

# Materials for renewable fuels production

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“Global warming of 1.5 °C to 2 °C will be exceeded during the 21st century unless deep reductions in CO<sub>2</sub> and other greenhouse gas emissions occur in the coming decades” states the United Nations Intergovernmental Panel on Climate Change (IPCC) in its Sixth Assessment Report.<sup>1</sup> In the recent years, IPCC published several reports and presented undisputable evidence associating greenhouse gas accumulation in the atmosphere with global average surface temperature increase and unprecedented changes in the weather patterns and the Earth’s ecosystems. The fact that the three climate scientists, Syukuro Manabe, Klaus Hasselmann, and Giorgio Parisi, who pioneered the studies relating climate change with greenhouse gases in the atmosphere and human activities, were awarded Nobel Prize in Physics in 2021 shows the relevance of the topic and the impact of their work on shaping a sustainable future.

The global average surface temperature has reached ~1.0 °C above the pre-industrial levels, and the consequences are already becoming apparent. Realizing the magnitude of the everlasting problems that the temperature rise would bring, the oil and gas companies have included aggressive measures in their business portfolio for carbon management and made decisions to achieve net zero emission by 2050. Many countries have intensified efforts to make a transition to low carbon or carbon-free fuels to achieve this target. The Hydrogen Shot program introduced in 2021 by the United States Department of Energy (US DoE) is an example. The goal of the program is to reduce the cost of hydrogen by 80% and achieve \$1 per 1 kilogram in 1 decade (also called “111”). Renewable energy based water splitting and low carbon pathways with effective measures for carbon management are being promoted for hydrogen generation.

Water splitting and carbon dioxide reduction are the prominent strategies pursued for fuel generation using renewable energy.

Electrochemical, thermochemical, photocatalytic, photoelectrochemical (PEC), biomass, biophotolysis, and hybrid approaches are being explored extensively for utilizing renewable energy to achieve low carbon emission. Although a few biomass-based technologies are mature and commercially used world-wide for fuel production, the biomass approaches are primarily limited by low sunlight-to-biomass conversion efficiency.

Water electrolysis is a mature electrochemical technology that has been commercially deployed to split water for hydrogen production for over a century. Nonetheless, grid electricity is commonly used to power the plants. Water electrolysis efficiency, defined as the ratio of the high heating value of hydrogen to the electrical energy consumed to generate it, as high as 98% have been reported.<sup>2</sup> The current interest is in drawing electric power generated from renewable energy sources, such as sunlight, wind, and geothermal, to operate the electrolyzers. The overall efficiency of electrolytic hydrogen production is primarily limited by the efficiency of the system that powers it. For example, with a solar module efficiency of 20% (ratio of electrical power output to solar power input), a polymer electrolyte membrane (PEM) electrolyzer operating at an efficiency of 80% can produce hydrogen at a solar to hydrogen (STH) efficiency of 16%. An efficiency in this range can be practically achieved by PEC as well as solar thermochemical approaches, but without employing an external electric power system. While commercial scale renewables powered electrolytic hydrogen production plants have been demonstrated, the two promising direct solar to fuel conversion technologies, PEC and thermochemical, have not yet reached the commercialization stage. Nevertheless, successful attempts have been made recently to scale up these processes.<sup>3,4</sup>

The H<sub>2</sub>O/CO<sub>2</sub> to fuel conversion reactions are energy intensive and efficient catalysts are inevitable to carry out the reactions at the

required high rates and under manageable operating conditions. For the commercial viability and sustainability of a technology, the catalysts should be efficient, affordable, stable for long-term operation, providing scalable fabrication methods and composed of earth abundant elements. Challenges in materials development are different for different technologies. Replacing noble metals with low-cost materials as electrocatalysts, finding stable and efficient photocatalysts, and developing catalysts that do not undergo sintering/deactivation at high temperatures are a few important challenges, respectively, in electrochemical, PEC, and thermochemical fuel generation technologies. Recent innovations in the materials and fabrication technologies, discovery of their unique physicochemical properties, and the enhanced scientific understanding obtained from fundamental studies show promise for addressing some of the challenges. The advent of novel two-dimensional (2D) materials with unique electrical, optical, and thermal properties is just an example. In order to capture in a timely manner the advances in this cutting edge area, particularly in the physics of such materials applied to the renewable fuel generation processes including solar water splitting, carbon dioxide conversion, and their hybrids using different forms of renewable energy, *Applied Physics Letters* launched this special collection.

