



Zinc complex formation of organic ligands on zinc oxide and titanium dioxide



Hiromasa Nishikiori^{a,*}, Daichi Natori^a, Hiroyoshi Ebara^a, Katsuya Teshima^a, Tsuneo Fujii^b

^a Department of Environmental Science and Technology, Graduate School of Science and Technology, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

^b Nagano Prefectural Institute of Technology, 813-8 Shimonogo, Ueda, Nagano 386-1211, Japan

ARTICLE INFO

Article history:

Received 15 February 2016

Received in revised form 1 May 2016

Accepted 9 May 2016

Available online 14 May 2016

Keywords:

Zinc oxide

Titanium dioxide

Organic ligand

Surface complex

Photoelectric conversion

ABSTRACT

Thin films consisting of zinc oxide or titanium dioxide particles dispersing an organic ligand, i.e., 1,2-dihydroxynaphthalene (DHN) or 8-hydroxyquinoline (HQ), on the surface were prepared by the sol–gel method with steam treatment. The crystalline phases were identified by XRD analysis. The UV–vis absorption and photocurrent spectra of the films were analyzed for their photoelectrochemical characterization. The complex formation of the ligands was confirmed by FTIR spectroscopy. The ligand molecules formed zinc complexes in the interlayer of the layered zinc hydroxide which was formed on the zinc oxide surface. The zinc complex did not efficiently generate electricity because the electron injection from the DHN moiety or the zinc complex of HQ into the zinc oxide was blocked by the layered zinc hydroxide. The ligand molecules formed titanium complexes on the titanium dioxide surface, and also zinc complexes in the presence of zinc ions on the titanium dioxide surface. The zinc complex formation increased the photocurrent. It is suggested that electrons were directly injected from the DHN moiety into the titanium dioxide conduction band and indirectly injected from the excited states of the metal complex of HQ into the titanium dioxide conduction band.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Ligand–metal interaction, such as electron and charge transfer in complexes, is an important behavior to utilize for applications of functional materials in electronic devices [1–6]. Many complexes are used as photofunctional materials such as in artificial photosynthesis [4,6], solar-energy conversion cells [2–4,6], and organic electroluminescence devices [1,5]. Metal oxide films containing metal complex molecules are expected to be actually used in photovoltaic cells [7–9]. Some processes include the electronic transition between the ligand and metal electronic states. The Ru complex dyes are frequently used as effective sensitizers of dye-sensitized solar cells based on titanium dioxide as a semiconductor [7]. The photoexcitation of the Ru complex dye is due to the electron transition of the metal-to-ligand charge transfer. The electrons in such excited states of the dye are injected into the titanium dioxide conduction band. On the other hand, the

HOMO electron is directly injected into the titanium dioxide conduction band when the titanium atom on the titanium dioxide surface becomes coordinated to the organic ligands that include the dihydroxy [10–13], dicyanomethylene [14–17], and carboxylic [18] compounds.

The electron transfer and transport efficiencies depend on the extent of the ligand–metal interaction, which originates from the electron donating force of the negative atom of the ligand molecule and the electron affinity of the metal ion [19,20]. Additionally, the complex structure also significantly influences the interaction. The complex is formed by covalent bonds between the ligand molecule and metal ion [8,21,22]. The metal ion state determines the coordination reaction of the other ligands in the catalysts.

In our previous study, thin films of organic ligand-dispersing titanium dioxide gels were prepared from titanium alkoxide sols containing ligand molecules by steam treatment without heating [20,23–27]. The formation of the ligand–titanium complexes and the photoinduced electron transfer process in the systems were investigated by photoelectrochemical measurements. The complex was formed between the 8-hydroxyquinoline (HQ) and titanium species, such as the titanium ion, on the titanium dioxide

* Corresponding author.

