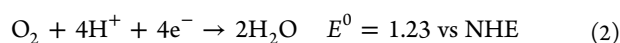


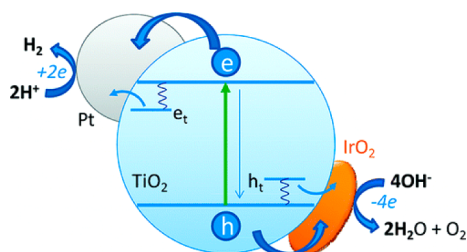
## Solar Fuels. Photocatalytic Hydrogen Generation

The necessity for developing clean energy technology has led to the surge in renewable energy research. A major effort is in discovering new approaches for producing transportable fuels. Hydrogen, which possesses the highest energy density (120 MJ/kg) known for any fuel and no carbon footprint, is regarded as the leading contender for meeting future fuel needs. The term *Hydrogen Economy* is often referred collectively to the topics of production, storage, and transport of hydrogen.<sup>1</sup> The grand challenge is to design a catalyst system that can effectively use sunlight and water to generate hydrogen and oxygen. During recent years many efforts have been made to develop new light harvesting assemblies, elucidate charge-transfer processes, and improve the efficiency of the water-splitting process. This Virtual Issue (<http://pubs.acs.org/page/jpcck/vi/solarfuels.html>) presents a few selected publications to highlight recent physical chemistry advances (Table 1). The readers should refer to recent reviews/perspectives for detailed developments in the area.<sup>2–5</sup>

Photocatalytic redox reactions with semiconductor nanostructures were first realized in the 1970s. The recent rejuvenation of this field has led to further exploration of new materials and hybrid assemblies. Theoretically, it requires an energy equivalent of 1.23 eV to split water into H<sub>2</sub> and O<sub>2</sub> (Reactions 1 and 2).



However, additional energy (the overpotential) is required to drive the photogenerated electrons and holes across the interface and to promote reduction and oxidation reactions. Cocatalysts such as Pt and IrO<sub>2</sub> are commonly employed to promote H<sub>2</sub> and O<sub>2</sub> generation in photoirradiated semiconductor systems (Figure 1).<sup>3,6</sup> Achieving greater efficiency

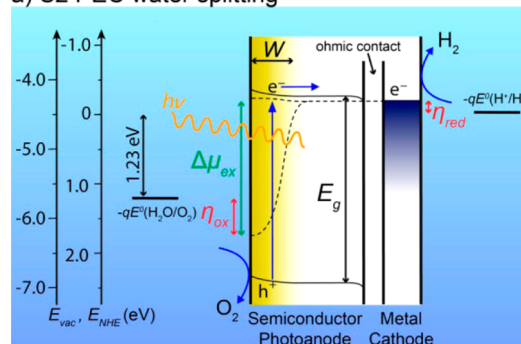


**Figure 1.** Illustration of semiconductor-assisted water-splitting reaction aided by Pt and IrO<sub>2</sub> cocatalysts. (Reproduced from reference 3).

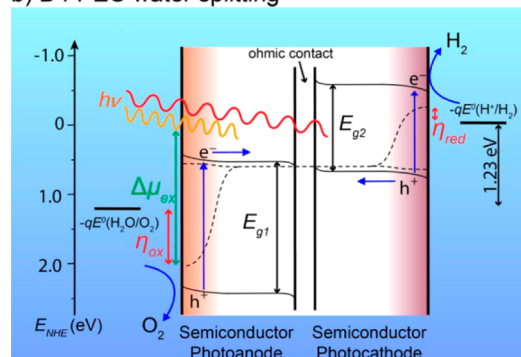
with oxygen-evolving catalysts to mediate the proton coupled electron transfer (reaction 2) remains a major challenge in the water-splitting process. The use of cobalt phosphate as a cocatalyst to boost the oxidative process of photocatalyst systems has drawn some attention.<sup>7</sup> Mimicking natural photosynthesis, recent efforts have also provided insights into Mn-based catalyst systems for oxygen generation.<sup>8,9</sup>