This special collection published 35 articles in the 2021–2022 period from many more received, which shows the current relevance of the topic. The collection covers developments in the experimental as well as computational/numerical simulation studies on materials for thermochemical, electrochemical, photocatalytic, and photoelectrochemical fuel generation. We discuss below the highlights of the articles in this special collection.

Thermochemical water splitting was originally envisaged to utilize the waste heat from nuclear power plants. Later it became a promising approach to convert concentrated solar energy to chemical energy. In the second half of the 20th century, several multi-step processes were developed to reduce the operating temperature of water splitting (a single step process requires a temperature over 4300 K for 100% conversion and above  $\sim 2000$  K for partial splitting). The current research focus is on concentrated solar two-step cycles as they offer the most efficient way to practically utilize concentrated sunlight (theoretical efficiency for redox-based two-step solar thermochemical cycles is in excess of 35%) and recently emerged redox materials that can function at manageable temperatures. The process can produce synthesis gas (syngas), a mixture of  $H_2$  and CO, if water and carbon dioxide are fed to the solar reactor system. The syngas can be a feedstock for Fischer–Tropsch process to produce liquid fuels. In a two-step cycle, a redox material, typically a binary oxide, is reduced to a metallic or oxygen deficient (non-stoichiometric) state at high temperatures and then exposed to water vapor or carbon dioxide or both where the catalyst gets oxidized with the formation of hydrogen and CO. ZnO is an example of a material that goes to metallic state during reduction. Cerium oxide (ceria;  $CeO_2$ ) is currently the most promising material in the category of materials that undergo transition to a non-stoichiometric oxide state during the reduction process. The non-stoichiometric materials outperform the stoichiometric oxides in terms of yield and lower process temperature in thermochemical processes. In their article, Lenarduzzi and Cooper analyzed the solid-state entropy change in stoichiometric and non-stoichiometric oxides during the reduction process.<sup>5</sup> Their study revealed that all non-stoichiometric oxides, ceria in particular, are uniquely benefited by a

large positive solid-state entropy change arising from the substantial configurational entropy change associated with the oxygen vacancy (reduced cation) formation. Their theoretical explanation for the superior performance of the nonstoichiometric oxides would be a foundation for the invention of new materials.

Abanades *et al.* developed a process involving ion-exchange resins to fabricate unique ceria microspheres with porosity 36% for syngas production from  $H_2O$  and  $CO_2$  feeds.<sup>6</sup> Their experiments using concentrated sunlight showed that individual spherical particles with well-defined geometry and micrometer-scale pores would increase the fuel production rate significantly in comparison with already explored ceria granules and reticulated foams. Furthermore, the catalytic activity of the material did not decline substantially although the material was subjected to 19 redox cycles between 1400 and 1050 °C or below for five days. Instead of  $H_2O$ , dry methane could be used along with  $CO_2$  to produce syngas and this way, one could address the issues associated with both  $CH_4$  and  $CO_2$ , if  $CH_4$  is biogenic. Nevertheless, the replacement of expensive noble metal catalysts with cheaper alternatives remains a challenge in the field. An example of such an alternative material is nickel; however, it quickly undergoes deactivation and agglomeration under thermochemical conditions. In order to address this problem, Wells *et al.* developed an *in situ* process to fabricate well dispersed  $xCeO_2-(1-x)Ni(OH)_2$  bimetallic nanoparticles (size  $\sim 1.6$  nm) inside mesoporous (3 nm) silica cages.<sup>7</sup> The catalyst was highly stable for over 50 h of high-rate stoichiometric production of syngas at 900 °C. The protection given by the silica encapsulation was critical to the stability of the catalyst.

