Heyrovsky or Tafel step) of intermediates from the surface and thereby overall reaction rate. Therefore, the necessary but not sufficient condition for an active hydrogen evolution catalyst is  $\Delta G_{\text{H}^*} \cong 0$  [272, 273]. The plot of experimentally determined current density against  $\Delta G_{\text{H}}$  of various catalyst material results in a volcano-type relationship as in Fig. 12.7 [274–276].

The critical step in designing any catalyst material evolved from the understanding of how to control the binding energies of the active intermediate species involved in any particular process to the active surface sites. Even though the volcano plots provide useful information regarding the catalyst design for HER, a quantitative measurement of



**Fig. 12.7** HER volcano curve of MoS<sub>2</sub> vs. metals. (Reproduced with permission from J.K. Nørskov, T. Bligaard, A. Logadottir, J.R. Kitchin, J.G. Chen, S. Pandalov, U. Stimming, *Trends in the exchange current for hydrogen evolution*, *J. Electrochem. Soc.* 152 (2005) J23–J26. ©2005 by ECS-The Electrochemical Society.)

absolute reaction rate is needed in each class of the materials. This quantification is because the kinetic barrier associated with a process varies according to the material employed as well as the pH of the electrolyte [277]. It is more of a surprise that the catalytic activity in the volcano curve changes up and down with pH or kinetic barrier and not in the left-right direction implies the applicability of the descriptor in designing material for HER at any conditions [278].

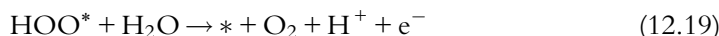
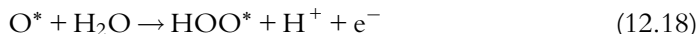
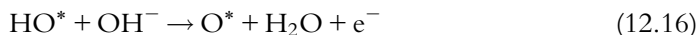
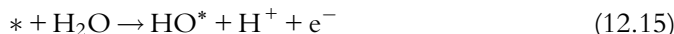
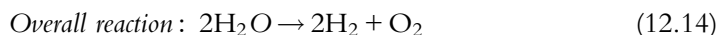
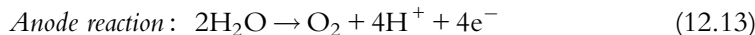
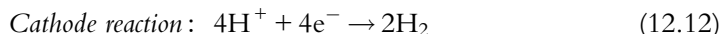
The best-performing catalyst toward HER is platinum that sits on the top of the volcano curve and needs only negligible overpotential in the acidic medium [269]. Nevertheless, the high cost and less abundance could limit the extensive use of the platinum-based electrodes. In search of new earth-abundant material, scientists have observed that the least explored surface of MoS<sub>2</sub> edge sites possesses  $\Delta G_{H^*} \cong 0.08$  eV at 50% hydrogen coverage near to the thermoneutral  $\Delta G_{H^*}$  value [279]. Further detailed studies [280, 281] on MoS<sub>2</sub>-based systems have revealed that the hydrogen evolution activity depends on the perimeter length of the edge sites and not on the increased surface area [280]. Nanostructuring the MoS<sub>2</sub> catalyst into a three-dimensional (3D) porous structure with double-gyroid morphology shows a marginal but two to fourfold increase in the turnover frequency [282]. The drawback of this kind of 3D structures is the longer transport distance to the active sites, which imparts resistance to the electron flow, indicating that well-designed lower dimensional materials are preferred for vectorial electron transfer reactions such as water splitting. Even though in-depth studies to increase the active edge sites on the MoS<sub>2</sub> surface reported, the overall activity of the electrode is still limited due to the small fraction of the edge sites responsible for the reaction rate. This limitation turned the study into other catalyst systems with higher intrinsic activity such as metal nitrides [283], carbides [284, 285], borides [284], phosphides [286, 287], and selenides [288]. All of which exhibit higher HER activity closer to that of Pt regarding overpotential required to reach a current density of 10 mA cm<sup>-2</sup>. The higher catalyst loading and surface area limit the non-precious catalyst system orders of magnitude behind Pt while considering the TOF<sub>avg</sub> under acidic conditions. In a basic medium, Ni-Mo [289] system shows lower overpotential to reach 10 mA cm<sup>-2</sup> but substantially lower TOF than that of Pt. Developing a catalyst system for HER evolution reaction needs more efforts and remains as a critical challenge. The design of a catalyst system should take care of the long-term stability, which is as important as the activity, to be viable technologically.

### 12.3.6 Oxygen evolution reaction

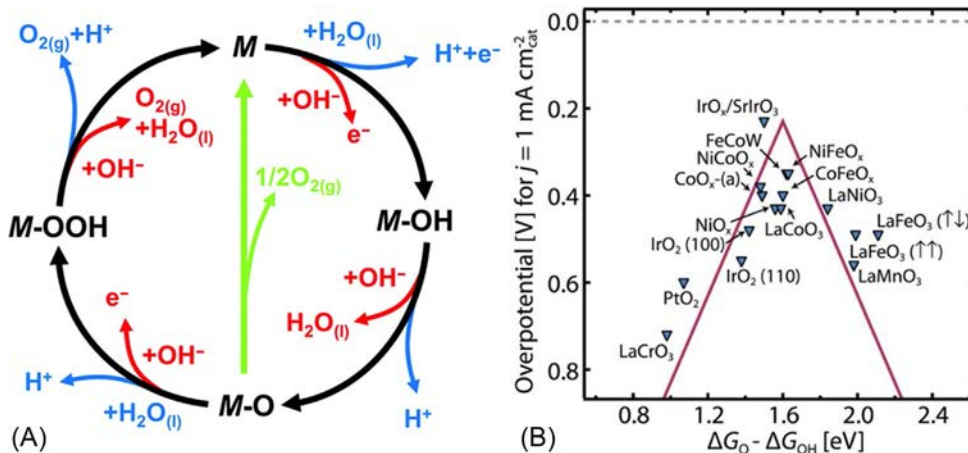
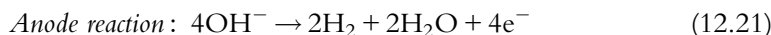
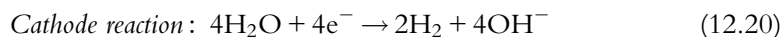
OER is one of the vital process involving the transfer of four excitons and responsible for the slower kinetics of the PEC water splitting process. O\*, HO\*, and HOO\* are the main intermediates observed in the OER [269]. Therefore, in OER reaction, the M-O bonding interaction has a significant role in stabilizing the reaction intermediates



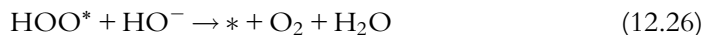
on the surface, and that has a pronounced impact on the overall water splitting efficiency. In acidic medium, the OER reaction mechanism (Fig. 12.8A) can be written as [290]



In alkaline medium (Fig. 12.8B),



**Fig. 12.8** (A) OER mechanism in acid (blue lines—gray in print version) as well as in alkaline medium (red lines—dark gray in print version). (B) Activity trends toward OER on metal oxides. ((A) Reproduced with permission from N.-T. Suen, S.-F. Hung, Q. Quan, N. Zhang, Y.-J. Xu, H.M. Chen, *Electrocatalysis for the oxygen evolution reaction: recent development and future perspectives*, *Chem. Soc. Rev.* 46 (2017) 337–365. ©2017 The Royal Society of Chemistry. (B) Reproduced with permission from Isabela C. Man, Hai-Yan Su, Federico Calle-Vallejo, Heine A. Hansen, José I. Martínez, Nilay G. Inoglu, John Kitchin, Thomas F. Jaramillo, Jens K. Nørskov, Jan Rossmeisl, *Universality in oxygen evolution electrocatalysis on oxide surfaces*, *ChemCatChem* 3 (2011) 1159–1165. ©2011 John Wiley & Sons, Inc.)