E-mail address: nishiki@shinshu-u.ac.jp (H. Nishikiori).

nanoparticle surface through the oxygen and nitrogen atoms of the quinolate [20,27]. A photocurrent was observed in the electrodes containing the complex due to the electron injection from the LUMO of the complex into the titanium dioxide conduction band. A bidentate ligand, 2,3-dihydroxynaphthalene (DHN), formed a complex on the titanium dioxide surface through dehydration between its two hydroxyl groups of DHN and two TiOH groups of the titanium dioxide [27]. The electron injection from the HOMO of DHN to the titanium dioxide conduction band was observed during light irradiation. This direct electron injection was more effective than the two-step electron injection.

Zinc is expected to exhibit a stronger interaction with ligands than titanium due to its high electron affinity [28]. In this study, the zinc complex formation of organic ligands on zinc oxide and titanium dioxide was investigated by photoelectrochemical measurements.

2. Experimental

2.1. Materials

The ligands (DHN and HQ), zinc acetate, zinc nitrate, titanium tetraisopropoxide, methanol, ethanol, sodium hydroxide, hydrochloric acid, nitric acid, diethylene glycol, iodine, and lithium iodide (Wako, S or reagent grade) were used without further purification. Water was ion-exchanged and distilled. Glass plates coated with the transparent ITO electrode (AGC Fabritech) were soaked in hydrochloric acid (0.10 mol dm^{-3}) for 2 h, then rinsed with water. The electrolyte for the photoelectric measurement consisted of a diethylene glycol solution of iodine ($5.0 \times 10^{-2} \text{ mol dm}^{-3}$) and lithium iodide (0.50 mol dm^{-3}).

2.2. Preparation of electrodes

Zinc acetate was dissolved in a mixture of 30.0 cm^3 of methanol and 0.60 cm^3 of a 1.0 mol dm^{-3} sodium hydroxide aqueous solution in which the concentration of zinc acetate was 0.20 mol dm^{-3} . This solution was labeled SZ0. The ligand, DHN, was dissolved in the SZ0 at concentrations of 1.0, 2.0, and $3.0 \times 10^{-2} \text{ mol dm}^{-3}$. They were labeled SZ-DHN1, SZ-DHN2, and SZ-DHN3, respectively. The ligand, HQ, was also dissolved in the SZ0 at concentrations of 1.0, 2.0, and $3.0 \times 10^{-2} \text{ mol dm}^{-3}$. They were labeled SZ-HQ1, SZ-HQ2, and SZ-HQ3, respectively.

The sol-gel reaction systems (sols) were prepared by mixing 5.0 cm^3 of titanium tetraisopropoxide, 25.0 cm^3 of ethanol, 0.21 cm^3 of water, and 0.21 cm^3 of nitric acid as the catalyst of the sol-gel reaction and labeled ST0. The ligands, DHN and HQ, were individually dissolved in the ST0 at the concentration of 0.20 mol dm^{-3} . They were labeled ST-DHN and ST-HQ, respectively. Zinc nitrate was dissolved in ST-DHN and ST-HQ, in which the concentrations were 0.20 mol dm^{-3} , and labeled STZ-DHN and STZ-HQ, respectively.

The dip-coated thin films were prepared from the systems in which the sol-gel reaction proceeded for 1 day in order to prepare the electrodes. Glass plates with the indium tin oxide (ITO) electrode were dip-coated 3 times with the SZ0 and then heated at 500°C for 30 min. These were dip-coated 5 times with SZ0, SZ-DHN1, SZ-DHN2, SZ-DHN3, SZ-HQ1, SZ-HQ2, and SZ-HQ3, then steam-treated at 100°C for 30 min. These were labeled EZ0, EZ-DHN1, EZ-DHN2, EZ-DHN3, EZ-HQ1, EZ-HQ2, and EZ-HQ3, respectively. Glass plates with the ITO electrode were dip-coated 3 times with the ST0 and then heated at 500°C for 30 min. These were dip-coated 5 times with ST0, ST-DHN, STZ-DHN, ST-HQ, and STZ-HQ, then steam-treated at 100°C for 30 min. These were labeled ET0, ET-DHN, ETZ-DHN, ET-HQ, and ETZ-HQ, respectively. The glass plates without the ITO were also coated with the sols in

order to measure the XRD pattern. The film samples were initially labeled "F" on the sample name substituted for "E" such as FZ0 and FZ-DHN1.