Water electrolysis has been used as a commercial process for hydrogen production. The three primary electrolyzer technologies are named alkaline, polymer electrolyte membrane (cation or anion exchange membranes), and solid oxide based on the electrolyte used. Alkaline electrolyzers are the conventional types. While alkaline and PEM electrolyzers are used for commercial-scale hydrogen production, solid-oxide electrolyzers are in the demonstration/pilot-plant stage. The current emphasis in the field is to reduce the cost of electrolytic hydrogen by reducing the use of noble metals while minimizing the overpotential losses and maximizing the current density. Recent efforts have been targeted at enhancing the performance and durability of advanced electrolyzers. For example, regular PEM electrolyzers operate typically at a pressure near 30 bar; however, Zhang *et al.* demonstrated that hydrogen could be produced at elevated pressures if the membrane electrode assembly design could be improved.<sup>8</sup> They developed a noble metal catalyst coated proton exchange membrane-electrode assembly and evaluated the performance in a 56 cell, 20 kW PEM electrolyzer. This membrane-loaded cell stack could operate at 1.785 V (efficiency 82.9%) with a current density of 1 A/cm<sup>2</sup> at 70 °C and produce hydrogen at a rate of 3.09 m<sup>3</sup>/h (normal) at 50 bar. Conventional and PEM water electrolyzers use strong alkaline or acidic electrolytes, which are corrosive. Shteplyuk *et al.* reported that a monolayer epitaxial graphene on a 4H-SiC substrate loaded with ultrathin silver islands would be promising as a cathode material for hydrogen evolution reaction (HER) at neutral pH ( $\sim 7$ ).<sup>9</sup> The study showed that the onset potential became less negative and the current density became high (low overpotentials) with the loading of silver nano-islands. The authors attributed the improved performance at neutral pH to the strong coupling between water reduction reaction on Ag nano-islands (thickness 2 nm, diameter 31 nm) and underlying

graphene as well as to strained graphene in the Ag free region, facilitating increased binding and charge transfer with water molecule.

Oxygen evolution reaction (OER) is a four-electron process and is thermodynamically more challenging than HER. Typically, iridium oxide or ruthenium oxide is used as the OER electrocatalyst. Nonetheless, such materials make the technology cost prohibitive. Layered double hydroxides (LDH) are cheaper and promising. Nevertheless, their stacking geometry limits the concentration of active sites and conductivity. Wang *et al.* addressed the problem by fabricating a 3D flower shaped core-shell structure on nickel foam.<sup>10</sup> The core-shell structure consisted of CoFe-PBA (Prussian blue analog) as the core and NiCoFe-layered ternary hydroxide nanosheets as the shell. This structure exposed spatially separated active sites to the electrolyte species and provided facile electron transport pathways leading to reduced Tafel slope and increased stability of the material as an OER catalyst in an alkaline medium. Cao *et al.* substituted Co in LaCoO<sub>3</sub> with Mn to achieve appropriate electron spin orientations and promote the electron transfer between the catalyst and the OER reaction intermediates.<sup>11</sup> About 25% substitution enabled the transfer of Co<sup>3+</sup> from a low spin state to a high spin state enhancing the hybridization between Co *e<sub>g</sub>* and O *2p* states near the Fermi level and thereby helping the transition of the material from a semiconductor to a half-metal with enhanced OER performance. Yang *et al.* discovered that VO<sub>x</sub> doping in a NeFe layer coated on a porous nickel cobalt phosphide (NiCoP) electrocatalyst supported by a titanium mesh would reduce the overpotential for both OER and HER.<sup>12</sup> This modified electrocatalyst could be employed as a low-cost bifunctional catalyst to construct both the positive and negative electrodes in an electrolyzer.<sup>12</sup> The doping with VO<sub>x</sub> made the NeFe surface superhydrophilic. It also increased the active surface area and concentration of oxygen vacancies. In a 1 M KOH electrolyte, the overpotentials measured at a current density of 10 mA/cm<sup>2</sup> were 45 and 215 mV, respectively, for HER and OER.

BiVO<sub>4</sub> is a known photocatalyst; however, the work of Mir *et al.* showed that it could function as an electrocatalyst upon tuning the morphology appropriately.<sup>13</sup> They found that the morphology had more influence on the electrocatalytic properties compared to the defect states and vacancies. A low OER overpotential of 170 mV at 10 mA/cm<sup>2</sup> was achieved. The material also showed potential for capacitive charge storage with high columbic efficiency.