Metal oxide catalysts such as perovskites,  $\text{RuO}_2$ ,  $\text{IrO}_2$ ,  $\text{IrOx/SrIrO}_3$ , Ni-oxides, Co-oxides, Mn-oxides, and others like tertiary oxyhydroxides are the well-known electrocatalysts for the OER [290]. Similar to HER, a volcano-type relationship (Fig. 12.8B) can be arrived at for OER reaction using  $(\Delta G_{\text{O}^*} - \Delta G_{\text{HO}^*})$  as a descriptor [291]. The fundamental overpotential of the reaction could be circumvented by stabilizing the  $\text{HOO}^*$  concerning  $\text{HO}^*$  intermediate on the catalyst surface.

## 12.4 Surface engineering of photoelectrodes

Surface engineering is a powerful technique for tuning the transport properties of the charge carriers and therefore, the design of new semiconductor materials [292–297]. This section intends to analyze the problems with surface engineering techniques and not to cover the state-of-the-art development. There exist significant studies on these aspects; it is recommended that the readers follow the following Refs. [293–297]. The application of doped semiconductors in the field of solar energy conversion started with a primary intention to enhance the photon-absorption cross section of the photoactive materials as well as the photoactivity. Understandably, surface engineering techniques help to enhance the photoactivity toward thermodynamically favorable reactions such as pollutant degradation that does not mean that the same can be true for all other solar energy utilization processes. It is also worth noting here that, any surface techniques used till date does not solve the problems that exist in water splitting or other thermodynamically unfavorable reactions such as photoreduction of carbon dioxide [298–300]. Moreover, the so-called statement “increases photoactivity” is still at the marginal level. In most of the studies on these aspects only taking care of the thermodynamic controls over the reaction and not the kinetics. It is worth remembering that a thermodynamically favorable reaction does not proceed well if the kinetics is sluggish. This is precisely the situation in PEC water splitting; consequently, we need the control over the thermodynamic as well as the kinetic aspects of the reaction for any further improvements in the process [301]. We would expect that a revisit into this may help to change the paradigm.

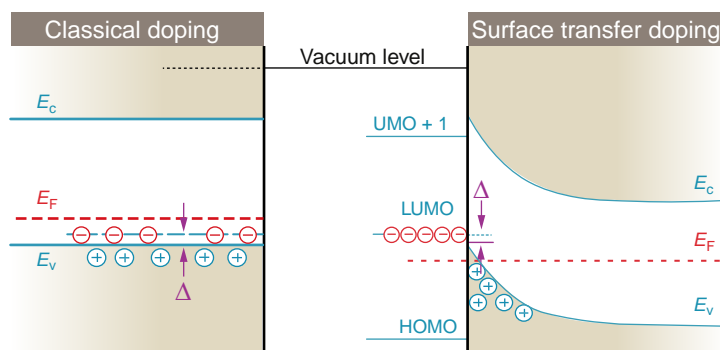
### 12.4.1 Doped photoelectrodes

The definition of doping is the intentional introduction of impurities into a semiconductor matrix to modulate the electrical properties [302, 303]. The doping strategy was first applied in the electronics industry for controlling the carrier generation and transport.

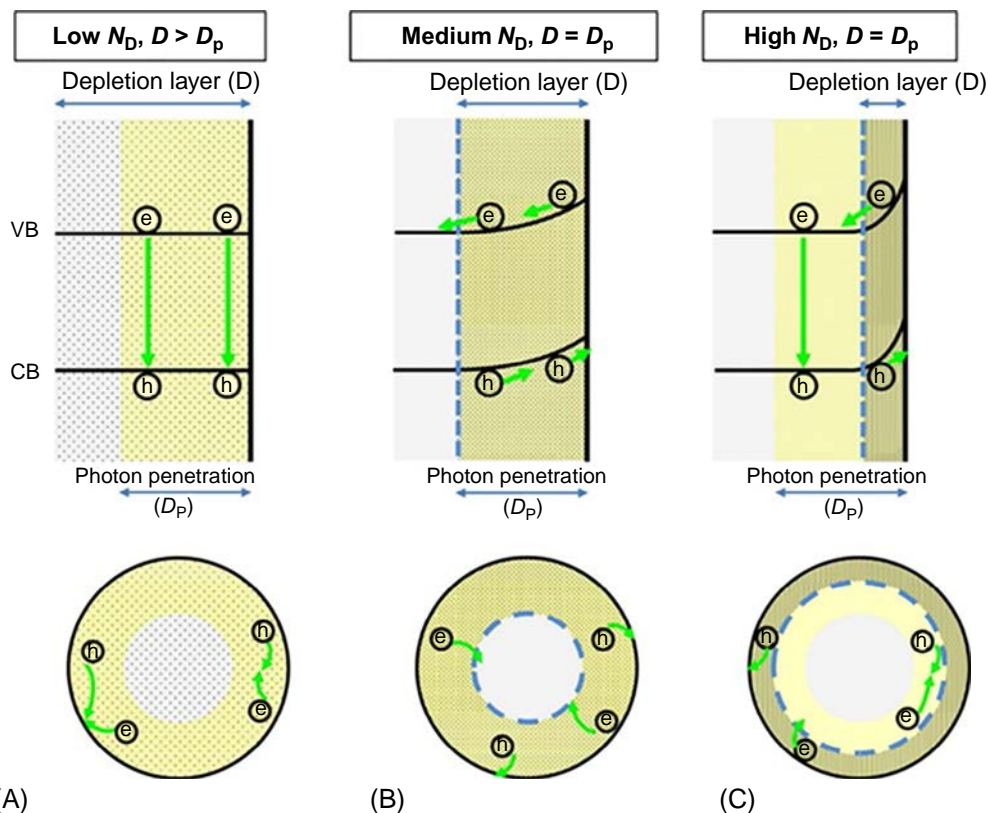
New generation electronic materials, such as a solid-state photomultiplier or resonant tunneling transistors emerged from these classical doping techniques where the impurities are directly introduced into the bulk of the semiconductor [303]. Doping can also be achieved by the electronic interaction of semiconductor with the dopant situated at the surface lattice (Fig. 12.9). Doping leads to fine-tuning of the light absorption properties as well.

Let us consider a photoelectrode such as titanium dioxide which is capable of splitting the water. We have seen in the previous section that the photovoltage required for efficient water splitting should be  $\sim 1.8$  V, and therefore, the band gap required will be more than 2 eV. As per the definition, the photovoltage is the potential difference between the two quasi-Fermi levels situated nearer to the conduction as well as valence band. The introduction of a dopant into the surface layer forms an intermediate state above the valence band that acts as a HOMO (highest occupied molecular orbital) level (Fig. 12.9) from where the electrons are excited to the conduction band. Therefore, the energy required to excite an electron in a doped system is less than that of the undoped system, but the oxidation potential of the later is more pronounced than the former. Consequently, the photovoltage generated in the doped system also will be less compared to the undoped one because of the shift of the valence band quasi-Fermi level to a less positive value. Then, the Fermi level changes occurred in the semiconductor alters the dark Fermi level equilibrium with the electrolyte, and therefore, the band bending at the interface will be different from that of the undoped system (Fig. 12.10) [304].

The interfacial changes could explain the effect of doping in a photoelectrode at the surface space charge layer. Addition of the optimal concentration of the dopant decreases



**Fig. 12.9** This band diagram illustrates classical p-type doping (left) and p-type surface transfer doping (right), using the energy of an electron in free space as a reference (vacuum level).  $E_c$  and  $E_v$  are the energies of the conduction band minimum and the valence band maximum, respectively. (Reproduced with permission from J. Ristein, *Surface transfer doping of semiconductors*, *Science* 313 (2006) 1057 LP-1058. ©2006 American Association for the Advancement of Science.)



