New $In_2O_3(ZnO)_m$ Photocatalysts with Laminal Structure for Visible Light-induced H_2 or O_2 Evolution from Aqueous Solutions Containing Sacrificial Reagents

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$In_2O_3(ZnO)_m$ powder with laminal structure like a superlattice showed photocatalytic activities for H_2 evolution from an aqueous methanol solution and O_2 evolution from an aqueous silver nitrate solution under visible light irradiation ($\lambda>420$ nm). Anodic photocurrent was also observed under visible light irradiation ($\lambda>480$ nm) when $In_2O_3(ZnO)_m$ sintered electrodes were employed. The band gaps of $In_2O_3(ZnO)_3$ and $In_2O_3(ZnO)_9$ were 2.6 and 2.7 eV, respectively, which were smaller than those of In_2O_3 and ZnO of starting materials.

CdS,[1] WO_3,[2,3] $RbPb_2Nb_3O_{10}$,[4] and $BiVO_4$[5] have been reported as visible light-driven photocatalyst materials with reasonable activities for H_2 or O_2 evolution from aqueous solutions containing sacrificial reagents. Water splitting is enhanced on Cu_2O powder under visible light irradiation.[6] However, the number of photocatalyst materials is still small. The development of new visible light-driven photocatalyst materials is urged for achieving an artificial photosynthesis by water splitting.

Mixed oxides consisting of In_2O_3 and ZnO, $In_2O_3(ZnO)_m$, have a unique structure. They consist of slabs of wurtzite-type ZnO separated by an In_2O_3 lamella with two metal-oxygen layer thickness as shown in Figure 1.[7,8] The thickness of the ZnO slab depends on the value of m in $In_2O_3(ZnO)_m$. This structure can be regarded as a superlattice and the photochemical property is of interest.

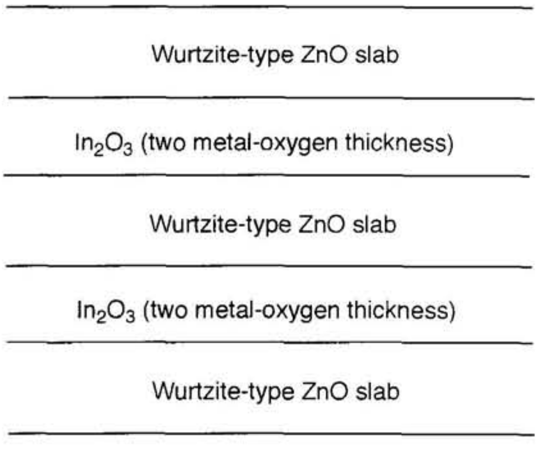

Figure 1. Schematic laminal structure of $In_2O_3(ZnO)_m$.[7]

This paper reports the photocatalytic activities and the photoresponse to the anodic current of $In_2O_3(ZnO)_m$ under visible light irradiation.

$In_2O_3(ZnO)_m$ powder was synthesized by calcination of a mixture of In_2O_3 (Kanto Chemicals, purity: 99.9%) and ZnO (Kanto Chemicals, purity: 99.0%) powder at 1620 K for 68 h with one grinding in between in air using a platinum crucible.[7,8] The product phases were confirmed by X-ray diffraction (Rigaku, RINT-1400).

Diffuse reflection spectra were measured by using a UV-VIS-NIR spectrometer with an integrating sphere (JASCO; Ubest V-570). The spectra were converted from reflection to absorbance by the Kubelka-Munk method.

Photoelectrochemical measurements were conducted in a conventional H type cell using a potentiostat (Hokuto Denko; HZ3000), a 300 W Xe illuminator (CERMAX; LX300), and cut-off filters. The reference and counter electrodes were Ag | AgCl | $KCl_{sat.}$ and Pt-black, respectively. Polycrystalline sintered disks were employed for the photoelectrochemical measurements. The ohmic contact of the oxide electrodes with lead wires was made by a Ga-In alloy. The electrolyte used was 0.3 mol/l K_2SO_4.

Photocatalytic activities for H_2 evolution from aqueous methanol solutions (H_2O 350 ml + CH_3OH 20 ml) and O_2 evolution from aqueous silver nitrate solutions (0.05 mol/l, 350 ml) were measured as test reactions for photocatalytic decomposition of water. 1 wt% of Pt was photodeposited on catalysts *in situ* when the photocatalytic H_2 evolution was tested. The photocatalytic reactions were carried out in a gas-closed circulation system connected to a gas chromatograph (Shimadzu; GC-8A, MS5A column, Ar carrier, TCD). 1 g of the catalyst powder was suspended using a magnetic stirrer and it was irradiated with visible light using a 300 W Xe illuminator and a cut-off filter.

