Review Article
Perovskite semiconductors for photoelectrochemical water splitting applications

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Perovskite oxide semiconductors have been used as efficient electrocatalysts for electrochemical reactions using an external applied bias. The review describes the different alternatives to use perovskite materials as photoelectrocatalysts for the conversion of solar energy into chemical bonds. The main requirements for a photoelectrochemical configuration are first discussed. Recent development in lead halide perovskite for photovoltaic applications has improved the understanding on the design rules that link chemical compositions with electrical and optical properties. It is shown that some recent literature examples using metal oxide perovskites support the validity of the design rules. The different alternatives in device configurations are discussed in terms of stability of the perovskite material.

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Introduction

The conversion of solar energy into chemical bonds using visible light absorbing semiconductors (SCs) is a major goal toward a society sustained by low carbon, clean and renewable energy. Photoelectrochemical (PEC) generation of fuels with SC materials offers a versatile strategy to efficiently capture and store the solar energy incident on the earth crust [1]. One of the most interesting approaches entails the utilization of solar photon to realize the reduction of water to H_2 or CO_2 to carbon-based molecules. In order to efficiently carry out these processes, an energy conversion device based on visible light absorbing

SCs that will capture solar photons and use them to carry out the required electrochemical reactions must be developed, e.g., oxygen evolution reaction (OER) for water oxidation and hydrogen evolution reaction (HER). Suitable SC materials must satisfy stringent conditions in terms of cost, stability under operating conditions, light absorption in the visible range, adequate alignment of band edges with the relevant redox potentials and overall efficiency. This is a major scientific and technological challenge and at the current date a single material has not been identified to accomplish all the requirements [1].

Perovskite oxide SCs have been used as efficient electrocatalysts for HER and OER promoted by the use of an external applied bias [2]. More recently, modification of the electrical properties of the SCs has allowed the generation of photoelectrocatalysts able to carry out HER/OER reactions induced by solar energy. In addition, the recent development in lead halide perovskite for photovoltaic applications has improved the understanding on the design rules that link chemical compositions with electrical and optical properties. The current review will focus on the requirements to convert solar energy into a fuel in a PEC configuration. In addition, recently published articles suggest that perovskite materials are adequate candidates to provide high solar to fuel efficiencies in different device configurations.

Requirements for PEC cells

There are several alternative systems to develop a low cost efficient device for the conversion of sunlight into chemical fuel. In all cases, the process relies on the capture of the solar energy by a SC that absorbs solar photons exciting carriers, which can be transported to the active reaction site where the desired chemical reaction will take place as shown in Figure 1a. Several redox reactions can be promoted such as OER for water oxidation and HER for H^+ reduction to gas molecules. This fundamental operation principle poses the main constraints to the SC properties. The extended energy levels carrying electron and holes limited by the conduction band (CB) and valence band (VB), respectively, must realize separately the two reactions. Separation in energy space, given by the SC band gap, facilitates adequate driving forces for performing the reactions.

With large band gaps the separation of electron and holes Fermi levels is facilitated, obtaining large photovoltages. However, a large band gap decreases the range of spectral

Figure 1
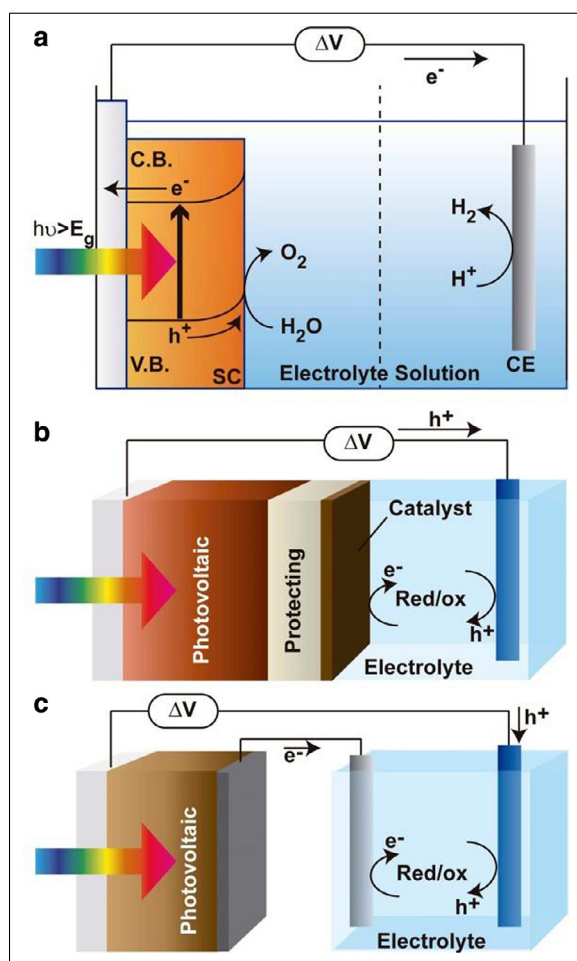
Representative device configurations to convert solar energy into a fuel. a) Photoelectrochemical configuration. b) Semiconductor or photovoltaic device with a buried junction. c) Photovoltaic device coupled with an electrolyzer.