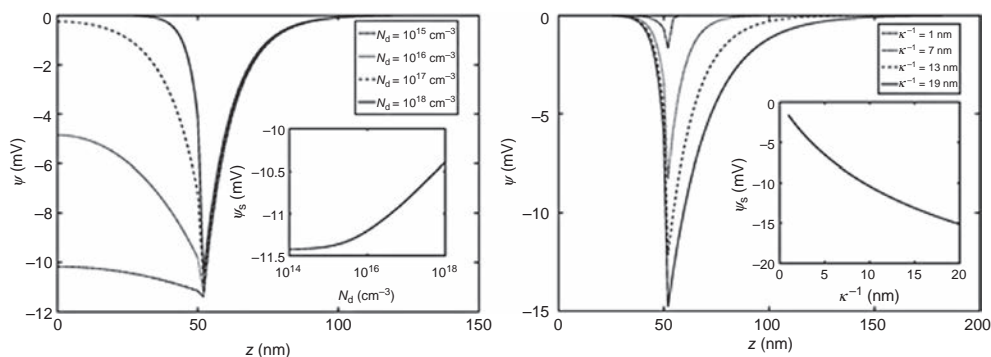
**Fig. 12.10** The effect of dopant concentration ( $N_D$ ) on the band bending and photogenerated carrier behavior in semiconductor nanoparticles: (A) the dopant concentration is low; depletion layer length ( $D$ )  $>$  photon penetration ( $D_p$ ); (B) the dopant concentration is medium; depletion layer length ( $D$ )  $=$  photon penetration ( $D_p$ ); and (C) the dopant concentration is high; depletion layer length ( $D$ )  $<$  photon penetration ( $D_p$ ). In panel C, where extreme upward band bending exists because of high  $N_D$ , holes transferred efficiently to the particle surface. (Reproduced with permission from Z. Zhang, J.T. Yates, *Band bending in semiconductors: chemical and physical consequences at surfaces and interfaces*, *Chem. Rev.* 112 (2012) 5520–5551. ©2012 American Chemical Society.)

the depletion region to the photon penetration depth of the semiconductor (Fig. 12.10). This enables a uniform generation of charge carriers in the space charge layer, reduces the recombination rate and enhances the charge transfer to the interface. At dopant concentration higher than the optimum level, the depletion layer width decreases beyond the photon penetration depth. Consequently, the charge carrier produced in that region will be less and therefore, at the interface. Excess dopant concentration increases the recombination of charge carriers in the bulk region within photon penetration depth, or it acts as recombination center [304].

The charge density inside the doped semiconductor plays a pivotal role and significantly alters the overall interaction with the electrolyte. The changes in the doped semiconductor concerning the potential in the electrolyte could have a dramatic effect on the kinetic stability of the material. The increased doping decreases the electrostatic repulsion between the particles. Consequently, the doped semiconductor colloids suspended in electrolyte solution should be less stable provided the surface chemical groups be the same. The latter condition is more critical because the doping procedure changes the surface chemistry, and therefore, it has a pronounced effect on the stability of the material. The drop in the electrostatic potential with doping witnesses the domination of the van der Waals force leads to the particle precipitation or coagulation [305, 306].

The electrostatic potential distribution of an n-doped semiconductor–oxide–electrolyte system concerning the dopant concentration is depicted in Fig. 12.11 [306]. We know that the oxide layer on the surface is charge free and behaves as a capacitor. The figure also reveals the variation in the surface potential at the oxide–electrolyte interface with doping. The doping has a dramatic effect on the potential distribution inside the semiconductor because of screening, but a comparatively small effect on the potential distribution in the electrolyte since the surface groups involved in charge regulation interact directly with the electrolyte [307].

The increase in the water splitting reaction or hydrogen production is only due to the increase in the carrier concentration at the interface and the reduction of electron–hole



**Fig. 12.11** The potential distributions plotted as a function of distance  $z$ . The semiconductor/oxide interface is at  $z=50$  nm, while the oxide/electrolyte interface is at  $z=52$  nm. The electrolyte has pH 3. The various lines depict varying doping concentrations. The inset is a plot of surface potential  $\Psi_s$  vs. doping  $N_d$ . Potential distributions plotted as a function of distance  $z$ . At constant doping of  $N_d=10^{18}$   $\text{cm}^{-3}$ . The inset is a plot of the surface potential  $\Psi_s$  vs. Debye length  $\kappa^{-1}$ . (Reproduced with permission from M.E. Fleharty, F. van Swol, D.N. Petsev, *Charge regulation at semiconductor-electrolyte interfaces*, *J. Colloid Interface Sci.* 449 (2015) 409–415. ©2015 Elsevier BV.)

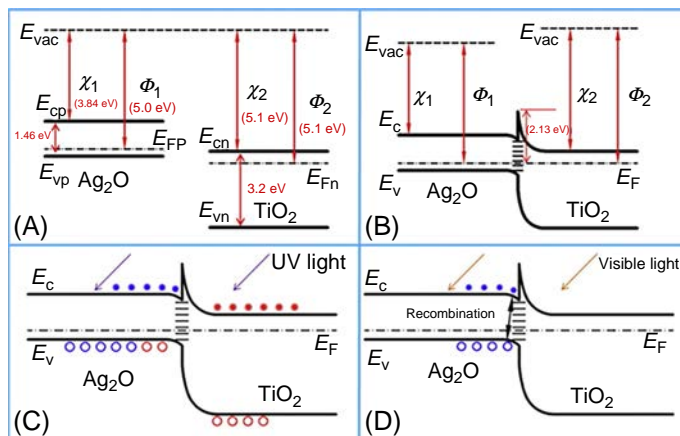
recombination. The increase is marginal mainly because dynamic effects at the interface are not considered. A detailed experimental study is required on the stabilities of doped semiconductor and its influence on the interfacial band energetics.

### 12.4.2 Heterojunction photoelectrodes

A heterojunction photoelectrode offers necessary photovoltage required for overall water splitting. Also, one can utilize the full range of semiconductors that do not have sufficient band positions to straddle past the water redox potentials. Using heterojunction photoelectrode is advantageous since the electric field formed in the interface of two semiconductors are capable of transporting the charge carriers in the opposite directions. Details on different aspects and application of heterojunction semiconductors as a photoelectrode have been covered in the literature [308–314]. A champion material for PEC water splitting should be capable of addressing the following: appreciable absorption characteristics, adequate band alignment about water redox potentials, faster reaction kinetics, and extended stability. Even though heterojunction photoelectrode helps to address the thermodynamic requirements of water splitting; it is observed that the increase in the rate of the reaction is marginal and is only due to the slight decrease in the rate of recombination of the charge carriers.

Let us consider the each of four characteristics of champion materials in the case of a heterojunction. The heterojunction extends the absorption of light radiation to a large extent depending on the semiconductor employed. However, the charge carrier transport between the semiconductors decreases the inherent potential of the charge carriers. Holes and electrons move toward the semiconductors having less oxidation/reduction potential. So, water oxidation will take place in a semiconductor having less oxidation potential, and similarly the reduction of water by electrons take place at semiconductor surface having lower reduction potential. In such a situation, the advantage of increased light absorption may not be realized fully in the heterostructure.

The nature of heterojunction in the photocatalytic or photoelectrocatalytic processes explained the band alignment of the individual semiconductors and classified into four; type I (straddling gap), type 2 (staggered gap) and type 3 (broken gap), and the conventional p–n junctions. In a real sense, one cannot accept the usage of these type of theories directly to interpret the nature of electron transfer across the semiconductor heterojunction [315, 316]. A more reasonable approach based on the electron affinity and the work function of the individual semiconductors is needed.  $\text{Ag}_2\text{O}/\text{TiO}_2$  belongs to the type 2 heterojunction (Fig. 12.12), and the respective band positions of  $\text{Ag}_2\text{O}$  lie above that of the  $\text{TiO}_2$  [317]. Therefore, after equilibrium, one could expect an electron transfer



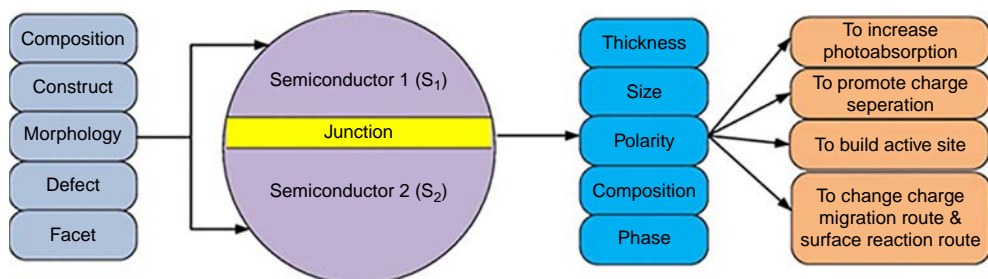
**Fig. 12.12** (A) The energy band structures of  $\text{Ag}_2\text{O}$  and  $\text{TiO}_2$  before the formation of the nano-heterojunction. (B) The energy band structures of  $\text{p-Ag}_2\text{O/n-TiO}_2$  nano-heterojunction at equilibrium. (C) The energy band structures of the  $\text{p-Ag}_2\text{O/n-TiO}_2$  nano-heterojunction under UV irradiation. (D) The energy band structures of the  $\text{p-Ag}_2\text{O/n-TiO}_2$  nano-heterojunction under visible light irradiation. (Reproduced with permission from Y. Lei, X. Lu, *The decisive effect of interface states on the photocatalytic activity of the silver(I) oxide/titanium dioxide heterojunction*, *J. Colloid Interface Sci.* 492 (2017) 167–175. ©2017 Elsevier Inc.)