2.3. Measurements

The crystalline phase of the film samples was determined using an X-ray diffractometer (Rigaku SmartLab). The surface morphology of the electrode samples was observed using a field emission scanning electron microscope (Hitachi S-4100). The layer thickness was estimated from their cross-section images. The UV-vis absorption spectra of the electrode samples were observed using a spectrophotometer (Shimadzu UV-3510). The amounts of the ligands existing in the electrode samples were estimated from the absorption spectra of the ligands eluted by the 0.1 mol dm^{-3} hydrochloric acid or sodium hydroxide aqueous solution. The flakes of the ligands and ligand-dispersing film samples were pressed in KBr pellets and their IR spectra were obtained using an FTIR spectrophotometer (Shimadzu FTIR-8300).

The iodine-based electrolyte was allowed to soak into the space between the electrode sample and the counter Pt electrode. Monochromatic light from a fluorescence spectrophotometer (Shimadzu RF-5300) with a 150 W Xe short arc lamp (Ushio UXL-155) irradiated the electrodes for the spectroscopic measurements. The area of the irradiated electrode was 0.4 cm^2 although that of the whole electrode was 10 cm^2 . During the light irradiation, the short circuit currents of the electrodes were measured in the electrolyte solutions by a digital multimeter (ADCMT 7461A). The J - V curves of the electrodes were measured by a potentiostat during visible light (0.40 W cm^{-2}) irradiation at a wavelength longer than 390 nm emitted by the 150 W Xe short arc lamp using a sharp cutoff filter (UV-39). The intensity at each wavelength of the light source was obtained using a power meter (Moletron PM500A) in order to estimate the incident photon-to-current conversion efficiency (IPCE) and quantum efficiency for the photocurrent from the excited ligands, i.e., the absorbed photon-to-current quantum efficiency (APCE), in the electrode samples. The visible absorbance of the present electrode samples was less than 1.0, which was sufficient to measure the number of absorbed photons in order to calculate the quantum efficiency.

3. Results and discussion

3.1. Surface structure of the ligand-dispersing films

The thickness of the ligand-containing layers prepared from the systems containing zinc acetate and titanium tetraisopropoxide was ca. 100 and 350 nm, respectively. The SEM images of the films prepared from the solutions or sols containing zinc acetate or titanium tetraisopropoxide are shown in Fig. 1. The films consisted of particles having about 5–10 nm diameters in all the films, independent of the zinc or titanium and with or without the ligands. The particles were aggregated and formed the secondary particles in each film. The crystal growth of the zinc oxide or titanium dioxide did not significantly proceed and the crystallinity was low because the films were prepared by the steam treatment at the low temperature of 100°C . Fig. 2 shows the XRD patterns of the films from the solutions containing zinc acetate with or without the ligands. All the films exhibited peaks at 31.7° , 34.3° , and 36.2° assigned to the (100), (002), and (101) planes of Wurtzite zinc oxide. The crystallite size was estimated from the full-width at half-maximum of the 36.2° peak using Scherrer's equation and was 18–19 nm in the present films. Additionally, a peak was observed at 6.6° in the ligand-free film. This peak was assigned to a layered zinc hydroxide containing acetate ions, $\text{Zn}_5(\text{OH})_8(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ [29–34], and shifted to the lower angle side with the DHN content

Download English Version:

<https://daneshyari.com/en/article/26098>

Download Persian Version:

<https://daneshyari.com/article/26098>

[Daneshyari.com](https://daneshyari.com)