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Summary: Solar energy is abundant and renewable energy: however, extensive conversion of the solar energy can only be achieved by large-scale collection of solar flux. The technology that satisfies this requirement must be as simple as possible to reduce capital cost. Overall water splitting (OWS) by powder-form photocatalysts directly produces H_2 as a chemical energy in a single reactor, which does not require any complicated parabolic mirrors and electronic devices. Because of its simplicity and low capital cost, it has tremendous potential to become the major technology of solar energy conversion. To achieve the OWS efficiently, the development of efficient photocatalysts is mandatory. The OWS photocatalysis involves the electrocatalysis for both water reduction and oxidation on the surafce of photocatalysts, which is driven by particular semiconductors that absorb photons to generate excited carriers. Such photocatalysts must be designed to maximize the charge separation efficiency at the catalyst-semiconductor and semiconductor-electrolyte interface. In addition the low-overpotential electrocatalyts towards water redox reactions should be insensitive to the back-reaction of the produced H_2 and O_2 that produces H_2O. In this presentation, some recent progress on the topic of the OWS in our group will be discussed.

Keywords: Solar energy conversion; Photocatalysis; Hydrogen evolution; Oxygen evolution; Electrocatalysis; Semiconductor

1 Introduction

Effective solar energy conversion is must to compensate the gap between energy production and its demand which is increasing with years [1]. Photocatalysis, using powder-form materials, is considered to be one of the most economical processes for solar energy conversion [2]. The photocatalytic reaction is initiated by the excited charge carriers (electrons and holes) that are generated by the absorption of the photons in the semiconductor materials (photocatalysts) [3]. Both the generated electrons and the holes move to the surface of the photocatalytic materials and subsequently initiate their respective redox reactions [3]. The photocatalytic process fully utilizes the electronic configuration occurring at the metal–semiconductor and semiconductor–electrolyte interfaces by constructing band structures (the formation of band bending and barriers) preferably without introducing p–n junctions that generally increase the process cost [4,5]. This electronic structure is essential in enhancing the charge separation and in achieving a highly efficient photocatalytic process because the photophysical process, including the generation and recombination of the excited carriers, occurs on a significantly shorter time scale (femto- to-microseconds) than surface electrocatalytic reactions, unless the process is separated effectively (microseconds to several seconds) [6]. The scheme of the photocatalytic process is depicted in Figure 1.

The design of the photocatalysts should be focused on the following points [7]:

1) Select suitable elements to be used as photocatalysts that possess the suitable band positions and band gaps with high absorption coefficients;
2) Synthesize highly crystalline bulk photocatalysts throughout the particle with appropriate concentrations of the majority carriers;
3) Construct ohmic contact (minimize the Schottky barrier) between the semiconductor and the cocatalysts;
4) Develop highly active cocatalysts for surface electrocatalysis;
5) Effectively locate the sites and maximize the concentrations of the reduction/oxidation cocatalysts on the photocatalyst surfaces.

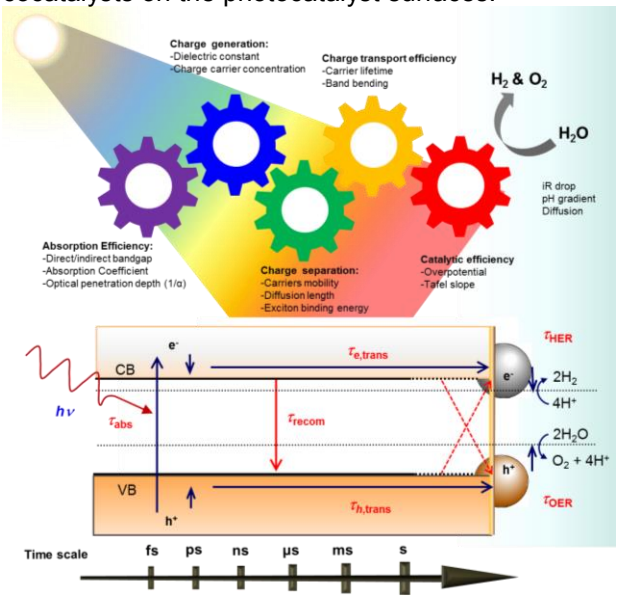

Fig. 1. Conceptual scheme for photocatalytic OWS reaction.

