CanApple ニュース（284）

カーボン・エネルギーコントロール社会協議会 (CanApple)
事務局：民秋均
発行責任者：石谷治
編集責任者：八木政行

Towards Solar Fuel Devices: Challenges and Scopes

Niigata University Debraj Chandra

For the sustainable development of human society, the supply of secure and clean energy is arguably the most important scientific and technical challenge in the 21st century.[1] Ever since, the French scientist Edmond Becquerel pioneered the photoelectric effect in 1839, researchers and engineers have been impassioned with the idea of converting light into electricity or chemical fuels. Water splitting by solar light energy using semiconductors, to produce clean hydrogen (H_2) fuel in an economically viable way could become a new industrial photosynthesis whose only waste product upon utilization is water. Back in 2010, when I started to research on solar water splitting by extending my expertise from nanomaterials development, my dedication to research remain unchanged in this field. In this newsletter, I would like to cover the basics of solar water splitting and then discuss the present challenges in this filed and prerequisite for materials development.

Production of H_2 and O_2 from water is an uphill reaction. The standard Gibbs free energy change for the conversion of one H_2O molecule into H_2 and 1/2 O_2 is $\Delta G°$ = 237.2 kJ/mol, which, according to the Nernst equation, corresponds to $\Delta E°$ = 1.23 eV per electron transferred. Therefore, for solar water splitting, the band gap energy (E_g) of the semiconductor should be >1.23 eV (photons wavelength of <1000 nm). However, to utilize visible light, E_g should be <3.0 eV (wavelength >400 nm). In semiconductors, solar light absorption induces charge separation to generate electron-hole pairs when the energy of the incident photons matches or exceeds the band gap. The valence-band (VB) holes exhibit an oxidative potential of +1.0 to +3.5 V versus the normal hydrogen electrode (NHE); hence can drive the oxygen evolution reaction (OER; $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$). The conduction-band (CB) electrons have a chemical potential of +0.5 to –1.5 V versus NHE; hence can act as reductants and drive the hydrogen evolution reaction (HER; $4H^+ + 4e^- \rightarrow 2H_2$). However, the photoinduced free charge carriers (electrons and holes), without recombination must travel to the semiconductor/aqueous interface and react with solution species to carry out OER and/or HER. Any other processes that consume free charge carriers should be evaded in order to maximize the efficiency of H_2 production.

To date, three kinds of solar water splitting systems have been well established: photocatalytic (PC), photoelectrochemical (PEC), and photovoltaic-electrolyzer (PVE) systems. At present scenario, the major challenges for commercialization of the water splitting devices are centralized on the development of materials that able to support efficient separation of charge carriers, provide rapid charge transfer at a semiconductor/aqueous interface, have fast surface-reaction kinetics, exhibit long-term stability, and can efficiently harvest a large portion of the solar spectrum.

Thus, factors such as chemical composition, nanostructures, crystallinity and electronic properties all of which determine the PC and PEC activity of materials, need to be further elucidated. Nanomaterials can provide advantages of large surface areas, abundant active sites, diverse morphologies, and easy device modeling. A small mesopore system of crystalline WO_3 photoanode has been attained by ligand assisted fabrication approach, which provided high surface area and a shorter carrier diffusion length than conventional photoanodes and highly improved the visible-light-driven PEC water splitting.[2] Band gap engineering of semiconductors by ion-doping, semiconductor sensitization etc. can expand the opportunities of visible light response. N_2-intercaleted WO_3 photoanodes through band gap engineering with improved visible-light absorption has been utilized for efficient PEC water oxidation.[3] Crystal-facet design is another way that can offer highly active atomic configuration on the surface of photoelectrodes.[4] Computational DFT calculations can provide useful insights to identify new materials. It is thus of great importance to recognize and design new semiconductor materials for solar water splitting that are efficient, stable and abundant. I believe, after commercialization of solar fuel devices in the future, our descendant will wonder at the “Fossil Fuel Wars” in this century.

[1] *Nature* ***2012***, *488, 294*
[2] *Angew. Chem. Int. Ed.* ***2013*** 52, 12606.
[3] *ACS Sustainable Chem. Eng.* ***2019***, 7, 17896.
[4] *ACS Appl. Mater. Interfaces* ***2023***, 15, 20885.