match with the solar irradiation. Hence, the large voltage obtained by the use of large band gap SC is accompanied by low photocurrents. As the output power is a product of photocurrent and photovoltage, there exists a value of about 1.1 eV that produces optimal electrical output, as calculated by Shockley–Queisser (SQ) approach, [3] that assumes additional optimal characteristics as minimal recombination and unity internal quantum efficiency. On the other hand, the PEC generation of fuel with a SC material poses somewhat different requirements than photovoltaic production of electricity. The SC band gap must be sufficient to exceed the difference of free energies of the desired reaction, including the overvoltage required by the given surface catalysts. For example, for the water splitting reactions resulting in hydrogen and oxygen evolution a voltage of about 1.8 eV is required as the result of the required free energy (1.23 eV) and the overpotential (0.4–0.6 eV). The second essential requirement that

marks a contrast with electricity production photovoltaics is the necessary contact of the system with the active electrolyte in which effective catalysts must carry out the fuel-producing reactions. This feature poses the need for stability at the reaction site that will determine the different device configurations schematically shown in Figure 1.

Interplay between SC stability and device complexity

In a first configuration the SC can be directly placed in the electrolyte solution to carry out a reaction photoelectrochemically whilst at the counterelectrode the complementary reaction is catalyzed by an electrocalalyst (Figure 1a). However, photocorrosion of SCs has long been discussed as a critical problem in PEC cells. It was shown that when the anodic (or cathodic) corrosion potential lies within the band gap, photocorrosion is competitive with water oxidation (or reduction). In these cases, the potential of the SC corrosion reaction is typically less energetic and thus thermodynamically more favorable than the HER/OER reaction, leading to unstable photoelectrodes [4]. For example, it has been shown that SCs such as Si, ZnO, Cu_2O or some binary metal sulfides are not stable in extreme pH electrolytes and/or at high oxidative or reductive potentials [5]. Alternatively, some metal oxides are kinetically stable under highly oxidizing conditions and some non-oxide SCs are kinetically stable to the reduction of photogenerated electrons [6].

Unstable SCs for a given chemical reaction require more complex device configurations. The use of a combination of semiconducting materials is typically described in a Z-scheme photocatalysis in which oxide materials like $SrTiO_3$, WO_3, $BiVO_4$, or Fe_2O_3 suitable for OER can be combined with chalcogenides containing CuI ions, such as $CuGaSe_2$, Cu_2ZnSnS_4, and $Cu(Ga,In)(S,Se)_2$, that are suitable for HER [7]. A second approach aims at converting photovoltaic devices into a PEC cell by using protecting layers to avoid the chemical reaction of the liquid solution with the materials used in the photovoltaic device (Figure 1b). In this case an additional catalytic layer may be needed to carry out the desired reaction, i.e. Pt for hydrogen production. Intensive research started protecting SCs using relatively thick layer of TiO_2 applied to Si, GaAs, GaP, or CdS single crystals and, more recently, very thin layers in the order of a few nanometers [8–9]. Several examples where stability of SCs has been enhanced by the use of protection layers can be found in the literature [10–12]. In addition, different photovoltaic technologies have been turned into PEC configuration by using protective layers including CIGS [13] and organic photovoltaic (OPV) [14, 15]. However, as far as we know this approach is totally unexplored for perovskite materials.

