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Photoanodic properties of sol–gel-derived iron oxide thin films with embedded gold nanoparticles: effects of polyvinylpyrrolidone in coating solutions

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Abstract

Fe_2O_3 thin films containing dispersed Au nanoparticles were prepared on nesa silica glass substrates, using $Fe(NO)_3 \cdot 9H_2O$–$HAuCl_4 \cdot 4H_2O$–$CH_3COCH_2COCH_3$–$CH_3OC_2H_4OH$ solutions containing polyvinylpyrrolidone (PVP). The photoanodic properties were studied in a three-electrode cell with the film sample as the working electrode and an aqueous buffer solution of pH=7 as the supporting electrolyte. The Au particles increased photoanodic quantum efficiency at wavelengths <500–600 nm. Quantum efficiency was further increased by modifying the microstructure of the film electrodes through the addition of PVP. The maximum incident photon to current efficiency (IPCE) of about 20% was achieved in an Au-dispersed film prepared from a solution containing PVP. PVP in coating solutions provided the fired films with an increase in size of the grains and voids between them and in donor density, either of which could contribute to the increased IPCE.

Keywords: Photoelectrode; Photoelectrochemistry; Iron oxide; Sol–gel

1. Introduction

A number of studies have been carried out on wet-type solar cells since the discovery of Honda–Fujishima effect [1]. Semiconductor electrodes for wet-type solar cells should have higher energy conversion efficiency and high photoelectrochemical stability in aqueous solutions. In spite of the photoelectrochemical stability in aqueous solutions, TiO_2 has a large bandgap of about 3 eV, and hence is photoexcited only by the ultraviolet light, which occupies 5% of the solar spectrum. Therefore, semiconductor electrodes that exhibit photoresponse to the visible light are strongly demanded. Sensitization of TiO_2 with Ru complexes [2] is the most well-known challenge on this issue.

α-Fe_2O_3, an n-type semiconductor, is another photoelectrode material for wet-type solar cells that has been studied for a long time [3]. α-Fe_2O_3 has relatively small bandgap of ca. 2.2 eV, and is photoelectrochemically stable in aqueous solutions. Also the Clarke number of Fe is the fourth largest at 4.70, which is attractive from the viewpoint of natural resources. However, because of the small optical absorption coefficient and of the low carrier mobility, α-Fe_2O_3 normally shows low quantum efficiency [3]. In order to overcome these problems Björksten et al. [4] prepared porous α-Fe_2O_3 thin films consisting of nanocrystals of 25–75 nm in size, reporting that the film electrode showed the maximum incident photon to current efficiency (IPCE) of 1.7% in a 0.1 M ethanolic solution of LiI at a potential of 0.4 V vs. SCE (saturated calomel electrode) with illumination from the rear side. Kahn et al. [5] prepared thin films comprising α-Fe_2O_3 nanocrystals by spray-pyrolysis, and optimized the preparation conditions, achieving the maximum IPCE of 22.5% at a potential of 0.6 V vs. SCE in a 1.0 M NaOH aqueous solution.

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Recently, our group prepared α-Fe_2O_3 thin films containing dispersed Au and Ag particles 5–20 nm in size by sol–gel method, finding that the metal particles, especially Au particles, enhance the quantum efficiency of the film electrodes [6]. IPCE increased by eight times up to 4% at wavelengths around 400 nm by embedding Au particles where the electrode was immersed in an aqueous buffer solution of pH=7, illuminated from the front side. The Au particles on the surface of the film were supposed to catalytically promote the hole transfer from the valence band of Fe_2O_3 to the supporting electrolyte.

Further increase in quantum efficiency is expected when the Au-dispersed Fe_2O_3 films are made porous, which can provide larger numbers of photoelectrochemical reaction sites. In the present study, polyvinylpyrrolidone (PVP), an organic polymer, was added to the coating solution to prepare porous Au-dispersed Fe_2O_3 films. The effect of the PVP content in solutions on the photoanodic properties of the films was studied as well as the effect of the Au content.