While electrolyzers split water to hydrogen and oxygen, in a fuel cell these gases are combined to form water with the production of electric power. Avoiding noble catalysts and reducing overpotential losses are important for fuel cells as well. Co-N<sub>x</sub> embedded graphene has been identified by several research groups as an active low-cost catalyst for oxygen reduction reaction (ORR) at the cathode of a proton exchange membrane fuel cell. Li *et al.* report the stable adsorption configurations and adsorption free energies of ORR intermediates on graphene co-doped with cobalt and nitrogen (CoN<sub>x</sub>C<sub>4-x</sub>-graphene).<sup>14</sup> Their calculations using Density Functional Theory (DFT) revealed that an increase in N doping concentration would decrease the average Co-C/N bond length as well as formation energy. CoN<sub>4</sub> was identified as the most stable among all configurations of the material. On the other hand, a decrease in doping concentration would weaken the hybridization among the cobalt d states, oxygen p states, and nitrogen p states. Consequently, the O adsorption would be weak.

Sunlight assisted photocatalytic and photoelectrochemical H<sub>2</sub>O splitting and CO<sub>2</sub> conversion processes are attractive because all relevant activities, primarily solar energy absorption, charge generation and transfer, and redox reactions take place in the semiconductor used as the photocatalyst and its interface with the electrolyte. A photocatalytic fuel production process can proceed spontaneously upon illuminating photocatalyst particles dispersed in an electrolyte or placed in a gaseous environment if thermodynamic and kinetic requirements are met. In a PEC cell, an external electrical bias is applied to drive the reaction when these requirements are not satisfied (e.g., the photovoltage produced is insufficient to cover thermoneutral voltage and overpotentials). PEC water splitting has similarity with the electrolysis, which is a commercial technology, that possesses the inherent ability to spatially separate gases evolved from reduction and oxidation processes (H<sub>2</sub> from cathode and O<sub>2</sub> from anode for water splitting). The anode or cathode or both in a PEC cell can be constructed using a semiconductor.

Titanium dioxide (titania; TiO<sub>2</sub>) has received the highest attention for PEC water splitting since Fujishima and Honda published the seminal work on solar water splitting using the material about five decades ago.<sup>15</sup> Although it is a powerful photocatalyst for OER, the wide bandgap (3.0–3.2 eV) of TiO<sub>2</sub> makes it inefficient for solar fuel generation. Nevertheless, it is superior in terms of stability, economic viability, scalability of fabrication methods, and abundance. With the introduction of low dimensional architectures as well as discovery of various physical phenomena appropriate for effective utilization of sunlight, there has been a surge in the activities to utilize this material for PEC fuel generation. TiO<sub>2</sub> can photocatalytically convert water vapor and/or carbon dioxide to fuels only at very low rates under 1 sun illumination. Nevertheless, Zhang *et al.* demonstrated that the yield could be enhanced more than a hundred fold with the use of concentrated light.<sup>16</sup> Their study conducted under natural sunlight concentrated to a ratio in the range 200–800 demonstrated that anodically grown TiO<sub>2</sub> nanotube array could generate CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> at enhanced rates in a low partial pressure CO<sub>2</sub>-H<sub>2</sub>O atmosphere. The temperature reached the range of 500 °C under illumination. The concentration ratio 400 yielded the maximum solar to chemical energy conversion efficiency (0.17%, if only UV conversion is considered).

Guan *et al.* used localized surface plasmon resonance (LSPR) to enhance the visible light photocatalytic activity of TiO<sub>2</sub>.<sup>17</sup> They decorated TiO<sub>2</sub> with gold (Au) nanocubes with exposed {100} facets or Au nano-tri-octahedrons with exposed {221} facets exhibiting LSPR. The hydrogen production rate doubled with the use of latter, which was ascribed to the synergy from LSPR and effective electron trapping facilitated by the specific tri-octahedron geometry and {221} facets. Using a study conducted with the help of time resolved absorption measurements, Inoue *et al.* verified that under visible light irradiation, platinum (Pt) nanoparticles would exhibit SPR and transfer electrons to TiO<sub>2</sub> at lower light intensities.<sup>18</sup> An interesting observation was that at an intensity above 50 mW/cm<sup>2</sup> some Pt particles would receive electrons from the TiO<sub>2</sub> conduction band. The authors believed that depending upon the particle size some Pt particles were receiving electrons from some other Pt particles through TiO<sub>2</sub> conduction band when the photoelectron density was high. Wang *et al.* doped TiO<sub>2</sub> rutile and anatase phases with rhodium (Rh) using an immersion calcination process and compared the photocatalytic hydrogen evolution activity.<sup>19</sup> Rh doping broadened the absorption spectra of both anatase

