

Short Communication

Cerium Doped Fluorescence into TiO₂ Photoelectrode for Enhancement of Electrochemical Response in Dye Sensitized Solar Cells

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We have used unique composition of yttrium aluminum garnet doped with cerium ion (combination of light adsorbing and photon emitting materials) to develop TiO₂ photoelectrode for high sensitivity dye sensitized solar cells. Fluorescence YAG:Ce based DSSC exhibits higher incident photon to current conversion efficiency (IPCE) between 500 nm and 600 nm wavelength region. Therefore, the use of Ce can support the adsorption of light at certain wavelength and this adsorbed energy was rearranged with YAG which can continuously emit photons at a certain wavelength (at 539 nm) to increase probability of interaction of photons with dye molecules. This process had enhanced the excitons in dye molecules and these were rapidly split into electrons and holes on TiO₂ nanostructure electrode surface. The energy conversion efficiency of TiO₂ electrode with optimum YAG:Ce complexes was 6.3% which is enhanced by a factor of two in compared to the only TiO₂ photoelectrode base DSSC.

Keywords: Fluorescence additive, Dye-sensitized solar cells, TiO₂ electrode, photovoltaic performance

1. INTRODUCTION

The uses of rare-earth doped fluorescence material in dye-sensitized solar cells (DSSC) have attracted considerable attention as cost efficient candidate to traditional photovoltaic device [1-4]. This utilization of the light-converting materials have enhanced surface area for higher amount of dye molecules adsorption and the properties of electron transport into photoanode materials for improving

their performance. Despite of several efforts by scientific community, there has been no report finding optimum nano-structures and/or materials for best solution to overcome issues associated with stability, efficiency and cost effective production. This is because the optimum material should have higher surface area, better light scattering properties and higher yield for electron transportation [5-7].

The photons interact with dye molecules to create excitons in DSSCs. These excitons come in contact with nanoparticle/nanostructures at surface of photoelectrons and are rapidly split with electrons and holes. Electrons inject into the photoelectrode and holes leaving the opposite side of the device by means of redox species (traditionally the I^-/I_3^- couple) in a liquid or solid-state electrolytes used in DSSC to ensure efficient electron transfer to the redox couple [8-14]. In DSSC process, extensive work has been carried out to enhance electron transportation, increasing surface area and improving the stability of electrolytes. However, a very little attention has been paid towards development of down- or up converting materials and structures which can enhance the light photon interaction with dye molecules to achieve higher proportion of excitons.

The fluorescence materials can be an ideal choice to enhance coupling of the light photon with dye molecules. Xu et. al. report the adsorption of light emitted from fluorescent materials by N3 dye to generate excitons, and considerably increase the light harvesting and the photocurrent of DSSCs [15]. Liu et al. had developed the Dy^{3+} doped $LaVO_4$ luminescent film onto back of the DSSC, and the overall conversion efficiency was improved by 23.3% relative to the referenced cell coated with an undoped $LaVO_4$ film [16].

The objective of this study was towards down-conversion of TiO_2 electrode containing a fluorescent and improvements in the short-circuit current density and the overall conversion efficiency. We have used Ce which can support the adsorption of light at certain wavelength and this adsorbed energy was rearranged with YAG to achieve continuous emission of photons at a certain wavelength to enhance interaction probability of photons with dye molecules. The effect of fluorescence YAG:Ce on TiO_2 photoelectrode to enhance conversion efficiency of dye-sensitized solar cells (DSSCs) was investigated. XRD and SEM were used to determine the structural and morphology of this hybrid photo-electrode. Absorption and luminescence properties of dye and fluorescence YAG:Ce ceramics were investigated using UV spectrophotometer and photoluminescence spectrometer. Electrochemical measurements were used to optimize the wt% of fluorescence materials in TiO_2 photo-electrode for higher conversion efficiency (η), fill factor (FF), open-circuit voltage (V_{OC}) and short-circuit current (I_{SC}).