from  $\text{Ag}_2\text{O}$  to  $\text{TiO}_2$  and hole transfer from  $\text{TiO}_2$  to  $\text{Ag}_2\text{O}$ . However, this is not true; the built-in an electric field is not continuous (interfacial spike formation in the conduction band edge) in the case of  $\text{Ag}_2\text{O/TiO}_2$  (Fig. 12.12). Illumination of such heterojunction enhances recombination of charge carriers at the interface resulting in a lower efficiency compared to the individual semiconductor systems, and the system becomes active in the visible light and not in UV. More details and understanding of the construction of heterojunction interfaces have been covered earlier [318–321].

Also, heterojunction photoelectrode does not address the kinetic factors such as the charge carrier mobility in two semiconductor systems as well as the surface kinetics aspects. Therefore, a heterojunction photoelectrode does not respond to appreciable water splitting reaction until one addresses the issues related to kinetic aspects effectively. Also, stability (of the material as well as the interface) is another critical aspect and has not considered in the literature.

While designing the electrode, apart from the electron affinity and work function characteristics, one needs to consider in detail, the interactions at three interfaces formed in the PEC cell, namely,

- photoelectrode/metal contact,
- heterojunction interface between the two semiconductors, and
- heterojunction photoelectrode/electrolyte interface.



**Fig. 12.13** Adjusting and controlling factors of the heterojunction. (Reproduced with permission from X. An, Y. Wang, J. Lin, J. Shen, Z. Zhang, X. Wang, *Heterojunction: important strategy for constructing composite photocatalysts*, *Sci. Bull.* 62 (2017) 599–601. ©2017 Science China Press. Published by Elsevier B.V. and Science China Press.)

Individual studies on each interface are required to interpret the nature of carrier transfer within the heterojunction photoelectrode. Also, to the best of the author's knowledge, there is no report on the behavior of these three interfaces in the presence of simultaneous electric and photon field or a photoelectric field. In addition to this, a variety of other issues (Fig. 12.13) are to be considered [321], which include:

- The optical and electric properties of the individual semiconductor. Do they meet all the necessary criteria for the desired application for water splitting?
- What is the nature of the electrostatic fields developed at the heterojunction interfaces and how the defects in the parent semiconductors would affect this?
- The interface formed during the heterojunction formation is thermodynamically stable or not?
- How to control the lattice mismatches at the interface?

It is to be remembered that the resulting built-in electric field and band bending would be symmetric only when the doping levels in the individual semiconductors are nearly equal [321]. That means an appreciable amount of homework is to be done to construct a highly active heterojunction photoelectrode. Otherwise, the interface would impede the carrier flow resulting in the instability of the interface. These issues suggest that there exists plenty of room for improvement in designing a heterojunction photoelectrode for overall water splitting [322].

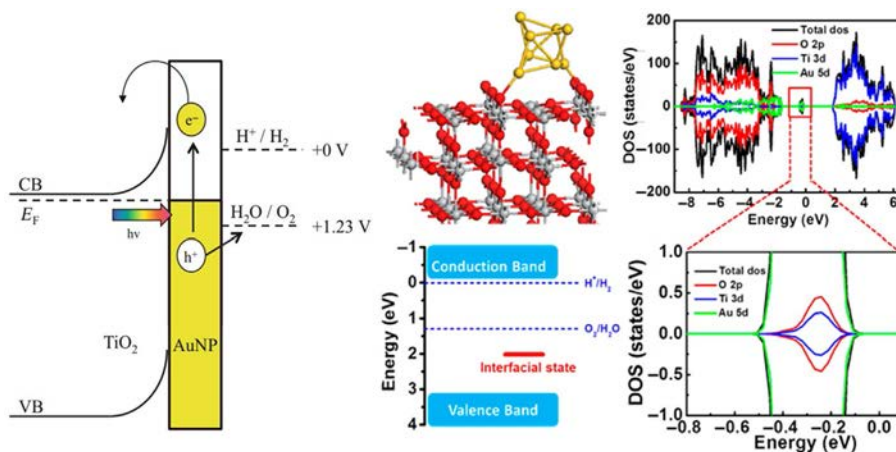
### 12.4.3 Plasmon-modified photoelectrodes

The main idea of incorporating plasmonic metals to a photoelectrode is to enhance its optical absorption characteristics in the visible region as well as to reduce the activation barrier toward the water splitting reaction [323–325]. However, the later has not been considered in detail in the literature. Plasmonic gold nanoparticles are the most studied photoelectrode systems among other plasmonic metals because of its resistive character toward oxidation [326]. The plasmon-enhanced PEC water splitting mechanism has not



yet been understood clearly, and the views on the mode of oxygen evolution on the plasmonic metal surface remain controversial. The proposed mechanisms based on the direct electron transfer (DET) and plasmonic resonant energy transfer (PRET) do not account a detailed clarification on the various phenomena occurring at the plasmonic interface [327–329]. Clarity on these aspects is needed to design better semiconductor plasmonic interfaces. A recent study (Fig. 12.14) suggested that the plasmon generated holes at the semiconductor/plasmonic metal interface are responsible and identified as the reaction site for water oxidation [330].

In many reports, the functioning of the plasmonic semiconductor has been compared with the dye sensitization mechanism [326]. However, such a comparison may not be relevant. In a dye-sensitized photoelectrode, the shape of the potential dependence of the photocurrent is more or less similar to that of the bare dye molecule. However, in a plasmonic semiconductor, the shape of the potential dependence of the plasmonic photocurrent is similar to that of the bare photoelectrode [331]. It could indicate that local surface plasmon resonance (LSPR) decayed as UV light rather than the hot electron and the efficiency of the overall process is dependent on the distribution of electric field and potential across the space charge layer. Also, there is a chance of some upconversion mechanism at the plasmonic interface due to energy pooling. Energy pooling like phenomena occurs between the particles with the same physical properties such as shape,



**Fig. 12.14** The proposed underlying mechanism of plasmon-mediated PEC water splitting. (Image of the left reproduced with permission from J.C. Alexander, Literature review, in: J.C. Alexander (Ed.), *Surface Modifications and Growth of Titanium Dioxide for Photo-Electrochemical Water Splitting*, Springer International Publishing, Cham, 2016: pp. 5–45, ©2017 Springer International Publishing AG. Moreover, on the right from S. Wang, Y. Gao, S. Miao, T. Liu, L. Mu, R. Li, F. Fan, C. Li, *Positioning the water oxidation reaction sites in plasmonic photocatalysts*, *J. Am. Chem. Soc.* 139 (2017) 11771–11778, ©2017 American Chemical Society.)

size, and distance of separation must be below the plasmon wavelength. This indicates the profound influence of particle shape, size, and concentration of the plasmonic metal on the photoelectrode surface on the hot electron injection efficiency (HEIE) [332]. Moreover, the HEIE depends on the nature of support semiconductor in the photoelectrode and the interface formed. The presence of surface defect enhances the Schottky barrier height with the plasmonic metal and leads to a lower HEIE. Therefore, careful surface treatment has to be done before depositing the plasmonic metal on the surface of the photoelectrode.