and rutile. While doping was homogenous in rutile,  $\text{Rh}_2\text{O}_3$  nanoparticles were observed on the surface of the anatase sample. Consequently, Rh-doped rutile exhibited significantly higher hydrogen evolution activity in the presence of ascorbic acid as a sacrificial agent. Antimony (Sb) and chromium (Cr) are also appropriate dopants to enhance the visible light absorption in  $\text{TiO}_2$ . Sb and Cr co-doped  $\text{TiO}_2$  ( $\text{TiO}_2\text{:Cr/Sb}$ ) is a promising  $\text{O}_2$  evolution photocatalyst with an ideal bandgap of about 2.2 eV. Nonetheless, the catalyst is not active in the presence of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  reversible redox mediator. Okada *et al.* dramatically altered this situation by dispersing  $\text{WO}_3$  on the surface of micrometer-size  $\text{TiO}_2\text{:Cr/Sb}$  particles.<sup>20</sup>  $\text{WO}_3$  promoted  $\text{O}_2$  generation as well as  $\text{Fe}^{3+}$  reduction. The authors applied this material in combination with  $\text{Ru/SrTiO}_3\text{:Rh}$  particles to a Z-scheme (photosynthesis like) system involving an aqueous  $\text{Fe}(\text{ClO}_4)_3$  solution and demonstrated that with the use of the  $\text{WO}_3$  modified photocatalyst, the  $\text{O}_2$  and  $\text{H}_2$  evolution rates would increase by approximately an order of magnitude. Khatun *et al.* fabricated ultrathin g- $\text{C}_3\text{N}_4$  with a surface area of  $190\text{ m}^2/\text{g}$  using an oxygen induced exfoliation method and formed  $\text{TiO}_2/\text{g-CN}$  nano-heterostructures with broad spectrum light absorption.<sup>21</sup> The carrier lifetime increased by 30% after the heterostructure formation. The hydrogen evaluation rate in an aqueous solution containing this heterostructure and a sacrificial agent (triethanolamine) was 15 fold greater than that with bare  $\text{TiO}_2$ .

Strontium titanate ( $\text{SrTiO}_3$ ) is another wideband gap material promising for photocatalytic/PEC fuel generation due its high photochemical stability. This material in the perovskite family also has appropriate band edge positions for spontaneous water splitting under illumination. This is the material used by Nishiyama *et al.* in the first demonstration of large area hydrogen generation using the PEC water splitting process.<sup>3</sup> Wen *et al.* used periodic DFT calculations to understand the impact of biaxial strains on the photocatalytic OER at the  $\text{SrTiO}_3$  (001) surface.<sup>22</sup> They made some interesting observations. The tensile strains would reduce the surface energy and OER overpotential by forming a surface O-O bond. The compressive strains would do the opposite. That means, the tensile strains intentionally introduced in the lattice could be used as a way to enhance the OER performance of  $\text{SrTiO}_3$ . Trivalent dopants such as indium can enhance the catalytic activity of  $\text{SrTiO}_3$ . The substitutional site,  $\text{Sr}^{2+}$  or  $\text{Ti}^{4+}$ , where the dopant settles has a decisive role in the enhancement or suppression of photocatalytic activity. Nevertheless, the dopant site had never been located through direct measurements/observations before Kitta *et al.* took this task.<sup>23</sup> They were successful in directly observing the location of indium in cubic  $\text{SrTiO}_3$  using analytical TEM imaging and EDS elemental mapping. They confirmed that In occupied the Ti sites in the lattice and this geometry would help charge separation and enhance photocatalytic activity.