2. EXPERIMENTAL

TiO_2 power was dispersed for 10 h at 300 rpm using a ball mill (Planetary Mono Mill, FRITSCH) by adding acetyl acetone, poly(ethylene glycol) (MW = 20,000), and Triton X-100 to obtain viscous TiO_2 paste. YAG doped with cerium ion as fluorescence materials was purchased from Sigma-Aldrich Co. To obtain fluorescence doped TiO_2 paste, different wt.% ratio of YAG doped with cerium ion were added in TiO_2 paste and ball mill mixed for 2 h. TiO_2 and fluorescence doped TiO_2 pastes were coated onto the fluorine-doped SnO_2 conducting glass plates (FTO, $10 \Omega \text{ cm}^{-2}$, Asahi

glass co.) using squeeze printing technique and followed by sintering at 450 °C for 30 min. About 10 μm thick TiO_2 film was deposited on the 0.25 cm^2 size FTO glass substrate. The glass-FTO/ TiO_2 and fluorescence doped TiO_2 electrodes were immersed overnight (ca. 24 h) in a 5×10^{-4} mol/L ethanol solution of $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$ (535-bis TBA, Solaronix), rinsed with anhydrous ethanol and dried. Few drops of the liquid electrolyte (which was composed of 0.3 mol/L 1,2-dimethyl-3-propylimidazolium iodide (Aldrich), 0.5 mol/L LiI (Aldrich), 0.05 mol/L I_2 (Aldrich), and 0.5 mol/L 4-*tert*-butylpyridine (4-TBP, Aldrich) and 3-metoxypionitrile as a solvent) were dispersed onto surface and a fully cell assembly was constructed for electrochemical measurements. Field emission scanning electron microscopy (FE-SEM, Hitachi, S-4700) was used to picture microstructures of films. UV–Vis spectrum of the N719 dye solution with UV–Vis spectrophotometer (Shimadzu UV-1601A, Japan) and luminescence property of YAG:Ce powder by a fluorescence spectrometer (LS 55, PerkinElmer, USA) were measured. Incident photon to current conversion efficiency (IPCE) was measured as a function of wavelength from 300 nm to 800 nm using a specially designed IPCE system for dye-sensitized solar cell (PV Measurements, Inc.). The photovoltaic properties were investigated by measuring the I-V characteristics under irradiation of 500 W Xenon lamp (Thermo Oriel Instruments, USA). The incident light intensity and the active cell area were 100 mWcm^{-2} .

3. RESULTS AND DISCUSSION

FE-SEM images of TiO_2 powder, YAG:Ce powder and TiO_2 film with YAG:Ce powder were shown in figure 1 a, b and c. Fluorescence powder particles were of non-uniform shapes and had size in the range of 5 to 7 μm . These non-uniform structures of powder had generated porous and higher surface morphology at fluorescence powder doped TiO_2 film surface. Fluorescence materials have advantages to achieve higher percentage of adsorption of dye molecules and can support deeper penetration of I^-/I_3^- redox used into the TiO_2 film based DSSC.

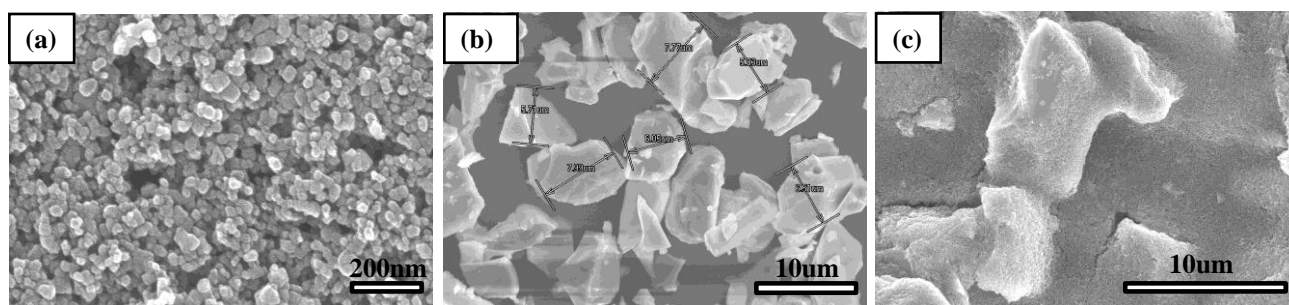


Figure 1. FE-SEM images of TiO_2 powder (a), fluorescence YAG:Ce powder (b) and fluorescence YAG:Ce powder doped TiO_2 electrode (c).

