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Efficient Production of Black Titania Thin Film Photoanodes for Solar Water Splitting

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Photoelectrochemical (PEC) solar water splitting has a big potential for providing future sustainable energy resource. Photoelectrodes using semiconductor films for the solar water splitting systems have been enormously studied, and the water splitting efficiency in the visible light region has been recently improved day by day. An n-type semiconductor TiO_2 is a well-known most popular photocatalyst in terms of high photocatalytic activity, stability and large amount of stock (low cost). Although the less photocatalytic response in the TiO_2 at visible light region, which is covered in the almost solar spectrum, is one of the big issues due to its wide band gap (~3.2 eV), the visible light response has been recently much improved by blackening of TiO_2 such as hydrogen-doped TiO_2 (TiO_2:H) [1], sulfur-doped TiO_2 (TiO_2:S) [2] and oxygen deficient TiO_{2-x} [3]. These modifications successfully realized to increase absorption of visible light wavelength, leading to a significant enhancement of photocatalytic activity under sunlight irradiation.

However, the blackening step from pristine TiO_2 takes long time (more than several hours at least) due to the low process temperature and needs hazardous conditions in some cases: an annealing at 200 °C for 5 days in high pressure H_2 gas at 20 bar for TiO_2:H, at 600 °C for 4 h in H_2S gas for TiO_2:S and at 500 °C for 6 h in low vacuum pressure at 0.5 Pa for TiO_{2-x}. Therefore, further straightforward and rapid process to obtain the black titania is demanded for application uses.

Recently, we have studied ultraviolet laser induced crystal nucleation and growth of oxide thin films from chemical solution [4], and the efficient polycrystalline growth of TiO_2 thin films from the precursor has been realized so far. In other case, emergence of oxygen deficiency was also revealed in a rutile TiO_2 single crystal surface by a pulsed UV laser irradiation. In this case, we have observed unconventional metallic state was realized by the oxygen deficient TiO_{2-x} that was not converted to Magnéli phases Ti_nO_{2n-1} but maintained the original rutile crystal structure with stacking faults [5]. This oxygen deficiency was realized by instantaneous photothermal heating under pulsed UV laser irradiation. Based on these results, we have tried an efficient production of black titania photoanodes using the UV laser irradiation to the TiO_2 films in this work, and realized very rapid conversion during several minutes from a pristine TiO_2 film to an oxygen deficient TiO_{2-x} film that showed 2.6-fold higher solar-to-hydrogen efficiency.

[1] X. Chen et al., Science 331 (2011) 746., [2] C. Yang et al., JACS 135 (2013) 17831., [3] Z. Wang et al., Energy Environ. Sci. 6 (2013) 3007. [4] T. Nakajima et al., Chem. Soc. Rev. doi:10.1039/c3cs60222b. [5] T. Nakajima et al., J. Solid State Chem. 182 (2009) 2560.