Iron oxide (hematite;  $\text{Fe}_2\text{O}_3$ ) is a photocatalyst with an ideal bandgap ( $\sim 2.2\text{ eV}$ ) for water splitting. This moderate bandgap helps the material absorb photons of sufficient energy to oxidize water. Nevertheless, sluggish charge transport and high carrier recombination rate are major problems in iron oxide. Rodriguez-Gutierrez *et al.* reported that the performance of thick mesoporous hematite photoanode would improve upon incorporating Ti in the hematite lattice and allowing it to segregate at the grain boundaries.<sup>24</sup> Intensity modulated photocurrent spectroscopy studies revealed that the titanium impurities made the electronic transport facile by reducing the energy barrier at the grain boundaries. Souza Junior *et al.*, in their perspective article,

discussed the prospect of utilizing the synergy of grain and grain boundary doping/co-doping in hematite photoanodes as a pathway to attaining benchmark efficiency required for commercialization.<sup>25</sup> They identified tetravalent impurities such as Ti, Si, and Sn as promising elements for reducing the grain boundary energy barrier via solute segregation without altering the depletion layer properties. Chen *et al.* noted that the insertion of thin  $\text{NiO}_x$  buffer layer between a Ti-doped  $\alpha\text{-Fe}_2\text{O}_3$  nanowire film and fluorine doped tin oxide glass substrate would reduce the interface defects and improve the charge transfer.<sup>26</sup> The photocurrent density doubled with the use of this interface layer in the absence of any co-catalysts on the surface or sacrificial species in the electrolyte.

Two other most investigated oxide semiconductors are  $\text{BiVO}_4$  and  $\text{WO}_3$  due to the abundance of elements and their visible light absorbing property. Choi executed first-principles hybrid functional calculations to investigate the effect of strain on the electronic and structural properties of  $\text{BiVO}_4$  polymorphs and found that strain effects could be used to enhance the photocatalytic/PEC water splitting activity of certain phases.<sup>27</sup> With tensile biaxial/hydrostatic strain, the bandgap increased and conduction band minimum shifted up and reached the same or a more negative potential (with respect to NHE) as the  $\text{H}^+/\text{H}_2$  potential in monoclinic scheelite and tetragonal zircon phases. On the other hand, the bandgap and band edges in tetragonal scheelite phase were unaffected by biaxial strain. Ma and Hu found copper doping as useful for enhancing the photocurrent density of  $\text{WO}_3$  photoanodes in PEC cells for water splitting.<sup>28</sup> The incident photon to current conversion efficiency (IPCE) increased substantially due to the enhancement in charge separation and charge transfer efficiencies as well as the reduction in Gibbs energy for OER caused due to  $\text{Cu}^{2+}$  incorporation.

A wide range of multinary oxide semiconductors capable of broad spectrum light harvesting have been reported for photocatalytic/PEC fuel generation. Werner *et al.* substituted Ti in  $\text{LiTi}(\text{O},\text{N})_3$  with Nb and found that the introduction of pentavalent Nb helped the incorporation of additional  $\text{N}^{3-}$ .<sup>29</sup> The charge compensation with N incorporation reduced the charge carrier density in the material.  $\text{LaTi}_{1-x}\text{Nb}_x(\text{O},\text{N})_{3\pm\delta}$  with  $x=0.01$  showed the highest improvement (30%) in the PEC performance compared to the original Nb free material and this was attributed to the enhanced crystallinity, increased substitution of O with nitrogen and reduced defect density.  $\text{La}_5\text{Ti}_2\text{AgS}_5\text{O}_7$  is a semiconductor with an optimum bandgap for efficient PEC water splitting. The material was not reported to exhibit promising performance as a photoanode due to the presence of oxide impurities and sulfur defects created during the fabrication process. Cai *et al.* developed a flash sintering method to address this issue.<sup>30</sup> The process formed a surface layer with sulfur defects that created a homojunction with bulk of the material. The electrical field at this junction caused effective charge separation and transfer. Their experimental results were supported by the results from DFT calculations.  $\text{BaTaO}_2\text{N}$  is another promising material with an absorption edge of  $\sim 660\text{ nm}$ . Takagi *et al.* demonstrated that this material could exhibit better PEC characteristics upon modifying the surface with  $\text{TiO}_2$  nanoparticles loaded with cobalt phosphate (CoPi).<sup>31</sup> The wideband gap of  $\text{TiO}_2$  nanoparticles allowed it to pass visible light into  $\text{BaTaO}_2\text{N}$  and its high surface area increased the number of CoPi active sites. As a result, the OER overpotential became low. Manipulating the surface and bulk oxygen vacancy concentration in photoanode materials is a