The above speculations on the mechanism of plasmon-mediated PEC water splitting should be evaluated in real time. Theoretical design of the interface considers only the work functions of the photoelectrode and the plasmonic metal. However, in a solution, the contact with water changes the work function of both photoelectrodes as well as the plasmonic metal [333]. These aspects are to be considered while interpreting the water oxidation reaction mechanism on plasmonic photoelectrode. The interface may behave differently compared to that of the photoelectrode/plasmonic interface designed on a theoretical basis.

#### 12.4.4 Cocatalyst decorated photoelectrodes

The decoration of cocatalyst efficiently reduces the overpotential barrier required for the water splitting reaction. For photoanode, various OER catalysts, such as Co-Pt, IrO<sub>2</sub>, CoO<sub>2</sub>, and NiO<sub>x</sub> [293] have been tried as cocatalyst. The negative shift in the current onset potential observed in all these cases indicates the suppression of overpotential on the decorated photoelectrode. The reduction in onset potential is an expected result, and the stability of cocatalyst/photoelectrode interfaces is a significant concern. As explained in the cases of the heterojunction, the excitons should readily migrate through the interface toward the cocatalyst/electrolyte interface. The initial enhancement in oxygen evolution does not mean that the reaction will sustain for a long time. The selection of an appropriate semiconductor/cocatalyst combination is necessary and should be based on the design principles proposed elsewhere [321, 334]. Photocathodes are usually decorated with Pt, MoS<sub>2</sub>, CoS<sub>2</sub>, and CoP<sub>x</sub> [293]. In these cases, also the extent of electron transfer depends on the work function of parent photoelectrode as well as the cocatalyst.

#### 12.4.5 Conductive material modified photoelectrodes

After exciton generation, the charge carriers have to migrate to the active site situated at the interface to proceed for respective OER and HER. Assembling a conductive material with a high surface density of carriers would facilitate transportation and continuous supply of the charge carriers to the surface-active sites. Typically used surface conductors are the monolayers of metal or metal oxides. The design principles adopted in the cases of

cocatalyst deposition as well as heterojunction can be extended to the design of conductive materials modified photoelectrodes. For OER, the hole formed in the valence band should move to the interface through the surface conductor only to the interface formed at the photoelectrode/conductor junction is a Schottky barrier. Similarly, the photocathode is active only when the photoelectrode/conductor interface obeys the Ohms law (ohmic contact). Also, the long-term stability of the nanolayer of the surface conductor is an issue. The metal monolayers will transform into its corresponding oxy(hydroxy) layers at the interface, which may be the reason for the increased oxygen evolution from the photoanode [335]. How the surface behaves at the interface is not explained [335]. It not only enhances the charge carrier transport but also acts as a better active site under reaction condition for the splitting of water.

It is worth noting here that the semiconductor surface usually limits the extent of Volmer step and the metal surface would limit the Heyrovsky/Tafel step [336]. The advantage of the use of conductive metal nanolayer is that it behaves as both semiconductor as well as the metal at the interface under reaction conditions. So, it may provide two active sites, one from the metal side and other from semiconductor side and the active site present on the metal surface activates the Volmer step, and the semiconductor activate the Heyrovsky/Tafel step [337, 338]. The detailed studies on these prospects offer a better chance of improvement in the water oxidation or reduction capability of the photoelectrodes.

As discussed, the surface modification has to be revisited more scientifically to enhance water splitting reaction thermodynamically as well as kinetically. The optoelectronic properties of the surface-engineered photoelectrode have to be studied in detail to resolve the interfacial issues exist in all these cases. The design of stable interface with the photoelectrode is the primary challenge in the case of heterojunction, cocatalyst deposition, conductive material deposition, surface states passivation, protective layer deposition, and plasmon-deposited photoelectrodes. Therefore, further studies on these aspects are needed.

## 12.5 Bonding characteristics and its role

The activity of metal oxides or sulfides or any other catalytic material depends on the nature of bonding, arising primarily because of the difference in the electronegativity between the constituent atoms. Usually, semiconductors exhibit mixed bonding characteristics (ionic or covalent) [339]. The bond polarity can be expressed in terms per cent ionic character or ionicity and derived using the well-known Pauling's equation.

$$\text{Percentage ionicity (\%)} = \left( 1 - e^{\frac{-(\chi_A - \chi_B)^2}{4}} \right) \times 100$$

where  $\chi_A$  and  $\chi_B$  are the electronegativity of the constituent atoms A and B. The ionicity of a bond is defined as the fraction of ionic character to the fraction of covalent character in a bond. More ionic compound shows larger band gaps, less polarizability, and smaller dielectric constant [340]. As the ionic character of the bond in the semiconductor increases, the negative charge accumulated on the oxide ion causes a less positive shift of the valence band and the positive charge on the metal shift the conduction band to more negative value makes the compound unfavorable for water splitting [341]. Therefore, the ionicity of a bond has a crucial role in the electron transfer ability of a material. In the case of water splitting, the ionicity of the bond should be just right, neither too ionic nor too covalent. Ideally, the ionicity of the bond should be in the range of 20%–30% for material to be active in the visible region of the solar spectrum. Semiconductors having percentage ionicity in the range of 20%–30% are given in Table 12.2. Together with the ionicity of the bond, the material should meet all the other necessary criteria for overall water splitting.

## 12.6 New generation materials: Perovskites

The use of quantum mechanical calculations helps to identify the new materials/structures for overall water splitting and avoids the expensive trial and error in the experimental process [342–344]. Essential criteria of a photoelectrode to be active toward PEC water splitting have been brought out in the earlier sections. Computational screening of different cubic perovskite materials such as oxides, oxynitrides, oxysulfides, and oxy-fluoronitrides as photocathodes, photoanodes, and transparent shield applications has been reported earlier [345–352].

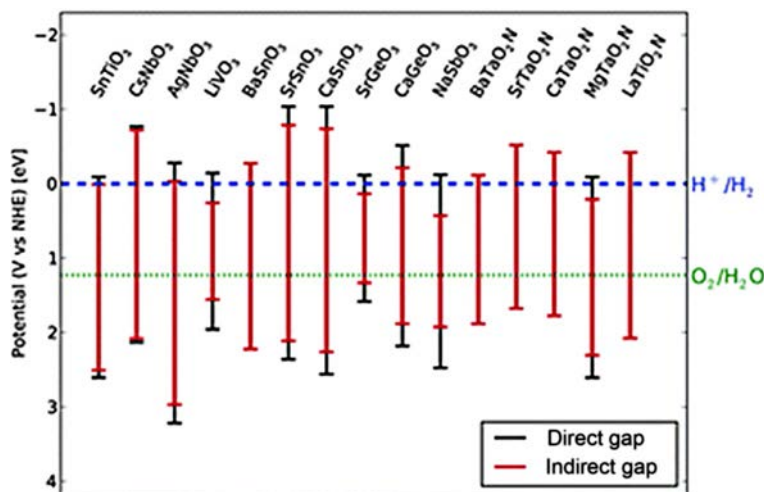
The design and discovery of low cost and highly efficient materials are the crucial issues at this juncture. In the last few years, substantial improvements have been reported in the highly active catalysts toward water splitting reaction by optimizing structural/electronic

**Table 12.2** Percentage ionic character of some conventional semiconductors used as photoelectrodes

Material	Electronegativity (eV)	Band gap (eV)	Electroactivity difference	% Ionic character
WO <sub>3</sub>	6.59	2.70	1.08	25.29
CdS	5.18	2.40	0.89	20
MnS	4.81	3.00	1.03	22.7
MnS <sub>2</sub>	5.24	0.50	1.03	22.7
TiS <sub>2</sub>	5.11	0.70	1.04	22.9
ZnS	5.26	3.60	0.93	20.75
ZnS <sub>2</sub>	5.56	2.70	0.93	20.75
ZrS <sub>2</sub>	5.20	1.82	1.25	26.84

properties of the transition metal-based oxides, usually called perovskites. Perovskites offer an alternative approach toward OER and have shown better activity than the state-of-the-art iridium oxide [353, 354]. Even though the perovskite structure provides good intrinsic activity toward the water oxidation, the low surface area inhibits the transfer of this substantial inherent activity toward the electrode. The speciality of perovskite structure ( $ABO_3/AA'BB'O_3$ ) is the flexibility to accept a wide variety of cations in the A- and B-sites, so that the electronic, as well as the structural properties, can be tuned, depending on the application [355]. Also, the layered structure of perovskites enhances the interfacial contacts with the substrate redox species.