Figure 2 shows diffuse reflection spectra of $In_2O_3(ZnO)_m$ (m=3 and 9), In_2O_3, and ZnO. The absorption edges of $In_2O_3(ZnO)_m$ were red-shifted to visible light regions compared with those of In_2O_3 and ZnO of starting materials. The broad absorption bands have no structure such as shoulders and

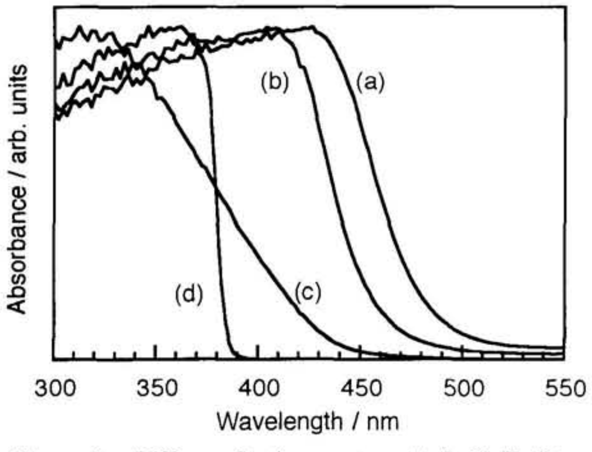

Figure 2. Diffuse reflection spectra. (a): $In_2O_3(ZnO)_3$, (b): $In_2O_3(ZnO)_9$, (c): In_2O_3, and (d): ZnO.

possess steep edges, suggesting that the absorption in the visible light region is due to not surface states but an intrinsic band transition. The onsets of spectra of $In_2O_3(ZnO)_3$ and $In_2O_3(ZnO)_9$ were about 485 and 460 nm, respectively, corresponding to 2.6 and 2.7 eV of the band gaps. These oxides were yellow or green-yellow. Distortion due to a mismatch at boundary between In_2O_3 and ZnO layers and/or superlattice structure seem to cause the red-shift. However, the detail is not clear at the present stage.

Such a red-shift is observed for a Bi_2O_3-Nb_2O_5 system.[9,10] When a solid solution is formed by Nb_2O_5 and Bi_2O_3, and the amount of Nb_2O_5 is less than ca. 30 mol%, the band gap of the solid solution becomes smaller than those of Bi_2O_3 and Nb_2O_5 of starting materials. The solid solutions show the activity for photocatalytic oxidation of 2-propanol.

Figure 3 shows a visible light response to the anodic current of an $In_2O_3(ZnO)_3$ sintered electrode. The anodic current was increased when visible light (λ>420 nm) was irradiated. The anodic photocurrent was also observed when a cut-off filter of λ>480 nm was employed, but not that of λ>520 nm. In the case of $In_2O_3(ZnO)_9$, the anodic photocurrent was observed when a cut-off filter of λ>420 nm was used, but not that of λ>480 nm. These responses agreed to the diffuse reflection spectra shown in Figure 2. The anodic photocurrent indicates that $In_2O_3(ZnO)_m$ has an n-type semiconductor characteristic.

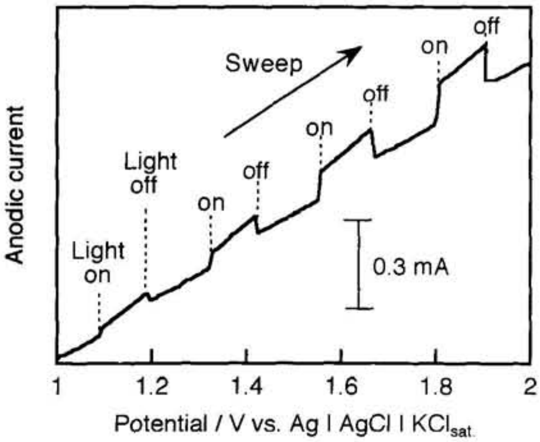

Figure 3. Visible-light (λ>420nm) response of an $In_2O_3(ZnO)_3$ sintered electrode to the anodic current.

Figure 4 shows photocatalytic H_2 evolution from an aqueous methanol solution and O_2 evolution from an aqueous silver nitrate solution under visible light irradiation (λ>420 nm) on $In_2O_3(ZnO)_9$ powder. Although solutions containing sacrificial reagents were employed, $In_2O_3(ZnO)_9$ produced H_2 or O_2 under visible light irradiation. The reaction stopped when the light was cut, showing the obvious visible-light response. An decrease in O_2 under dark is probably due to the adsorption on the catalyst surface. The adsorbed O_2 was partially recovered by photodesorption when visible light was irradiated again. When $In_2O_3(ZnO)_3$ was used, the activities of the H_2 and O_2 evolution were 1.1 and 1.3 μmol/h, respectively. Thus, it was found that the $In_2O_3(ZnO)_3$ and $In_2O_3(ZnO)_9$ photocatalyst have potentials for H_2 and O_2 evolution from aqueous solutions. However, the photocatalytic decomposition of pure water into H_2 and O_2 is not succeeded at the present stage.

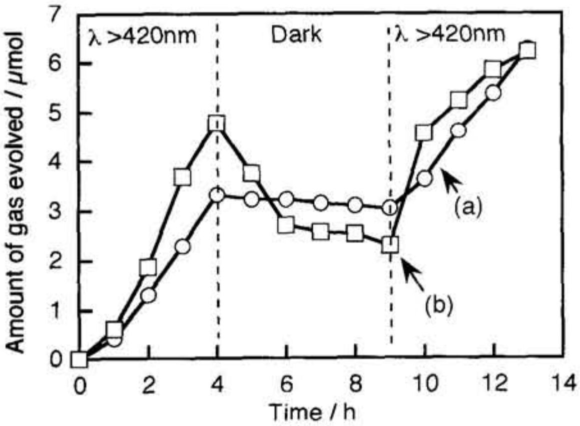

Figure 4. Photocatalytic reactions on $In_2O_3(ZnO)_9$ powder under visible light irradiation (λ >420 nm).
(a): H_2 evolution from an aqueous methanol solution,
(b): O_2 evolution from an aqueous silver nitrate solution.

In conclusion, $In_2O_3(ZnO)_m$ with laminal structure like a superlattice has arisen as structurally new type photocatalysts working under visible light irradiation.

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