2 Discussion

To understand the properties that affect photocatalytic process, various forms of photocatalytic materials are needed [8]. For example, thin film configuration is effective to measure absorption properties, such as absorption coefficient, refractive index, dielectric constant, and charge carrier concentration, carrier mobility, carrier lifetime and diffusion length. Calculations including density functional theory provide useful information, such as electronic structure (direct/indirect band gap), absorption coefficient, exciton binding energy, and dielectric constant. Photoelectrochemical configuration is effective to measure photoelectrochemical performance at different potential (Fermi level) and at different excitation wavelength. Semiconductor-electrochemistry is also effective to learn flat-band potential and majority carrier concentrations of the semiconductor. Measurements of the electrocatalytic performance give information of overpotential required for the respective redox reactions, and concentration gradient and diffusion of electrolyte. As a consequence of these parameters, photocatalytic powder configuration can only measure hydrogen and/or oxygen with and without sacrificial reagents [9].

Interface between two phases is critical to achieve charge separation and transport properties. Two components that have different chemical potentials lead to new electronic structure gradient with and without barrier (e.g., Schottkey or ohmic contacts). For sufficiently large space charge layer associated with a given carrier concentration, significant band bending is present, which may be utilized to separate the excited carriers. In sufficiently small semiconductor particulates, the bending may be minimal [3]. Without the band bending as a driving force for the charge transfer, the photogenerated charge carriers should transfer from the bulk to the particle surface simply by diffusion [7].

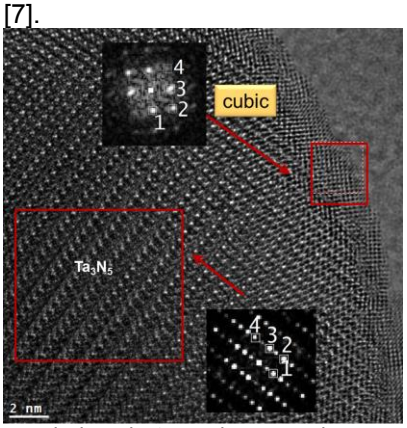

Fig. 2. Transmission electron microscope image and electron diffraction pattern of Ta_3N_5 powder [10].

The surface itself is defect by definition, consisting of dangling bonds. The surface recombination on the semiconductor is therefore expected at large quantity. Also, mainly due to the extra surface energy, the semiconductor surface may differ in its structure from that of the bulk. An example is shown in Fig. 2, where the cubic structure of the surface is observed, in contrast to the orthorhombic Ta_3N_5 bulk structure [10]. As expected, this type of semiconductor completely alter the semiconductor properties and resultant photocatalytic performance [10].

Cocatalysts are essential components to achieve high efficiency photocatalysis, which cause an enhanced charge separation and improved rates in the surface reactions towards products [6]. The cocatalysts are electrocatalysts that enhance the rates of water redox reactions. The recent efforts are to develop catalysts with non-noble metals. Water electrolyzer, a commercial technology operated at extreme pH condition, is beneficial if it can adapt various conditions relevant to the photocatalysis, such as neutral pH conditions. Indeed electrolyte effects give significant impact on the electrochemical performance [12]. The knowledge of electrocatalysis, which can be separately investigated, needs to be transferred to photocatalysis, focusing on establishing effective semiconductor interface.

3 Perspectives

While understanding various properties of known semiconductor materials, challenges should also be aimed at developing new semiconductors, knowing the requirements discussed above. The efforts should focus on 1) synthesis of crystalline semiconductor, 2) development of low-overpotential electrocatalysts, and 3) construction of effective interface for charge separation and transfer. To achieve efficient photocatalysis for OWS, all of these parameters should be effective because the overall efficiency is obtained as the multiplication of all these fundamental efficiencies. Accumulation of knowledge from solid-state physics to electrochemistry and multidisciplinary approach to conduct various measurements are inevitable to fully understand the photocatalysis and to improve the efficiency.

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