Characterization of Metal Oxides Serving as Photocatayst for Water Splitting under Light Illumination

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Fujishima and Honda in 1972 first showed that n-TiO_2 can be used as a photoanode for the photoelectrolysis of H_2O in a photoelectrochemical cell (PEC) as shown in Figure 1. Since then, a large number of semiconductor materials have been investigated for photoelectrocatalytic electrodes for H_2 production. However, the PEC cell suffers from the instability of semiconductor in aqueous media. Metal oxide semiconductors with wide bandgap (2.5–4.0 eV) such as TiO_2, ZnO, $NaTaO_3$, Fe_2O_3, $SrTiO_3$, WO_3 and Cu_2O are typically more stable compared to those narrow band gap materials (0.8–2 eV) in aqueous media.

Thermodynamically, the energy requirement for the water splitting reaction is 1.23 eV. However, considering the loss mechanisms such as series resistance and the electrocatalytic overpotential, the optically produced electron hole pairs need an energy difference of approximately 2 eV for efficient photoelectrolysis. Most metal oxide semiconductors are semiconductors having a band gap bigger than 2 eV and have been studied previously for application in water splitting. A major attraction of metal oxide is that it is inexpensive, non-toxic, and readily available.

Manufacture of metal oxide semiconductors by sol-gel (SG), traditional solid-state (SS) technique is an inexpensive and convenient method. The objective of this study is to investigate the material structural properties, which have a great influence on the efficiencies of water splitting.

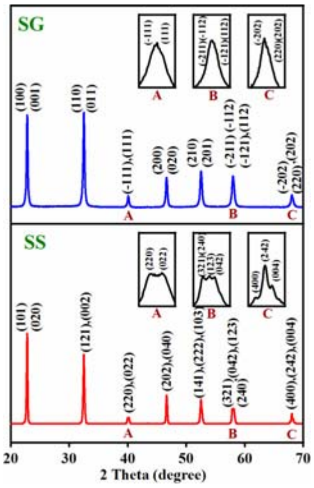

Figure 1. X-ray diffraction spectrum of sodium tantalate synthesized by sol-gel and solid state method (Rigakue, RINT2000).

Perovskite-type $NaTaO_3$ derived from a sol-gel (SG) synthesis exhibited a larger surface area and a remarkably higher photocatalytic activity in water splitting than the solid-state (SS) synthesized $NaTaO_3$. The sol-gel and solid-state $NaTaO_3$ had different crystalline structures of monoclinic P2/m and orthorhombic Pcmn, respectively. The different crystalline structures were observed by X-ray diffraction spectrum as shown in Figure 1. The monoclinic and orthorhombic phase $NaTaO_3$ were confirmed by X-ray diffraction pattern (Figure 2).

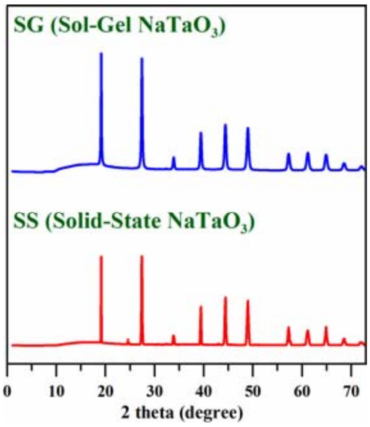

Figure 2. X-ray diffraction spectrum of sodium tantalate synthesized by sol-gel and solid-state method (NSRRC).

The differences in the XRD peaks observed might result from the difference in the preparation temperature because the crystalline structure of $NaTaO_3$ is sensitive to temperature.

Fig. 3 shows H_2 and O_2 evolutions from the photocatalytic reaction system. In principle, H_2 and O_2 were evolved in the ratio of ca. 2/1. The evolution was slow initially and accelerated to reach a stable rate after 50 min of reaction. The mean rates of H_2 formation were estimated to be ca. 1,940 and 13 μmol $h^{-1}g^{-1}$ for the SG and SS $NaTaO_3$, respectively.

The difference in the crystalline structure and surface area explained the higher photocatalytic activity of the sol-gel $NaTaO_3$.

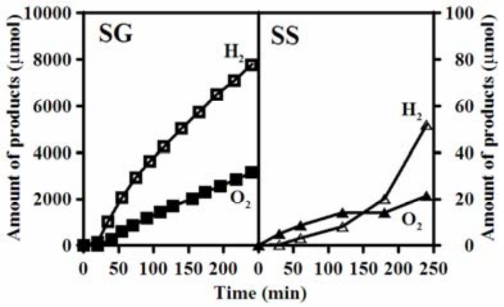

Figure 3. Photocatalytic H_2 (empty) and O_2 (full) evolution from 900 mL pure water suspended with 1 g photocatalysts of SG and SS $NaTaO_3$. Light source: 400W high-pressure mercury lamp.