Oxide-based perovskite materials with the structure ABO_3 have been reported as stable and suitable materials as electrocatalyst for OER as shown in Figure 2a [2,16].

Figure 2
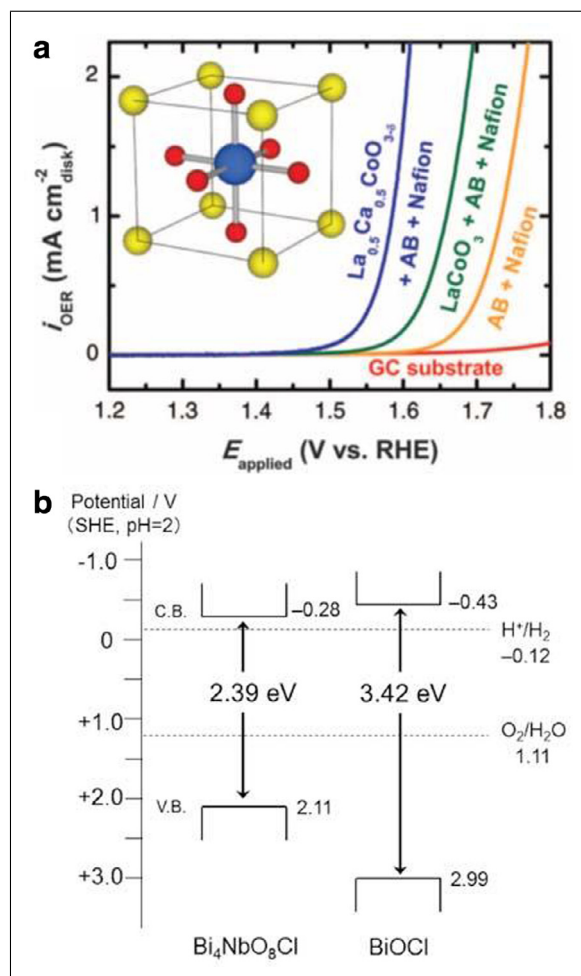
a) Exemplary OER currents of $La_{1-x}Ca_xCoO_3$ and $LaCoO_3$ thin films on GCE in O_2-saturated 0.1 M KOH and perovskite crystal structure (inset). Figure reproduced with permission from ref. [16]. b) Energy level diagram of perovskites based on Bi-oxides showing different electronic properties as a function of the composition. Reprinted with permission from ref. [17].

In the crystal structure, A is an alkali or a rare earth that is located at the vertices of a cube, B is a transition metal centered in the cube and O is oxygen that coordinates B generating octahedras. Suntivich *et al.* reported 10 different metal oxides that are active as OER such as $LaCoO_3$, $LaMn_{0.5}Cu_{0.5}O_3$ or $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$. Among these, the later material is the most active one showing intrinsic activity that is at least an order of magnitude higher than that of the state-of-the-art iridium oxide catalyst. This material is produced by a high temperature process (1100 °C during 24 h) yielding thermodynamically stable materials. In addition, a general theoretical method to design catalyst with reduced required overpotential to carry out the OER reaction was described. This is based on the occupancy level of the 3d electron with

an e_g symmetry of surface transition metal cations in an oxide. As a first approach these oxide perovskites could potentially be used as the catalyst shown in Figure 1b in a PEC cell configuration.