commonly used to strategy to improve the PEC performance. Yu *et al.* created oxygen vacancies in dual-source electron beam evaporated BiFeO<sub>3</sub> films by annealing them in argon atmosphere.<sup>32</sup> BiFeO<sub>3</sub> is a ferroelectric material with a bandgap of  $\sim 2.6$  eV. The authors coated the material with p-type conductive poly 3, 4-ethylenedioxythiophene (PEDOT) for passivating the surface recombination centers and then loaded with a borate-intercalated nickel cobalt iron oxyhydroxide (NiCoFe-B<sub>2</sub>) co-catalyst. Although the surface modification improved the photocurrent notably, it was further enhanced with ferroelectric polarization.

While oxide photocatalysts offer better stability, non-oxide semiconductors such as III-V compounds and chalcopyrites have the proven ability to split water at high efficiency. Ravi *et al.* fabricated visible light absorbing n-type InGa<sub>0.53</sub>N<sub>0.47</sub> nanowires of composition In<sub>22</sub>Ga<sub>78</sub>N and In<sub>30</sub>Ga<sub>70</sub>N on Si (111) substrates using a custom-made low-cost chemical vapor deposition (CVD) reactor.<sup>33</sup> The photocurrent generated by the In<sub>30</sub>Ga<sub>70</sub>N photoanodes absorbing photons of wavelength up to 700 nm was 5 times higher than that produced by the UV absorbing GaN nanowire photoanodes. The applied bias photon to current conversion efficiency (ABPE) was 5.8% and the hydrogen evolution was 42  $\mu\text{mol}/\text{cm}^2/\text{h}$  (bias voltage 0.15 V) when water splitting was performed in a 1M NaOH electrolyte. Navid *et al.* developed Mg doped InGa<sub>0.53</sub>N<sub>0.47</sub> (nanowire)/Si double-junction photocathodes with each nanowire in the configuration, p<sup>+</sup>-InGa<sub>0.53</sub>N<sub>0.47</sub>(Pt decorated)/p<sup>+</sup>-InGa<sub>0.53</sub>N<sub>0.47</sub>/n<sup>+</sup>-InGa<sub>0.53</sub>N<sub>0.47</sub>/n<sup>+</sup>-InGa<sub>0.53</sub>N<sub>0.47</sub>, on n<sup>+</sup>-p Si wafer using plasma assisted molecular beam epitaxy.<sup>34</sup> The p-type doping (Mg) in the top p<sup>+</sup>-InGa<sub>0.53</sub>N<sub>0.47</sub> region of the nanowire facilitated vertical transport of photogenerated holes to the tunnel junction. It also created a downward band bending near the surface of the nanowire, which helped the top layer drive photogenerated electrons efficiently to the electrolyte-nanowire interface for proton reduction. The optimum composition, In<sub>0.32</sub>Ga<sub>0.68</sub>N, yielded a maximum ABPE of 9.5%. A modeling work performed by Kolbach *et al.* deciphered the effect of the water layer in contact with a III-V/Si double junction PEC device on its maximum attainable STH efficiency, which is often ignored while designing the device.<sup>35</sup> While decreasing the water layer thickness would reduce the optical losses, it could increase transport losses as well. By optimizing the top absorber bandgap and water layer thickness, the STH efficiency could be increased by 1%.