Wide bandgap semiconductors such as TiO<sub>2</sub>, which show good photostability, respond only to the UV region of the

a) S2 PEC water splitting



b) D4 PEC water splitting



**Figure 2.** Electron energy scheme of (a) S2 PEC water splitting using a photoanode and (b) D4 PEC water splitting using a photoanode and photocathode in tandem. The absorption of a photon ( $h\nu$ ) by the semiconductor with a band gap of  $E_g$  creates an electron–hole pair that can be separated by the space charge layer,  $W$ , to generate a free energy of  $\Delta\mu_{\text{ex}}$ . This free energy must be greater than the energy needed for water splitting (1.23 eV) plus the overpotential losses at both the anode and cathode,  $\eta_{\text{ox}}$  and  $\eta_{\text{red}}$ , for the water-splitting reaction to occur. Two photons must be absorbed in the S2 mechanism to produce one H<sub>2</sub>, while four are needed for the D4 approach. (Reproduced from reference 5).

spectrum. Efforts to dope these semiconductors with N or S to extend the photoresponse into the visible have produced limited success. Other efforts to couple such semiconductors with sensitizing dyes extend the concepts of dye-sensitized solar cells into photoelectrolysis systems. Such an approach assists in extending the photocatalyst response into the visible, though the dye regeneration remains a limiting factor. Another approach to harvesting visible photons is through the design of new materials. Recent efforts to develop tantalates, vanadates, and oxinitrides have gained significant attention because of the ability of these ternary semiconductors to respond to visible photons.<sup>7,10,11</sup> Earth-abundant hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) remains another popular photocatalysis material, but its conduction band is too low to drive H<sub>2</sub> production. An electrochemical bias potential needs to be applied to drive the oxidation reaction.<sup>12,13</sup> Intrinsic imperfections due to electronic structure and ultrashort lifetime

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Table 1. Selected Readings of Physical Chemistry Advances in Photocatalytic Hydrogen Production