In a cubic perovskite ( $ABO_3$ ), 12 co-coordinated cations are located at the A-sites and the six-coordinated cations in the B-sites. In such a structure, the valence band is mainly due to the contribution of  $O_{2p}$  orbitals, so that all the cubic perovskites with  $ABO_3$  structure possess more or less the same valence band position. Therefore, the bandgap of the materials and thereby the band edges can be tuned using A- and B-site cations or substituting the one or two oxygen atoms in the perovskite structure with other electro-negative elements such as nitrogen, sulfur, or fluorine. The substitution of other elements into the perovskite structure (Fig. 12.15) is governed by some selection rules so that the overall stability of the resultant perovskite structure is maintained [356].



**Fig. 12.15** 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—gray in print version) and indirect (black) gaps. (Reproduced with permission from I.E. Castelli, T. Olsen, S. Datta, D.D. Landis, S. Dahl, K.S. Thygesen, K.W. Jacobsen, *Computational screening of perovskite metal oxides for optimal solar light capture*, *Energy Environ. Sci.* 5 (2012) 5814–5819. ©The Royal Society of Chemistry.)

Some of the possible oxidation numbers of the metal to be substituted should be equal to 6 since the three oxygen atoms in the perovskite structure require two electrons each for the formation of a compound without any free charge.

- The ionic radii of the metal cations must be reasonably equivalent.
- Fewer electronegative elements should be chosen for the bond formation with oxygen in the lattice.
- The bandgap of the resultant perovskite structure must reasonably be higher than the photovoltage ( $\sim 1.8\text{--}3\text{ eV}$ ) required, and the band position should straddle the water redox potentials.

The bandgap of the resultant material decreases with an increase in the electronegativity of the B-site cation or adjusting the site of the A-site cation. Also, one can replace one or two oxygen from the  $\text{ABO}_3$  structure with nitrogen to tune the bandgap of the material. The introduction of nitrogen into the  $\text{ABO}_3$  perovskite structure causes an upward shift in the valence band position due to the higher energy of the  $\text{N}2p$  orbital than the  $\text{O}2p$  orbitals and forms oxynitrides with a perovskite structure  $\text{ABO}_2\text{N}$ . The smaller electronegativity of the nitrogen reduces the size of the oxynitride compound, and it ultimately destabilizes the cubic perovskite symmetry by creating some excess charge on the corners of the octahedron [349].

Instead of nitrogen, one can also replace the oxygen in the perovskite structure with fluorine ( $\text{ABO}_2\text{F}$ ) or sulfur ( $\text{ABO}_2\text{S}$ ) atoms or a combination of both ( $\text{ABONF}$ ) and can be used for one photon water splitting [345, 348]. The stability of the system is also the same as the oxynitrides, but less stable than the parent perovskite structure.

Some of the perovskite structures possess a higher band gap and inherent stability. Such kind of materials can be used as a shielding material for the photoelectrodes [348]. Those structures having lower valence band positions could use as a photoanode protecting material. Since the band gap is above  $3\text{ eV}$ , the material is transparent to the radiations below  $3\text{ eV}$ . The same idea can be utilized to design a protective shield for photocathode. The photocathode protective shield must have a conduction band position in between  $0$  and  $-0.7\text{ V}$ , and band gap above  $3\text{ eV}$ . Other sets of perovskites structure having lower band gap and bandgap position do not straddle the water redox potential and could be utilized for two-photon water splitting in a tandem cell [348].

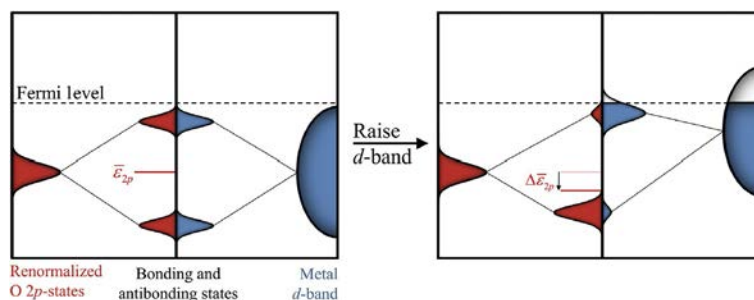
Another type of perovskites structure, also designed as a photoelectrode for water splitting is a prototype structure of  $\text{A}_2\text{BO}_3\text{N}$ ,  $\text{A}_3\text{B}_2\text{O}_7$ . The former is composed of  $\text{ABO}_3$  by slabs with oxygen atom that lies in its terminal position of the octahedra and separated by a layer of A metal atoms. In the latter structure,  $\text{A}_3\text{B}_2\text{O}_7$  is composed of two  $\text{BO}_6$  octahedra units, and the unit cell of both of these structures has 14 and 24 atoms, respectively [356].

Detailed theoretical analysis of the various possible perovskite structures and the data can be found elsewhere [357]. Most of the theoretical studies show that perovskites are

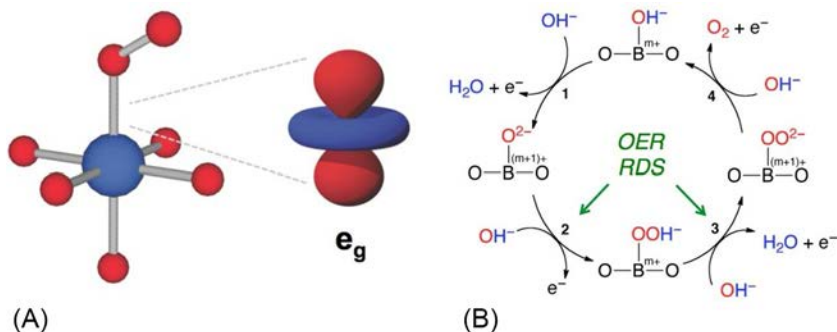
excellent candidates for overall water splitting. However, the question is how long it could be used in a real sense because the descriptor used here is the bandgap as well as band edge positions. The theoretical analysis does not consider the kinetics of the water splitting reaction. Also, the thermodynamic stability of the perovskite structure could be obtained from Pourbiax diagram [358], but in a real sense, the kinetic stability of the perovskites also has to be taken into account, and apparently, such kind of studies have not been reported yet.

In water splitting reaction, the major challenge is the sluggish kinetics of OER, and the state-of-the-art catalyst active toward this step is costly noble metal oxides. There are different options available, based on both theory and experimentation for oxygen evolution catalysis by perovskites. Theoretically, the activity of perovskites toward OER is mainly derived by adsorption energies of the reaction intermediates on the catalyst surface. Recent operando studies indicate that the catalyst surface behaves differently under reaction conditions so that the dynamic changes on the catalyst surface also have to be considered for the design of better catalysts [335].

The oxygen interaction to the surface of the perovskite is the crucial step because all the intermediates involved in the water oxidation reaction interact with the surface through the oxygen atom that leads to the formation of  $^*O$  or  $^*OH$ . The optimum binding of oxygen to the surface controls the overall rate of the reaction, which follows the Sabatier principle as shown in a volcano shaped-dependence toward the reaction rate (Fig. 12.16A). In perovskites, the surface-to-oxygen interaction energy correlated to the occupancy of d symmetry components such as  $t_g$  and  $t_{2g}$  (Fig. 12.16B) [353, 354].



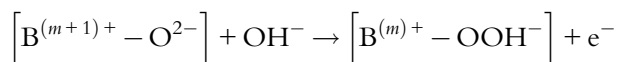
**Fig. 12.16** The schematic illustration represents the influence of metal d-band on the 2p state of oxygen on the transition metal surfaces. The O 2p-states couple to the metal d-band form a normalized 2p states. The formed oxygen O 2p-states couple with the metal d-band results in the formation of bonding as well as antibonding states (shown at left) projected either toward the oxygen 2p states or the metal d states (shown at left). The average energy ( $\bar{\epsilon}_{2p}$ ) of the bonding and antibonding states projected to the 2p state of the oxygen, represented using a red (gray in print version) horizontal line. (From J.K. Nørskov, F. Studt, F. Abild-Pedersen, T. Bligaard, *The electronic factor in heterogeneous catalysis*, in: J.K. Nørskov, F. Studt, F. Abild-Pedersen, T. Bligaard (Eds.), *Fundamental Concepts in Heterogeneous Catalysis*, John Wiley & Sons, Inc., Hoboken, New Jersey. <https://doi.org/10.1002/9781118892114.ch8>.)