Can chalcopyrites based PEC tandem cells be efficient, yet durable and economically viable? This question is discussed by Gaillard in his perspective article.<sup>36</sup> The author pointed out the major issues to be addressed and urged the community to use theoretical modeling to identify new wide bandgap ordered vacancy compound absorbers (the copper deficient chalcopyrites) possessing high stability per thermodynamics and improved energetics. The article also describes with examples how understanding the semiconductor corrosion to a fundamental level using techniques such as advanced x-ray photoelectron spectroscopy could help identify effective passivation layer materials for solving the long-term durability problem in chalcopyrites. Ikeda *et al.* demonstrated that a thin copper deficient layer of CuGaSe<sub>2</sub> at the interface of a CuGaSe<sub>2</sub> film and a Pt loaded CdS film would dramatically enhance the efficiency of hydrogen generation when used as a photocathode in a PEC cell consisting of 0.1 M KH<sub>2</sub>PO<sub>4</sub>/K<sub>2</sub>HPO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub> (pH 6.8) electrolyte.<sup>37</sup> The copper deficient layer helped in reducing the carrier recombination rate. The onset potential increased consistently with the thickness of the copper deficient layer; however,

the photocurrent reduced beyond a certain thickness as it reduced the number of photons reaching the absorber. Tellurium addition during the co-evaporation of elements to form ZnSe-Cu(In,Ga)Se<sub>2</sub> films helped Minegishi *et al.* to lower the deposition temperature by 70 °C and introduce indium into the Ga-rich layer to form a composition gradient for effective charge separation.<sup>38</sup> Moreover, it facilitated columnar growth of grains that reduced the grain boundaries impeding the charge transport. Consequently, the maximum IPCE measured from ZnSe:CIGS photocathodes rose to 89% in the visible spectral region.

Passivating the surface and developing materials with high inherent stability are among the primary strategies used to address the photo-corrosion problem in non-oxide electrode materials in PEC cells. Zhang *et al.* reported that a 1 nm thick layer of HfO<sub>2</sub> could passivate a P<sup>+</sup>/n/n<sup>+</sup> silicon photocathode surface and improve the stability in an alkaline medium (1 M KOH).<sup>39</sup> The photocathode fabricated in the metal-insulator-semiconductor configuration by depositing a Ni<sub>3</sub>N/Ni co-catalyst atop the HfO<sub>2</sub> layer on silicon showed a 100 mV enhancement in the onset potential and 3 mA/cm<sup>2</sup> increase in photocurrent with stability verified for 6 h of operation. The improvement was attributed to the electron tunneling pathways provided by the ultrathin HfO<sub>2</sub>. Using DFT calculations, Liu *et al.* discovered a new material, Sn<sub>2</sub>S<sub>2</sub>P<sub>4</sub>, with high stability for overall water splitting.<sup>40</sup> A Sn<sub>2</sub>S<sub>2</sub>P<sub>4</sub> monolayer with an indirect bandgap of 1.77 eV, appropriate band edge positions that straddle the water redox potentials, and high electron mobility ( $\sim 1900$  cm<sup>2</sup> V/s) is predicted to perform both OER and HER and offer a sunlight-to-hydrogen efficiency up to 17% in an acidic electrolyte.

Overall, the articles in this special collection would help the readers get an idea of the research directions in the study of materials for the production of fuels using renewable energy. Although the research focus may appear more oriented toward solving the scientific problems with solar PEC process than electrochemical and thermochemical, that does not imply that the other two technologies are less attractive. PV assisted electrochemical water splitting technology has already been commercially implemented, and therefore, the challenges are more in the technology improvement side than in the technology development or science part. Thermochemical process has the unique advantage that it enables high rate production of syngas, which can be used directly or as a feedstock for gaseous or liquid fuels. Although many materials challenges remain to be solved, specific expertise and equipment are required to run the experiments at very high temperatures. PEC experiments are relatively easy to execute with low-cost infrastructure; however, the scientific and technological challenges before the researchers are substantial. While during the transition from fossil fuels to sustainable energy technologies the world may rely on the solar electrochemical water splitting approach, we believe that in future the PEC and thermochemical approaches will also have major roles in shaping the global energy economy.

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## AUTHOR DECLARATIONS

## Conflict of Interest

The authors have no conflicts to disclose.

## Author Contributions

**Oomman K. Varghese:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Writing – original draft (equal); Writing – review & editing (equal). **Kazunari Domen:** Formal analysis (supporting); Writing – review & editing (supporting). **Wojciech Lipinski:** Writing – review & editing (supporting). **Joost Smits:** Writing – review & editing (supporting).

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