With these impressive catalytic activities the question is whether this type of electrocatalysts can be chemically modified to provide energy levels adequate to be used as photoelectrocatalysts. Recently, lead halide perovskites in the formulation ABX_3 have been studied as efficient SCs for photovoltaic applications and extensive studies have been focused to understand the connection between structural composition and the electronic properties. The effect of each of the cations and anions in the perovskite has been systematically studied. A detailed discussion is complex and here it is intended to provide general design rules [18]. First, the cation A mainly contributes to the structural part maintaining the integrity of the perovskite phase. Thus, the size is crucial to fill the gaps left by the octahedra generated in the center by the cation B and in each vertex an X anion. Although the cation A does not contribute to the band structure, the size affects the symmetry of the octahedron and the overlap between bands B and X. Thus, using a cation BXB a greater angle is closer to a linear configuration by increasing the overlap of the orbitals between BX and the band gap becomes smaller. For example, the band gap follows this trend $FAPbI_3 < MAPbI_3 < CsPbI_3$. Furthermore, the anion X contributes more to the electronic part as it contributes in overlapping bands of frontier orbitals. Very importantly, it appears that the design rules that determine the electronic properties of lead halide perovskites also seem to be applicable to different oxide materials. In particular, $BaNiO_3$, Bi_4NbO_8Cl and $BiOCl$ have been shown to be suitable photocatalytic materials [17,19]. The band gap depends very much on the size of the cation, becoming smaller with the use of the smaller Nb cation (72 pm) in comparison to Bi (103 pm) from 3.42 eV for $BiOCl$ to 2.39 eV for Bi_4NbO_8Cl (Figure 2b). Similarly, if the chloride in $BiOCl$ is replaced by a more electronegative and bulky Br, a shift of about 100 nm is observed in the absorption spectra indicating that the band gap for $BiOBr$ ($\approx$2.85 eV) is smaller than for $BiOCl$. Overall, it appears that there exist two set of design rules to improve optical, electronic and catalytic abilities of the perovskite materials.

The highly demanding requirements of PEC can be relaxed by placing a photovoltaic device outside the electrolytic solution while the catalytic fragment will be in direct contact with water (Figure 1c). Both portions of the device are connected by a wire. By using this approach the photovoltaic part does not need to be solvent/water resistant and the catalytic fragment of the system does not need to offer good optical properties, i.e. fulfill all the band gap requirements. Indeed, a PV device connected to an electrolyzer electrode is taking the lead in solar

hydrogen research [20]. Using this approach we find a lead halide perovskite photovoltaic device the solar to hydrogen efficiency world record of 12.3% achieving stable photocurrents of $\approx 10 \, \text{mA/cm}^2$ for the production of H_2/O_2. In order to achieve this record, two hybrid perovskite solar cells containing the cation methyl ammonium and lead halides are connected in series in a tandem configuration. In addition, an electrolyzer is connected by an external wire with an electrode containing earth-abundant catalysts like NiFe-LDH which carries out the desired electrochemical reaction [21]. Similarly, monolithic tandem solar cells based on lead halide perovskites and $BiVO_4$ have also been described with photocurrents of $\approx 2 \, \text{mA/cm}^2$ for the production of H_2/O_2 [22]. In this respect, tandem devices where the bottom cell is based in crystalline silicon and the top cell a perovskite device offer up to 19.9% incident light to electron efficiency seems promising for water splitting applications. In particular a photocurrent of $14 \, \text{mA cm}^2$ and voltage of 1.78 V may suffice to efficiently carry out the water splitting reaction. These results highlight the enormous potential of perovskite materials for solar fuel generation.

Conclusions and outlook

Perovskite materials are adequate electrochemical catalysts using external applied bias. Recently, the design rules that connect chemical composition and electronic properties have been studied for lead halide perovskites. These design rules seem to be applicable for more robust metal oxide perovskites enabling their use in the PEC configuration. For more reactive perovskite materials, alternative routes to provide PEC applications are discussed. These include the use of protective layers, relatively unexplored for perovskites, or the combination of a photovoltaic device and electrolyzer. The use of lead halide perovskite solar cells in the later configuration currently delivers the highest reported solar to hydrogen efficiency.

Acknowledgments

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- • Paper of special interest
- •• Paper of outstanding interest.

1. Gimenez S, Bisquert J: *Photoelectrochemical Solar Fuel Production. From Basic Principles to Advanced Devices*. Springer; 2016.

2. Peña MA, Fierro JLG: **Chemical structures and performance of perovskite oxides**. Chem Rev 2001, **101**(7):1981–2018.

3. Shockley W, Queisser HJ: **Detailed balance limit of efficiency of p–n junction solar cells**. J Appl Phys 1961, **32**:510–519.

4. Chen S, Wang L-W: **Thermodynamic oxidation and reduction potentials of photocatalytic semiconductors in aqueous solution**. Chem Mater 2012, **24**(18):3659–3666.

