Extended Abstracts of the 2012 International Conference on Solid State Devices and Materials, Kyoto, 2012, pp354-355

Surface Plasmon Resonance Enhanced Photocurrent Properties of Ag-loaded Titanium Dioxide Composite/Dye on Metallic Grating Surface

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1. Introduction

Dye-sensitized solar cells (DSSCs) are one of the most promising candidates for inexpensive solar cells based on organic materials. A number of studies have been reported for the improvement of the efficiency, which include the development of dye [1], metal oxides [2], Metal oxide / nano-metal composite [3] in cells. The use of nanoscale metal particles can excite localized surface plasmon resonance (SPR), which enhance the optical field of incident light near the particles [4]. Recently, we have reported the use of grating surface with propagating surface plasmon excitation the improvement of light scattering and light trapping to increase photocurrent of DSSCs [5].

In this work, we fabricated dye/Ag-loaded TiO_2 films on a metal grating surface to couple with surface plasmon resonance for the enhancement of photocurrent in DSSCs.

2. Experimental and Results

Synthesis

The bare TiO_2 and Ag-TiO_2 nanoparticles were prepared through a flame spray pyrolysis (FSP) route with starting material of titanium isopropoxide and silver nitrate as starting materials. This solution was added drop wise into a dilute acetonitrile/xylene solution (20% vol. / 80%vol.) under stirring material. The dopant concentrations in at% fraction of silver were set as 0.5%, 1.0% and 3% respectively. In a typical run, the precursor is fed into a FSP reactor by a syringe pump with a rate of 5 ml/min while 5 l/min O_2 was being dispersed (5/5 flame).The gas flow rates of methane and O_2 supporting flamelet were 1.19, and 2.46 l/min respectively. The pressure drop at the capillary tip was kept constant at 1.5 bars by adjusting the orifice gap area at the nozzle. Finally, the product nanoparticles were collected on a glass microfiber filters with the aid of a vacuum pump[6].

Fabrication of the DSSCs

We cut the BD-Rs (TAIYO YUDEN) into a pieces and then the bare polycarbonate grating (Λ = 320 nm) substrates were cleaned. The substrates were immersed in nitric acid and washed in deionized water to remove the dye layer deposited on the polycarbonate grating side. They were then covered with a gold layer of approximately 150 nm by a vacuum evaporation technique. Ag/TiO_2 solution was prepared in an ethanol. The Ag/TiO_2 solution was spin-coated on BD-Rs grating substrates (1000rpm, 60s). The deposited Ag/TiO_2 film was annealed at 100 ^oC for 3 hours under ambient conditions. The dye layer was deposited by layer-by-layer deposition method with 5,10,15,20-Tetrakis (1-methyl-4-pyridinio) porphyrin tetra(p-toluenesulfonate) (TMPyP, 0.25 mg ml^{-1}), sodium copper chlorophyllin (SCC, 0.25 mg ml^{-1}) using the Decher approach. The grating/Au/Ag-TiO_2 substrates were immersed in aqueous solutions of TMPyP and SCC alternately for 15 min each until the desired number of layers was achieved. Two min rinses with deionized water were performed twice between the depositions. The electrolyte used was 0.1 M sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) and 1 M sodium sulfate (Na_2SO_4) in deionized water. An ITO glass substrate with a sheet resistance of 10 Ω/sq was used as the cathode[5].

X-ray diffraction

Fig.1 shows the X-ray diffraction patterns of flame-spray-made bare TiO_2 and 0.5–3.0 at% Ag/TiO_2 nanopowders. All samples were highly crystalline, and all peaks can be confirmed to be the Anatase and Rutile phase of TiO_2. Ag peaks were found in these patterns. It can be assumed that the amount of Ag concentration was very low, Ag peaks were not found.

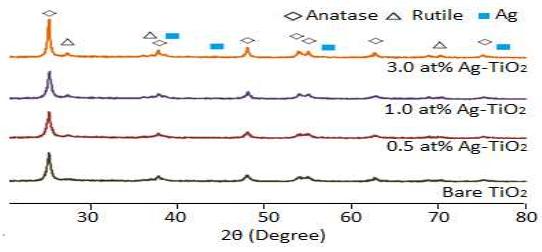

Fig. 1 XRD patterns of the investigated bare TiO_2 and Ag-TiO_2 samples

Scanning electron microscopy (SEM) and Energy- dispersive X-ray spectroscopy (EDS)

The surface morphology image and EDS spectrum of elements for 3.0 at% Ag-TiO_2 nanoparticles are shown in Fig. 2 It can be seen that the film surface is highly porous

and contains high-density nanoparticles with diameters smaller than 50 nm. In addition, nanoparticles are uniformly distributed on the surface. The EDS spectrum in the inset of Fig. 2 clearly shows elemental signals corresponding to Ti, O and Ag. The EDS data confirms the existence of Ag and the Ag content in this region is found to be 0.66 at%, which is in good agreement with the intended concentration