2. Experimental details

2.1. Preparation

$Fe(NO_3)_3 \cdot 9H_2O$, $HAuCl_4 \cdot 4H_2O$, PVP (K-90, viscosity average molecular weight of 6.3×10^5), $CH_3COCH_2COCH_3$ and $CH_3OCH_2CH_2OH$, all purchased from Wako, Osaka, Japan, were used as the starting materials. Thin film electrodes were prepared from solutions given in Table 1 via the procedure shown in Fig. 1. The mole ratio for PVP in Table 1 is defined for the monomer (polymerizing unit). Hereafter the solutions are called, for instance, P15A60 when PVP/Fe and Au/Fe mole ratios are 1.5 and 0.06, respectively. Prescribed amount of $HAuCl_4 \cdot 4H_2O$ was dissolved in $CH_3OC_2H_4OH$, and then PVP, $CH_3COCH_2COCH_3$, $Fe(NO_3)_3 \cdot 9H_2O$ were added and dissolved in this sequence. The resultant homogeneous solutions were used as the coating solutions. Gel films were deposited on silica glass substrates ($20 \times 40 \times 1.2$ mm^3) coated with nesa (Sb-doped SnO_2), where dip-coating was conducted at a substrate withdrawal speed of 3 cm min^{-1}. The gel films were pre-heated at 100°C for 2 min and then fired at 700°C for 10 min. Gel film deposition and heat-treatment were not repeated unless otherwise noted.

Table 1
Molar composition of the starting solutions

Solutions	Molar ratio				
	$Fe(NO_3)_3 \cdot 9H_2O$	PVP	$HAuCl_4 \cdot 4H_2O$	$CH_3COCH_2COCH_3$	$CH_3OC_2H_4OH$
P00A00	1	0	0	2	20
P08A00	1	0.8	0	2	46
P12A00	1	1.2	0	2	46
P15A00	1	1.5	0	2	46
P00A60	1	0	0.06	2	20
P12A60	1	1.2	0.06	2	46
P15A15	1	1.5	0.015	2	46
P15A30	1	1.5	0.03	2	46
P15A50	1	1.5	0.05	2	46
P15A60	1	1.5	0.06	2	46

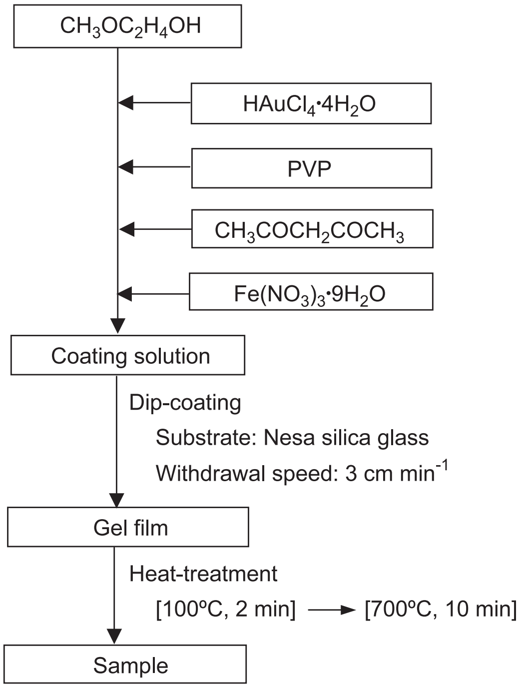

Fig. 1. Flow chart showing preparation of Fe_2O_3 thin films containing dispersed Au particles.

2.2. Characterization

The thickness of the films was measured using a contact probe surface profilometer (SE3400, Kosaka Laboratory, Tokyo, Japan) in a manner described elsewhere [7]. Crystalline phase identification was conducted by X-ray diffraction (XRD) measurement using an X-ray diffractometer with a thin film attachment (RAD IIA, Rigaku, Osaka, Japan) and with Cu Kα radiation operated at 40 kV and 40 mA. Electron microscopic observation was made using an field emission type scanning electron microscope, FE-SEM (JSM-6500F, JEOL, Tokyo, Japan). Optical absorption spectra were measured on the film samples using an optical spectrophotometer (UV-2400PC, Shimadzu, Kyoto, Japan), where a bare nesa silica glass substrate was used as the reference.

2.3. Photoelectrochemical measurement

Photoanodic properties of the films were evaluated in a three-electrode cell using a potentiostat (HZ3000, Hokuto Denko, Osaka, Japan). The three-electrode cell consisted of the film electrode sample, a platinized Pt electrode and SCE as the working, counter and reference electrodes, respectively, and of a buffer solution of pH 7, an aqueous solution of 0.2 M $Na_2B_2O_4$, 0.14 M H_2SO_4 and 0.3 M Na_2SO_4, as