**Fig. 12.17** (A) The geometry of  $e_g$  orbital in the octahedral-metal-oxygen complex. (B) The proposed mechanism of OER on perovskite transition-metal catalysts. *Reproduced with permission from J. Suntivich, K.J. May, H.A. Gasteiger, J.B. Goodenough, Y. Shao-Horn, A perovskite oxide optimized for oxygen evolution catalysis from molecular orbital principles, Science 334 (2011) 1383 LP-1385. ©2018 American Association for the Advancement of Science.*

More precisely, the contribution from the occupied valence and conduction bands out of which later is predominant. The occupancy of  $e_g/t_{2g}$  is due to the reactive sites present near to the Fermi level (interaction between oxygen  $2p$  level adsorbate and surface states near the Fermi level). The adsorption strength of oxygen to the surface of the perovskite depends on the occupancy of oxygen bonding and antibonding states (Fig. 12.16C); the interaction is too strong when the bonding states of the adsorbate fully occupied leaving the antibonding orbital unoccupied [353, 354].

Suntivich and coworkers derived a universal volcano dependence of the rate of OER to the oxygen binding strength of various perovskites structures (Fig. 12.17A) and found that the  $e_g$  filling in the transition metal cations ( $-B$  sites) shows (Fig. 12.17B) a pronounced influence on the surface stabilization of the OER intermediates which enhance the overall rate of the reaction [359]. The rate-determining step involves the formation of the  $\text{O}-\text{O}$  bond, followed by the proton absorption by the oxy-hydroxide group (Fig. 12.17E). The higher activity of perovskites toward OER also manifested using the covalency of  $-B$  sites and  $\text{O}-2p$  bonds (Fig. 12.17D) which enhances the charge transfer to the intermediates involved in the rate-determining step.



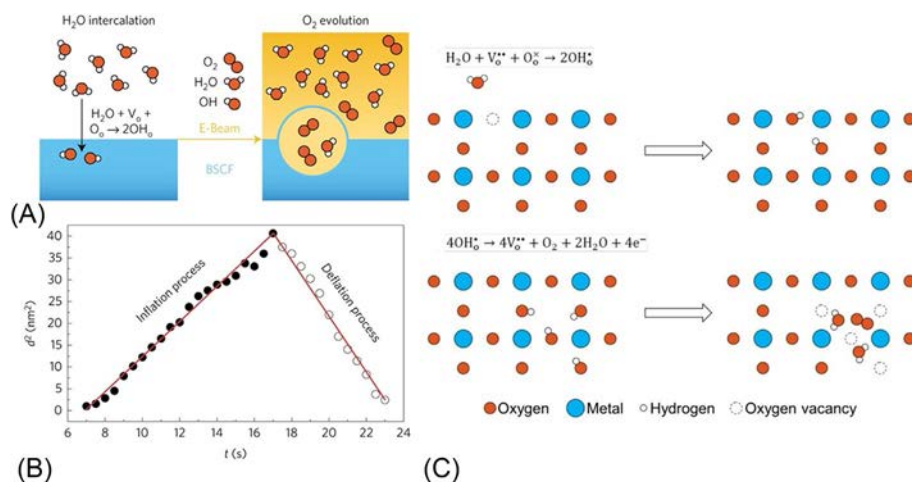
The increased oxygen evolution activity in the perovskite structure,  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ , can be attributed to the nanoscale structural oscillations and dynamic restructuring of the perovskite surface (Fig. 12.17C) under operando conditions [360]. The high oxygen non-stoichiometry that exists in the perovskite structure enables significant adsorption of water and the production of hydroxyl ions on the surface, which then diffuses to the bulk as a result of proton hopping between the neighboring oxide ions.



The high-energy electrons on the surface of BSCF ( $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ) [in situ environmental transmission electron microscopy (ETEM) study] can impart a positive potential approximately 2 V vs. SHE, which is considerably more significant than the oxygen evolution potential ( $E_{\text{OH}/\text{O}_2} = 0.82$  V vs. SHE (standard hydrogen electrode) @ pH 7), hence, it is evolved. In such cases, the water is also oxidized by the electron beam induced holes or by the oxygen from the perovskite lattice.

The oxygen vacancy generated during the reaction can be immediately replenished with the water uptake from the solution. This mechanism allows a continuous liberation of oxygen from the lattice, unique to the BSCF perovskite particles (Fig. 12.18). The accumulation of  $\text{O}_2$  in the BSCF lattice causes inflation of gas bubbles. The increased bubble size during the process makes the surface skin below some critical thickness to leak the oxygen gas molecule through the skin via the deflation process. These oscillation processes continue during the reaction and allow to capture more oxygen from the solution and reinflate again.

A first-order approximation can be used to explain the theoretical model of oxygen evolution in BSCF perovskite particles.



**Fig. 12.18** (A) A schematic representation of water incorporation accompanied by water splitting within BSCF particles, which leads to structural oscillations observed on BSCF in  $\text{H}_2\text{O}$  vapor under e-beam irradiation. (B) The plot of the square of the bubble size ( $d^2$ ) vs. the time ( $t$ ) during the first inflation process (filled) and the first deflation process (open) of particle A. The red lines (gray in print version) are a linear fit of the inflation and deflation processes, with  $R^2$  values of 0.98 and 0.99, respectively. (C) Water uptake process and the oxidation of hydroxyl group on lattice oxygen site into molecular  $\text{O}_2$  under the e-beam induced oxidative potential. (Reproduced with permission from B. Han, K.A. Stoerzinger, V. Tileli, A.D. Gamalski, E.A. Stach, Y. Shao-Horn, *Nanoscale structural oscillations in perovskite oxides induced by oxygen evolution*, *Nat. Mater.* 16 (2016) 121. ©2016 Macmillan Publishers Limited, part of Springer Nature.)

Considering the oxygen at the interface as an ideal gas,

$$P_{bubble} V_{bubble} = n_{O_2} RT$$

where  $P_{bubble}$  is the pressure inside the bubble and  $V_{bubble}$  is the volume of the bubble,  $n_{O_2}$  is the number of moles of oxygen present in the bubble, and  $R$  is the universal gas constant at a temperature  $T$ . In classic bubbles, the relation between  $P_{bubble}$  and the pressure in the transmission electron microscopy (TEM) ( $P_{TEM}$ ) and diameter ( $d$ ) of the bubble can be expressed as

$$P_{bubble} - P_{TEM} = \frac{4S_{BSCF}}{d}$$

Inside a TEM,  $P_{bubble} \gg P_{TEM}$ . Therefore,

$$P_{bubble} = \frac{4S_{BSCF}}{d}$$

Substituting the value of  $P_{bubble}$  in the former equation,

$$n_{O_2} = \frac{2\pi S_{BSCF}}{3RT} d^2$$

Assuming that oxygen evolution and oxygen leakage are the rates determining steps ( $\alpha_{OER}$  and  $\beta_{OER}$ ) in the inflation and deflation process, then one can express the relation as

$$\Delta n_{O_2} = \alpha_{OER} \Delta(t) \text{ for inflation process}$$

$$\Delta n_{O_2} = \beta_{OER} \Delta(t) \text{ for deflation process}$$

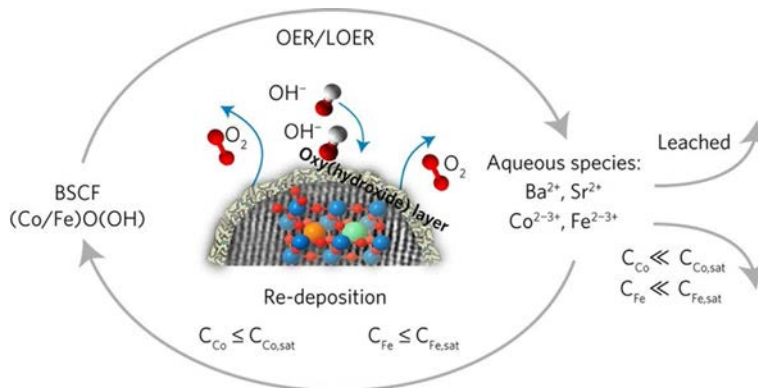
If one treats the oxygen evolution rate and deflation rate as constants, then we get