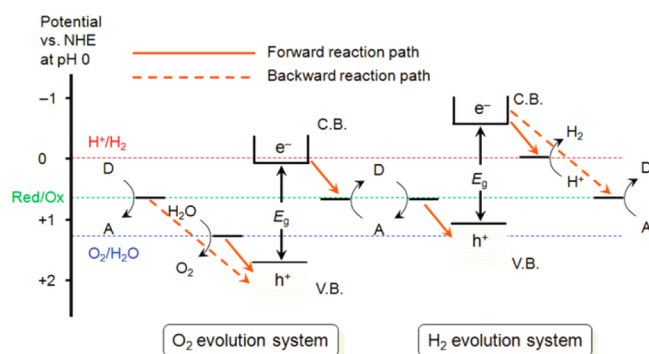
Reference Number	Title	Citation
(1)	The Hydrogen Economy.	Crabtree, G. W.; Dresselhaus, M. S.; Buchanan, M. V. <i>Phys. Today</i> <b>2004</b> , <i>57</i> , 39–44.
(2)	Photocatalytic Water Splitting: Recent Progress and Future Challenges.	Maeda, K.; Domen, K. <i>J. Phys. Chem. Lett.</i> <b>2010</b> , <i>1</i> , 2655–2661. doi:10.1021/jz1007966
(3)	Manipulation of Charge Transfer Across Semiconductor Interface. A Criterion That Cannot Be Ignored in Photocatalyst Design.	Kamat, P. V. <i>J. Phys. Chem. Lett.</i> <b>2013</b> , <i>3</i> , 663–672. doi:10.1021/jz201629p
(4)	Progress in Heterogeneous Photocatalysis: From Classical Radical Chemistry to Engineering Nanomaterials and Solar Reactors.	Teoh, W. Y.; Scott, J. A.; Amal, R. <i>J. Phys. Chem. Lett.</i> <b>2012</b> , <i>3</i> , 629–639. doi:10.1021/jz3000646
(5)	Metal Oxide Photoelectrodes for Solar Fuel Production, Surface Traps, and Catalysis.	Sivula, K. <i>J. Phys. Chem. Lett.</i> <b>2013</b> , <i>4</i> , 1624–1633. doi:10.1021/jz4002983
(6)	Synthesis and Activities of Rutile IrO <sub>2</sub> and RuO <sub>2</sub> Nanoparticles for Oxygen Evolution in Acid and Alkaline Solutions.	Lee, Y.; Suntivich, J.; May, K. J.; Perry, E. E.; Shao-Horn, Y. <i>J. Phys. Chem. Lett.</i> <b>2012</b> , <i>3</i> , 399–404. doi:10.1021/jz2016507
(7)	Photocatalytic Water Oxidation on BiVO <sub>4</sub> with the Electrocatalyst as an Oxidation Cocatalyst: Essential Relations between Electrocatalyst and Photocatalyst.	Wang, D. E.; Li, R. G.; Zhu, J.; Shi, J. Y.; Han, J. F.; Zong, X.; Li, C. <i>J. Phys. Chem. C</i> <b>2012</b> , <i>116</i> , 5082–5089. doi:10.1021/jp210584b
(8)	Proton-Coupled Electron Transfer versus Hydrogen Atom Transfer: Generation of Charge-Localized Diabatic States.	Sirjoosingh, A.; Hammes-Schiffer, S. <i>J. Phys. Chem. A</i> <b>2011</b> , <i>115</i> , 2367–2377. doi:10.1021/jp111210c
(9)	Water Oxidation Catalysis using Amorphous Manganese Oxides, Octahedral Molecular Sieves (OMS-2), and Octahedral Layered (OL-1) Manganese Oxide Structures.	Iyer, A.; Del-Pilar, J.; King'ondo, C. K.; Kissel, E.; Garces, H. F.; Huang, H.; El-Sawy, A. M.; Dutta, P. K.; Suib, S. L. <i>J. Phys. Chem. C</i> <b>2012</b> , <i>116</i> , 6474–6483. doi:10.1021/jp2120737
(10)	Role and Function of Ruthenium Species as Promoters with TaON-Based Photocatalysts for Oxygen Evolution in Two-Step Water Splitting under Visible Light.	Maeda, K.; Abe, R.; Domen, K. <i>J. Phys. Chem. C</i> <b>2011</b> , <i>115</i> , 3057–3064. doi:10.1021/jp110025x
(11)	Photocatalytic Hydrogen Production from Water Using N-Doped Ba <sub>3</sub> Ta <sub>4</sub> O <sub>15</sub> under Solar Irradiation.	Mukherji, A.; Sun, C. H.; Smith, S. C.; Lu, G. Q.; Wang, L. Z. <i>J. Phys. Chem. C</i> <b>2011</b> , <i>115</i> , 15674–15678. doi:10.1021/jp202783t
(12)	The Transient Photocurrent and Photovoltage Behavior of a Hematite Photoanode under Working Conditions and the Influence of Surface Treatments.	Le Formal, F.; Sivula, K.; Grätzel, M. <i>J. Phys. Chem. C</i> <b>2012</b> , <i>116</i> , 26707–26720. doi:10.1021/jp308591k
(13)	Direct Observation of Two Electron Holes in a Hematite Photoanode during Photoelectrochemical Water Splitting.	Braun, A.; Sivula, K.; Bora, D. K.; Zhu, J.; Zhang, L.; Grätzel, M.; Guo, J.; Constable, E. C. <i>J. Phys. Chem. C</i> <b>2012</b> , <i>116</i> , 16870–16875. doi:10.1021/jp304254k
(14)	Mechanism of O <sub>2</sub> <sup>-</sup> Production from Water Splitting: Nature of Charge Carriers in Nitrogen Doped Nanocrystalline TiO <sub>2</sub> Films and Factors Limiting O <sub>2</sub> <sup>-</sup> Production.	Tang, J. W.; Cowan, A. J.; Durrant, J. R.; Klug, D. R. <i>J. Phys. Chem. C</i> <b>2011</b> , <i>115</i> , 3143–3150. doi:10.1021/jp1080093
(15)	Charge Carrier Dynamics on Mesoporous WO <sub>3</sub> during Water Splitting.	Pesci, F. M.; Cowan, A. J.; Alexander, B. D.; Durrant, J. R.; Klug, D. R. <i>J. Phys. Chem. Lett.</i> <b>2011</b> , <i>2</i> , 1900–1903. doi:10.1021/jz200839n