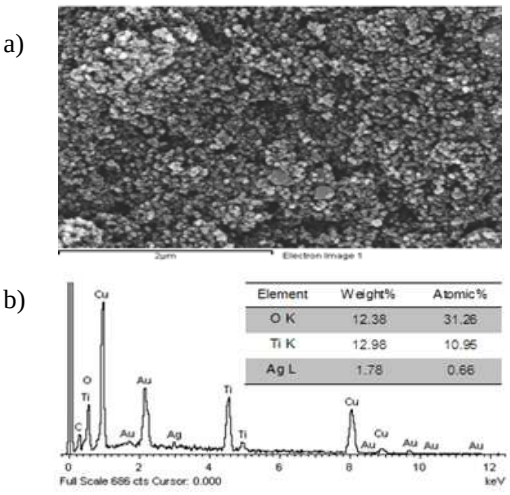

Fig. 2 SEM image of 3.0 at% Ag-TiO_2 nanoparticles(a). Inset shows EDS spectrum for the region indicated the white arrow (b).

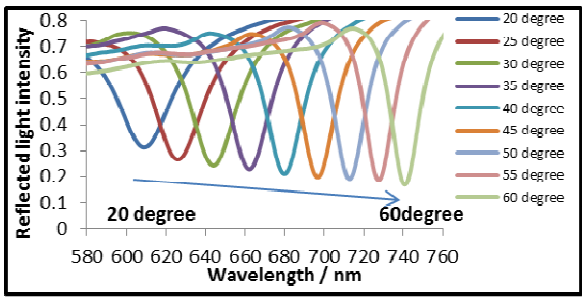

Fig. 3 Surface plasmon resonance reflectivity curves of the fabricated dye-sensitized solar cell, measured at fixed incident angles from 20 to 60 degree.

Surface plasmon resonance properties

As shown in Fig. 3, the SPR dip wavelength of all samples were shifted to the longer wavelength with increasing the incident angle. These results indicate that the grating-coupled surface plasmon can be excited in the cells. In addition, The SPR dips in the range of 20-60^o of incident angles were corresponded with the absorption peak of TMPyP-SCC LBL at 640 nm.

Short-circuit photocurrent properties

Short-circuit photocurrent properties of the dye-sensitized cell composed of the Au grating/ Ag-TiO2/TMPyP-SCC LbL (10 bilayers)/electrolyte/ITO substrates were measured. The measurements were investigated by irradiating the collimated light from a 350 mW xenon lamp. The p-polarized light was used for the excitation of SP, while s-polarized light was used for the non excitation of SP to compare the results. The effect of surface plasmon (SP) excitation on the short-circuit photocurrent was studied by the irradiation of the visible light (490-740) on the fabricated DSSCs. From the results, short-circuit photocurrents of fabricated DSSCs with Ag-loaded TiO_2 thin films were higher than that with unloaded TiO_2 thin film. Furthermore, the highest photocurrent was obtained at 25-30^o of incident angle in all DSSCs that corresponded to the SPR excitation wavelength and absorption peak of the dye. The enhancement of the short-circuit photocurrent by the excitation of surface plasmon with the Ag loading was studied by using p/s factor, the ratio of the current with SP excitation to the current without SP excitation as shown in Fig. 4. From the results, the p/s factor increased with increasing the amount of Ag-loading into TiO_2. These resulted from the strong field enhancement of surface plasmon excitation due to the interaction between the grating structure and the nanoparticle.

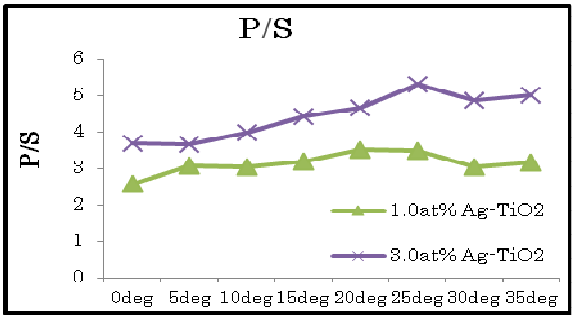

Fig. 5 Enhanced factor p/s, that is, the ratio of the current with surface plasmon excitation (p-pol.) to the current without surface plasmon excitation (s-pol.).

3. Conclusions

DSSCs consisted of an indium-tin oxide (ITO)/Ag-TiO2/dye/electrolyte/gold structure as shown in figure in the right. SPR excitation was observed in the fabricated cells upon irradiation with visible light. Short-circuit photocurrent was increased when surface plasmon (SP) was excited on the silver nanoparticles.

Acknowledgements

The authors gratefully acknowledge the financial support from the Niigata University, under the program Strategic Scholarships for Global circus Program, Japan. The International Research University Project under Center for Transdisciplinary Research, Niigata University, Japan and Graduate School, Department of Chemistry, Faculty of Science, Chiang Mai University.

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