$$\Delta(n_{O_2}) = \Delta(t)$$

By combining the two equations formerly written, we can write as

$$\Delta(d^2) = \Delta(t)$$

In contradiction to the existing models of oxygen evolution based on the adsorption energies of the intermediates on the catalyst surface, recent experiments suggest a diverged approach toward the state-of-the-art according to the dynamic nature of the surface interface [335]. The experiment is based on the flexible, dynamic structural variation of BSCF perovskites under OER real-time conditions. At OER conditions, BSCF perovskites surface with high oxygen vacancy favors the formation of a highly OER active oxy(hydroxide) layer at the surface interface. The lattice oxygen evolution reaction (LOER) is responsible for the formation of highly OER active layer on the surface (Fig. 12.19). The  $OH^-$  ions present in the interface act as an oxygen refiller. These results



**Fig. 12.19** The LOER process leads to cation dissolution. Ba<sup>2+</sup> and Sr<sup>2+</sup> cations are highly soluble, and thus, they can readily leach out from the perovskite structure. LOER also triggers the dissolution of Co and Fe cations. However, being slightly insoluble species, Co and Fe redeposition on the catalyst surface can take place, especially when near the electrode surface, the cation concentration (due to the initial dissolution) becomes significant. Furthermore, the lattice oxygen consumed by the LOER can be replenished by OH<sup>-</sup> from the electrolyte. Therefore, a stable dynamic cycle is established, permitting the coexistence of a self-assembled active surface layer with the original BSCF perovskite structure. (Reproduced with permission from E. Fabbri, M. Nachtegaal, T. Binninger, X. Cheng, B.-J. Kim, J. Durst, F. Bozza, T. Graule, R. Schäublin, L. Wiles, M. Pertoso, N. Danilovic, K.E. Ayers, T.J. Schmidt, *Dynamic surface self-reconstruction is the key of highly active perovskite nano-electrocatalysts for water splitting*, *Nat. Mater.* 16 (2017) 925. ©2018 Macmillan Publishers Limited, part of Springer Nature.)

suggest that the dynamic changes happening in the operando conditions are the real responsible factors and the intermediate formation and its interaction with the oxy(hydroxide) layer should be considered to describe the OER reaction experimentally as well as theoretically.

The modification of the surface and structural property of BSCF by A-site praseodymium-doping could tune the perovskite oxide as an efficient catalyst toward hydrogen evolution [361]. The overpotential required in the case of Pr<sub>0.5</sub>(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3- $\delta$</sub>  (Pr<sub>0.5</sub>BSCF) is almost 100 mV less than that of the BSCF at a current density of 10 mA cm<sup>2</sup> and a Tafel slope of 45 mV dec<sup>-1</sup>. Although the values do not match even with the Pt/C catalyst, the activity is comparable with other non-platinum HER catalysts such as bulk MoB, Mo<sub>2</sub>C, C<sub>3</sub>N<sub>4</sub>@NG, CoO@CN, NiFe LDH, and metallic Ni in the basic medium [362]. However, the stability of the praseodymium-doped BSCF is only up to a day, which is the main drawback of the electrocatalyst.

The flexibility of the inorganic oxide perovskite structure toward surface restructuring and modification allows tuning the electrical as well as optical properties of the material toward water splitting. The main problem to be addressed is to prolong the stability of

material under dynamic conditions and incorporation of BSCF perovskite oxide system into the PEC cell.

## 12.7 Prospects on photodecomposition of water decomposition

A semiconductor photoelectrode in contact with an electrolyte develops an inherent internal electric field at the interface because of the charge redistribution across the interface called Fermi level equilibration. The resultant band bending affects charge carrier transfer that follows, through the interface. Also, it alters the redox properties of the surface of the semiconductor because the change in the Fermi level will change the density of states of the semiconductor. The band position that we use to interpret the result is in the free state of the semiconductor and not at the interface. The interfacial band alignment will be different from that in the free state, which is yet to be determined with the help in situ techniques.

The fundamental problem associated with water decomposition process is the lack of understanding of the real-time semiconductor/electrolyte interface in the presence of an optoelectrical field [363]. The irradiation of light with appropriate wavelength matching to the band gap of the photoelectrode causes a charge carrier transition from the valence band to conduction band states. That means the net charge density is altered during the illumination process, and therefore, the field gradient present at the interface also will change accordingly. More precisely, the photoexcitation changes the conduction band wave functions contributed by the d orbital of the metal ions and the valence band wave functions which are added by the p orbital of the oxide ions, in the case an oxide photoelectrode system. The loss of an electron from the valence band may change its binding energy and will cause an expansion of the valence band states to a more negative value or less positive values. At the same time, the addition of electrons to the conduction band may shift its position to more negative values. This might give an explanation of the increased pace of hydrogen evolution than that of the stumbling block oxygen evolution. These assumptions infer that the interface would behave differently in the presence and absence of a photon field. So, the net alteration in the charge density could alter the surface interaction with water. Then, we need to consider the further effect of the applied bias on the photon-induced changes. The externally applied bias also changes the net charge density of the photoelectrode which would have a profound impact on the field gradient present (Garrett Brattain space charge region) in the electrolyte side as well as in the semiconductor side [363].

The accumulation of the species such as charge carrier or others at the interface changes the wave function overlap between the water molecule and the photoelectrode under equilibrium conditions. This may change as a result of the introduction of the optoelectrical field. These may include the change in the density of states, photoadsorption capacity, and perturbation of the surface states. These changes influence

the other factors such as refractive index, dielectric constant, and the capacity of the double layer formed across the interface.

The change in the density of states at the interface under the optoelectrical field could change photo-adsorption behavior. Any displacement in the Fermi level or the nature band curvature or both get simultaneously altered, the sign of the photo-absorption effect at the interface gets reversed [364].

Theoretically, the mapping of the interaction of the defect sites with the substrate (water) wave functions would be complicated because of the difficulty in tracing the wave function overlap regarding contour maps. Also, the nature of the frontier wave function of the defect states will be different from that of the semiconductor surface. The theoretical treatment in this regard will give only a rough estimate of the eigenvalues and eigenfunctions of the frontier orbitals. The lack of knowledge in this regard may be the central obstruction in the theoretical design of the suitable materials.

While we follow the thermodynamics of water splitting, the kinetic factors involved therein are not considered. The changes in the band alignment only reflect the free change and not the kinetics of the gas evolutions at the interface. The evolution of gas from the surface depends on a variety of steps such as the formation of the molecule from the atomic species, bubble formation, and desorption of gas from the surface. Any of these processes may be rate-determining step which is beyond the control of electron transfer steps. Accordingly, we need to reconsider whether the bandgap engineering alone is the correct footstep we took toward the development of photoelectrodes. Also, the materials design should consider the environmental factors such as the electrolyte ionic strength, composition, and pH, which affect the water splitting reaction.

## 12.8 Conclusion

The photoelectrocatalytic water decomposition continues to be a primary research area in the past five decades. Even though significant advances have been registered, still the efficiency of the process is too low for a commercial level utilization of the process. The knowledge on the nature of interface formed under the optoelectrical at the semiconductor/electrolyte junction is still in infancy. The dynamic nature of the interface has to be tackled precisely for the better treatment of the overall water splitting process. Besides the conventional bandgap engineering approach to increase the photo-response of the process thermodynamic as well as kinetic aspects of the process are to be addressed in detail. There is an urgent need for the design of in situ techniques that can visualize the changes at the interface under the photon and electric field. Reframing the sentences of G N Lewis again; it is not the semiconductor, but the semiconductor in the excited state/ at the interface causes a PEC cell to operate. Without the knowledge on the dynamic nature of the interfaces, the field of water splitting can no longer be improved.

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