DIRECT WATER SPLITTING BY NEW OXIDE SEMICONDUCTOR PHOTOCATALYSTS UNDER VISIBLE LIGHT IRRADIATION

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Hydrogen production by direct splitting of water using photocatalysts under solar light is one of the most attractive research subjects in terms of a clean energy supply in future. Therefore, a number of researches on photocatalytic splitting of water have been conducted so far. As a result, several oxide semiconductor photocatalysts, such as Na_2CO_3-Pt/TiO_2,[1] $NiO_x/K_4Nb_6O_{17}$,[2] NiO_x/Ta_2O_5[3], and $NiO_x/NaTaO_3$[4], which were able to split water under UV light irradiation, were reported. However, photocatalysts, which can utilize visible light for stoichiometric splitting of water, have not been developed so far. We have been investigating such new photocatalytic systems using two different approaches. The one is to design and synthesize narrow band gap oxide semiconductor photocatalysts which are able to split water under visible light irradiation. The other is to design the two-step water splitting system which is composed of the combination of two different oxide semiconductor photocatalysts for H_2 and O_2 production, respectively, and a shuttle redox mediator between two photocatalysts. This system mimics the Z-scheme mechanism in natural photosynthetic process. These new approaches are introduced and discussed.

We have synthesized various kinds of new mixed oxide semiconductor materials which could absorb visible light. The first group is Bi_2MNbO_7 (M= Al^{3+}, Ga^{3+}, In^{3+}, Y^{3+}, Rare $Earth^{3+}$) [5]of $A_2B_2O_7$ pyrochlore structure. The second group is $BiMO_4$ (M=Nb^{5+}, Ta^{5+})[6] of stibotantalite structure and the third group is InMO4 (M=Nb^{5+}, Ta^{5+}) [7]of wolframite structure. These materials crystallize in the different structures, however, they contain the same octahedral TaO_6 and/or NbO_6 in the structures. The band structure of these materials is estimated that the conduction band is composed of Ta/Nb *d*-level mainly and the valence band is composed of O *2p*-level mainly. The band gaps of these materials determined by UV-visible reflectance spectra were between 2.7 and 2.4 eV. Among these materials, NiO_x (surface oxidized Ni) or RuO_2 promoted $InTaO_4$ and $InNbO_4$ photocatalysts, such as $NiO_x/InTaO_4$, $RuO_2/InTaO_4$ and $NiO_x/InNbO_4$, showed photocatalytic activities for pure water splitting under visible light irradiation ($\lambda > 420$ nm, 300W Xe-lamp). However, the activities were very low.

In order to improve water splitting activity, transition metal doped $InTaO_4$ and $InNbO_4$ were synthesized.[8] Among these doped materials, Ni-doped $InTaO_4$ and Ni-doped $InNbO_4$ photocatalysts such as $NiO_x/In_{0.9}Ni_{0.1}TaO_4$, $RuO_2/In_{0.9}Ni_{0.1}TaO_4$, $NiO_x/In_{0.9}Ni_{0.1}TaO_4$ and $RuO_2/In_{0.9}Ni_{0.1}TaO_4$ showed the highest activities. The rate of H_2 and O_2 evolution were 16.6 and 8.3 μ mol/h, respectively, and the quantum efficiency at 402 nm was 0.66% in the case of 1wt%$NiO_x/In_{0.9}Ni_{0.1}TaO_4$ photocatalyst. [9] The absorption band due to Ni-doping was observed at 420-520nm in addition to that of $In_{0.9}Ni_{0.1}TaO_4$. This is one of reasons of activity increase. The stability of this photocatalyst and reproducibility of photocatalytic water splitting reaction were fairly good. TEM photographs of $In_{0.9}Ni_{0.1}TaO_4$ photocatalyst showed the particles size were 300 to 500 nm and NiO_x particles on $In_{0.9}Ni_{0.1}TaO_4$, were 15 to 30 nm. A clear formation of stepped- structure was also observed in $In_{0.9}Ni_{0.1}TaO_4$ particles and TEM-EDAX analysis showed $In_{0.9}Ni_{0.1}TaO_4$ has a homogeneous atomic distribution.[10]

The first principle calculations were conducted to determine of the band structure of $In_{0.9}Ni_{0.1}TaO_4$ using of $In_{14}Ni_2Ta_{16}O_{64}$ model. The electrons from the Ni-$3d^8$ dopant seem to be somewhat delocalized, thus contributing to the formation of the new band with the O-*2p* electrons. Based on a comparison with the light absorption and photocatalytic activity, we think the e_g state of the Ni-$3d^8$ plays a significant role in the photocatalytic splitting of pure water under visible light irradiation.

In natural photosynthesis, carbohydrate and O_2 are formed from CO_2 and water under solar light using so-called Z-scheme reaction composed of two photo-excitation centers, PSI and PSII, and many redox mediators. In order to develop the photocatalytic water splitting into H_2 and O_2 stoiciometrically under visible light irradiation, the mimicking system of the Z-scheme mechanism using reversible redox mediators (Ox/Red) was investigated. To look for the stable shuttle redox mediator and its appropriate reaction condition is very important. We found IO_3^-/I^- redox system could work for water splitting using the mixture of Pt/TiO_2(anatase) and TiO_2(rutile) photocatalysts as PSI[H_2] and PSII[O_2], respectively. The H_2 evolution took place over Pt/TiO_2 (anatase) with the oxidation of I^- to IO_3^-, and O_2 evolution took place over TiO_2 (rutile) with the reduction of IO_3^- to I^- in the one reactor under UV light irradiation.[11]

Various kinds of visible light responding oxide semiconductor photocatalysts, such as Fe_2O_3, Bi_2WO_6, $In_2O_3(ZnO)_9$, $CrTaO_4$, $InTaO_4$, $SrTiO_3$ and so on, were screened for H_2 evolution from water including I^- ion as a reversible electron donor. On the other hand, O_2 evolution from water including IO_3^- as a reversible electron acceptor was also tested using various kinds of oxide semiconductor photocatalysts such as WO_3, In_2O_3, Bi_2O_3, $BiVO_4$, $CuWO_4$, $NiWO_4$ and so on. Finally, we found both H_2 and O_2 evolution with a stoichiometric ratio of H_2/O_2=2/1 occurred stably for more than 250 h under visible light irradiation using a mixture of Pt/WO_3 photocatalysts for O_2 evolution and $Pt/StTiO_3$(Cr, Ta-doped) photocatalyst for H_2 evolution in NaI aqueous solution. We established a new visible light water splitting system with a two-step photo-excitation mechanism using a pair of I^-/IO_3^- shuttle redox mediator. The quantum efficiency at 420 nm was about 0.1%.[12,13]

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