Photocatalytic Water Splitting Reactions Based on Tantalum Oxynitrides

Hyo Na Kim Literature Seminar October 15, 2013

Photocatalytic water splitting reaction involves in formation of hydrogen and oxygen molecules from water when irradiated with solar energy. Use of titanium dioxide for electrochemical photolysis of water was first reported by A. Fujishima and K. Honda in 1972.[1] Since then, there have been a lot of researches and progress made in this field. The overall water splitting reaction is thermodynamically unspontaneous (ΔG° = 237. 13 kJ mol^{-1}).[2] In order to overcome such unfavorable energy barrier efficiently, there are several factors to consider when designing photocatalyst. Firstly, a material has to have suitable band edge positions. The conduction and valence band have to be located at more negative and more positive potential, respectively.[3] Also, small bandgap energy is essential as the main component of the solar spectrum (~50%) consists of visible light region ($400 < \lambda < 800$ nm).[2] In addition, a material has to be stable to generate hydrogen and/or oxygen continuously by avoiding electron-hole recombination or photocorrosion.[4]

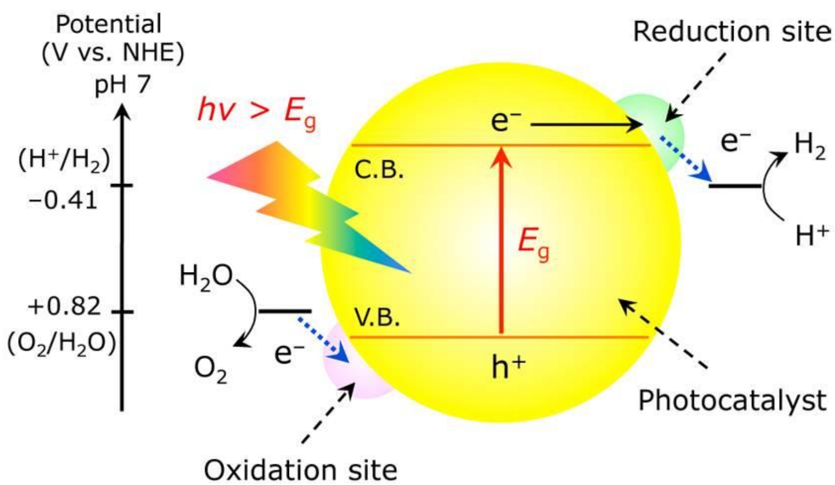

Figure 1: Schematic energy diagram of photocatalytic water splitting

There have been constant efforts to find a suitable photocatalyst which has all of these properties with high quantum yield, but it has not been reported yet. Instead, there have been heavy investigations of improving photocatalytic activities of materials by other means. The most common way is the usage of cocatalysts such as platinum, ruthenium, iridium, etc. Another way is doping of foreign elements to make n- or p-type doped materials. Electron-hole transferring system of heterostructures is also used to enhance the photocatalytic hydrogen and/or oxygen generation.[2,3]

Oxynitride has suitable conduction and valence band positions to produce hydrogen and oxygen from water. It contains nitrogen that forms the tops of the valence band, and it makes its band gap energy smaller than those of metal oxides. As a result, it absorbs visible light more effectively and has better photocatalytic ability. Also, it is stable, harmless and easy to obtain.[3] It is usually combined with Ti^{4+}, Nb^{5+} and Ta^{5+}. Tantalum oxynitride is one of the most attractive materials not only for the half reaction, which generates hydrogen or oxygen molecules from water, but also for the full reaction, which generates simultaneously hydrogen and oxygen molecules from water in the same reactor.[5-7] Its crystal structure is usually monoclinic baddeleyite (β-TaON), but there is also monoclinic VO_2(B) (γ-TaON) that is metastable.[8,9]

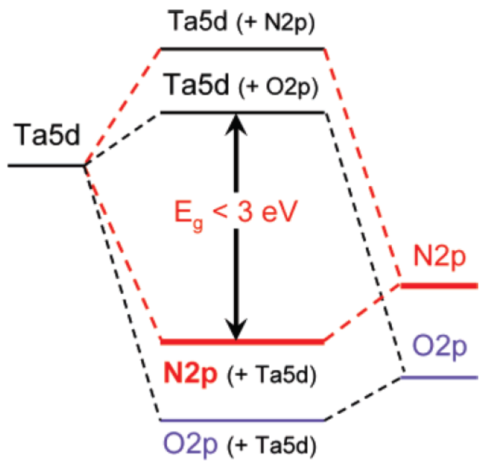

Figure 2: Schematic band structures of a tantalum oxynitride

Although, in these days, there are some researches related to the full reaction, there are still plenty of articles only focused on activities of tantalum oxynitrides for the photocatalytic hydrogen generation. They introduce various morphologies of tantalum oxynitrides such as hollow urchin structure[10], nanosheets[11], core-shell structure[12] and so on. Due to the diverse synthetic methods and their morphological changes, they have various changed physical and chemical properties, and enhanced photocatalytic activities.

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