(16)	Interpretation of Cyclic Voltammetry Measurements of Thin Semiconductor Films for Solar Fuel Applications.	Bertoluzzi, L.; Badia-Bou, L.; Fabregat-Santiago, F.; Gimenez, S.; Bisquert, J. <i>J. Phys. Chem. Lett.</i> <b>2013</b> , <i>4</i> , 1334–1339. doi:10.1021/jz400573t
(17)	Charge Transfer across the n-Type GaN–Electrolyte Interface.	Schäfer, S.; Koch, A. H. R.; Cavallini, A.; Stutzmann, M.; Sharp, I. D. <i>J. Phys. Chem. C</i> <b>2012</b> , <i>116</i> , 22281–22286. doi:10.1021/jp302000x
(18)	Multi-Bandgap-Sensitized ZnO Nanorod Photoelectrode Arrays for Water Splitting: An X-ray Absorption Spectroscopy Approach for the Electronic Evolution under Solar Illumination.	Chen, H. M.; Chen, C. K.; Lin, C. C.; Liu, R. S.; Yang, H.; Chang, W. S.; Chen, K. H.; Chan, T. S.; Lee, J. F.; Tsai, D. P. <i>J. Phys. Chem. C</i> <b>2011</b> , <i>115</i> , 21971–21980. doi:10.1021/jp204291b
(19)	Harnessing Infrared Photons for Photoelectrochemical Hydrogen Generation. A PbS Quantum Dot Based “Quasi-Artificial Leaf.”	Trevisan, R.; Rodenas, P.; Gonzalez-Pedro, V.; Sima, C.; Sanchez, R. S.; Barea, E. M.; Mora-Sero, I.; Fabregat-Santiago, F.; Gimenez, S. <i>J. Phys. Chem. Lett.</i> <b>2013</b> , <i>4</i> , 141–146. doi:10.1021/jz301890m
(20)	Graphene-Based Nanoassemblies for Energy Conversion.	Kamat, P. V. <i>J. Phys. Chem. Lett.</i> <b>2011</b> , <i>2</i> , 242–251. doi:10.1021/jz101639v
(21)	Graphene-Based Photocatalysts for Hydrogen Generation.	Xiang, Q. J.; Yu, J. G. <i>J. Phys. Chem. Lett.</i> <b>2013</b> , <i>4</i> , 753–759. doi:10.1021/jz302048d
(22)	Plasmon-Enhanced Photocatalytic Activity of Cadmium Sulfide Nanoparticle Immobilized on Silica-Coated Gold Particles.	Torimoto, T.; Horibe, H.; Kameyama, T.; Okazaki, K.; Ikeda, S.; Matsumura, M.; Ishikawa, A.; Ishihara, H. <i>J. Phys. Chem. Lett.</i> <b>2011</b> , <i>2</i> , 2057–2062. doi:10.1021/jz2009049
(23)	Near-Infrared Plasmon-Assisted Water Oxidation.	Nishijima, Y.; Ueno, K.; Kotake, Y.; Murakoshi, K.; Inoue, H.; Misawa, H. <i>J. Phys. Chem. Lett.</i> <b>2012</b> , <i>3</i> , 1248–1252. doi:10.1021/jz3003316
(24)	Doping of WO <sub>3</sub> for Photocatalytic Water Splitting: Hints from Density Functional Theory.	Wang, F. G.; Di Valentin, C.; Pacchioni, G. <i>J. Phys. Chem. C</i> <b>2012</b> , <i>116</i> , 8901–8909. doi:10.1021/jp300867j
(25)	First-Principles Study of Photoinduced Water-Splitting on Fe <sub>2</sub> O <sub>3</sub> .	Hellman, A.; Pala, R. G. S. <i>J. Phys. Chem. C</i> <b>2011</b> , <i>115</i> , 12901–12907. doi:10.1021/jp200751j
(26)	Theoretical Design of Molecular Electrocatalysts with Flexible Pendant Amines for Hydrogen Production and Oxidation.	Fernandez, L. E.; Horvath, S.; Hammes-Schiffer, S. <i>J. Phys. Chem. Lett.</i> <b>2012</b> , <i>4</i> , 542–546. doi:10.1021/jz3020277
(27)	Prediction of Silicon Nanowires as Photocatalysts for Water Splitting: Band Structures Calculated Using Density Functional Theory.	Zhang, R. Q.; Liu, X. M.; Wen, Z.; Jiang, Q. <i>J. Phys. Chem. C</i> <b>2011</b> , <i>115</i> , 3425–3428. doi:10.1021/jp111182c
(28)	Electronic Structure and Reactivity of Ce- and Zr-Doped TiO <sub>2</sub> : Assessing the Reliability of Density Functional Theory Approaches.	Iwazuk, A.; Nolan, M. <i>J. Phys. Chem. C</i> <b>2011</b> , <i>115</i> , 12995–13007. doi:10.1021/jp203112p
(29)	Effect of Compensated Codoping on the Photoelectrochemical Properties of Anatase TiO <sub>2</sub> Photocatalyst.	Ma, X.; Wu, Y.; Lu, Y.; Xu, J.; Wang, Y.; Zhu, Y. <i>J. Phys. Chem. C</i> <b>2011</b> , <i>115</i> , 16963–16969. doi:10.1021/jp202750w
(30)	Coincorporation of N and Ta into TiO <sub>2</sub> Nanowires for Visible Light Driven Photoelectrochemical Water Oxidation.	Hoang, S.; Siwei Guo, S.; Mullins, C. B. <i>J. Phys. Chem. C</i> <b>2012</b> , <i>116</i> , 23283–23290. doi:10.1021/jp309743u