5. McCafferty E: *Introduction to Corrosion Science*. New York: Springer-Verlag; 2010.

6. Khaselev O, Turner JA: **A monolithic photovoltaic–photoelectrochemical device for hydrogen production via water splitting**. *Science* 1998, **280**(5362):425–427.

7. Hisatomi T, Kubota J, Domen K: **Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting**. Chem Soc Rev 2014, **43**(22):7520–7535.

8. Hu S, Shaner MR, Beardslee JA, Lichterman M, Brunschwig BS, Lewis NS: **Amorphous TiO_2 coatings stabilize Si, GaAs, and GaP photoanodes for efficient water oxidation**. *Science* 2014, **344**(6187):1005–1009.

9. Kohl PA, Frank SN, Bard AJ: **Semiconductor electrodes: XI. Behavior of n- and p-type single crystal semiconductors covered with thin films**. J Electrochem Soc 1977, **124**(2):225–229.

10. Liu R, Zheng Z, Spurgeon J, Yang X: **Enhanced photoelectrochemical water-splitting performance of semiconductors by surface passivation layers**. Energy Environ Sci 2014, **7**(8):2504–2517.

11. Paracchino A, Laporte V, Sivula K, Grätzel M, Thimsen E: **Highly active oxide photocathode for photoelectrochemical water reduction**. *Nat Mater* 2011, **10**(6):456–461.

12. Morales-Guio CG, Tilley SD, Vrubel H, Gratzel M, Hu X: **Hydrogen evolution from a copper(I) oxide photocathode coated with an amorphous molybdenum sulphide catalyst**. *Nat Commun* 2014, **5**:3059.

13. Kumagai H, Minegishi T, Sato N, Yamada T, Kubota J, Domen K: **Efficient solar hydrogen production from neutral electrolytes using surface-modified $Cu(In,Ga)Se_2$ photocathodes**. J Mater Chem A 2015, **3**(16):8300–8307.

14. Guerrero A, Haro M, Bellani S, Antognazza MR, Meda L, Gimenez S, Bisquert J: **Organic photoelectrochemical cells with quantitative photocarrier conversion**. Energy Environ Sci 2014, **7**(11):3666–3673.

15. Haro M, Solis C, Molina G, Otero L, Bisquert J, Gimenez S, Guerrero A: **Toward stable solar hydrogen generation using organic photoelectrochemical cells**. J Phys Chem C 2015, **119**(12):6488–6494.

16. Suntivich J, May KJ, Gasteiger HA, Goodenough JB, Shao-Horn Y: **A perovskite oxide optimized for oxygen evolution catalysis from molecular orbital principles**. *Science* 2011, **334**(6061):1383–1385.

17. Fujito H, Kunioku H, Kato D, Suzuki H, Higashi M, Kageyama H, Abe R: **Layered perovskite oxychloride Bi_4NbO_8Cl: a stable visible light responsive photocatalyst for water splitting**. J Am Chem Soc 2016, **138**(7):2082–2085.

18. Yusoff ARbM, Nazeeruddin MK: **Organohalide lead perovskites for photovoltaic applications**. J Phys Chem Lett 2016, **7**(5):851–866.

19. Lee JG, Hwang J, Hwang HJ, Jeon OS, Jang J, Kwon O, Lee Y, Han B, Shul Y-G: **A new family of perovskite catalysts for oxygen-evolution reaction in alkaline media: $BaNiO_3$ and $BaNi_{0.83}O_{2.5}$**. J Am Chem Soc 2016, **138**(10):3541–3547.

20. Brillet J, Yum J-H, Cornuz M, Hisatomi1 T, Solarska R, Augustynski J, Graetzel M, Sivula K: **Highly efficient water splitting by a dual-absorber tandem cell**. Nat Photonics 2013, **6**:2012.

21. Luo J, Im J-H, Mayer MT, Schreier M, Nazeeruddin MK, Park N-G, Tilley SD, Fan HJ, Graetzel M: **Water photolysis at 12.3% efficiency via perovskite photovoltaics and Earth-abundant catalysts**. *Science* 2014, **345**(6204):1593–1596.

22. Chen Y-S, Manser JS, Kamat PV: **All solution-processed lead halide perovskite-$BiVO_4$ tandem assembly for photolytic solar fuels production**. J Am Chem Soc 2015, **137**(2):974–981.