of the charge separated state are cited as major limiting factors in attaining efficiencies comparable to other semiconductor materials. As pointed out by Braun and co-workers, a basic understanding of

the role of surface states in interfacial charge transfer as well as charge recombination are key to developing hematite-based photocatalyst assemblies.<sup>13</sup>

Significant advances have been made towards understanding of photoinduced charge separation and interfacial charge-transfer processes in semiconductor photocatalyst assemblies.<sup>3,14,15</sup> Both thermodynamic and kinetic aspects dictate the efficiency of electron and hole transfer in semiconductor systems. The existence of surface traps and the nature of the surrounding medium dictate the net charge-transfer yield. A kinetic model has been developed to discriminate between trap-assisted recombination and charge-transfer processes. This makes it possible to formulate the results for the interpretation of the current–potential curve under photogeneration.<sup>16</sup>

The nature of electronic states, the accumulation of photogeneration carriers, and the modification of charge-transfer kinetics by surface treatment or catalyst layers have been examined using different experimental methods.<sup>5,13,17</sup> One example is transient absorption spectroscopy that enables direct monitoring of the reactivity of photogenerated electrons and holes. Pesci et al. have probed the reactivity of holes toward water oxidation using a commonly employed semiconductor photocatalyst  $\text{WO}_3$  and identified limitations through the charge recombination process.<sup>15</sup> Unfortunately the conduction band of  $\text{WO}_3$  is not energetic enough to induce  $\text{H}^+$  reduction. As a result of this limitation researchers have invoked a Z-scheme in which two different semiconductors are assembled in a hybrid configuration to carry out reduction and oxidation on two separate semiconductor particles.<sup>10</sup> Since both particles absorb light it opens up new opportunities to modulate the two-photon process and thus overcome many of the energetic barriers (Figure 3). Designing hybrid assemblies that can utilize



**Figure 3.** Two-photon excitation of semiconductors to induce photocatalytic evolution of  $\text{H}_2$  and  $\text{O}_2$ . (Reproduced from reference 10).

the multiphoton process to induce the water-splitting reaction will be a major challenge that needs to be tackled in the future.

There have also been significant efforts to utilize narrow bandgap semiconductors such as metal chalcogenides. Because of facile anodic corrosion these semiconductors cannot generate oxygen. A sacrificial donor to evolve hydrogen must be used in order to overcome this adverse problem. Hence, photocatalytic evolution of hydrogen using short bandgap semiconductors only provides partial information related to the reduction process.<sup>18,19</sup>

New approaches in designing different shapes of nanostructures or creating hybrid assemblies have also dominated photocatalysis research.<sup>20–23</sup> Such hybrid assemblies enable better charge separation as well as extension of the photoresponse into the visible. By careful design and selection of nanoparticles it is possible to improve the efficiency and selectivity of the photocatalytic process. Graphene oxide based carbon support offers the opportunity to improve charge separation and spatially segregate

reduction and oxidation processes.<sup>20,21</sup> The enhanced electric field produced by photoexcitation of the localized surface plasmon resonance (LSPR) peak of Au particles has been shown to improve the photocatalytic activity as seen by increased  $\text{H}_2$  production rate.<sup>22,23</sup> The optimal distance between Au and the semiconductor core, viz., CdS, remains an important factor in achieving plasmon-induced enhancement of the photocatalytic process.

In parallel, theoretical efforts have emerged to evaluate the energetics and predict the water-splitting ability of different semiconductor systems.<sup>24–27</sup> In particular, DFT studies are useful in identifying the properties of doped semiconductors as well as in the design of new semiconductor photocatalysts. Theoretical<sup>28</sup> and experimental efforts<sup>29,30</sup> are currently leading the way in designing codoped semiconductor nanostructures. The enhanced photoconversion efficiency in  $\text{TiO}_2$  nanowires codoped with N and Ta was attributed to fewer recombination centers from charge compensation effects.<sup>30</sup>

The discussion of a few representative papers in this Virtual Issue provides recent physical chemistry advances in photocatalytic generation of hydrogen. Finding new approaches to overcome some of the energetic and kinetic barriers will be key to developing new photocatalysts and to tackling the renewable energy challenge effectively.

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