Figure 2 shows XRD pattern of TiO_2 powder, fluorescence doped TiO_2 films on FTO substrate after heating at 450 °C and fluorescence powder. Rutile phase of TiO_2 can easily distinguish by diffraction peaks at 25.5° 2θ value assigned to reflections from (101) crystal plane. Rutile phase of Ti

was also observed. Additional peaks associated with fluorescence particle structures were also observed in fluorescence doped TiO₂ films. The XRD positions were also confirmed by taking XRF spectra of fluorescence powder spectra and this confirms dispersion of fluorescence powder with TiO₂ in photo electrode.

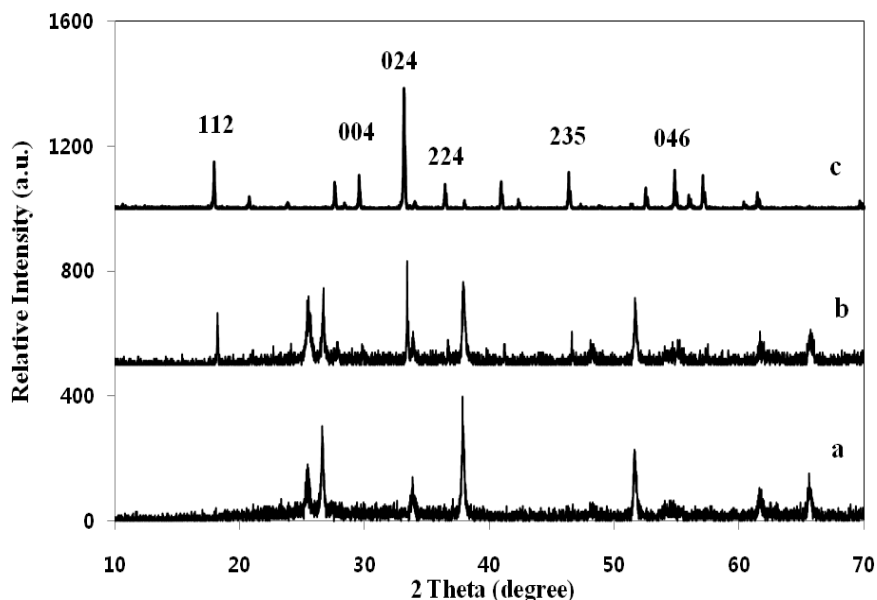


Figure 2. XRD pattern of TiO₂ electrode (a), fluorescence powder doped TiO₂ electrode (b), and fluorescence powder (c)

Figure 3A shows the optical property of N719 dye by UV-Vis spectroscopy in ethanol solution and the photoluminescence (PL) emission spectrum of YAG:Ce phosphors using a fluorescence spectrophotometer (LS 55, PerkinElmer, USA). The UV-Vis spectrum of N719 dye shows two absorption bands (385 nm, 530 nm) as metal-to-ligand charge transfer (MLCT) transitions ($4d-\pi^*$) between 300 nm and 580 nm. A broad emission spectrum with a peak at 539 nm was observed under the excitation of 456 nm, it is a typical $5d^1 \rightarrow 4f^1$ transition broad emission of Ce³⁺. The photoluminescence at 539 nm matches in the good absorption range of the N719 dye. This result indicates that YAG:Ce can be used as effective light down-converting materials to improve the light harvesting for DSSCs [7].

The action spectra shown in Figure 3B demonstrate increases in IPCE values in the visible region for the DSSC prepared with YAG:Ce based materials. The effect of YAG:Ce additive is clearly seen when comparing IPCE of without YAG:Ce. Specially, fluorescence YAG:Ce based DSSC exhibits higher IPCE between 500 nm and 600 nm wavelength region. A broad emission peak at 539 nm in photoluminescence spectra of YAG doped with cerium ion was observed. Photons from this broad emission spectrum can interact with dye molecules and can create additional excitons. The intensity had increased with increasing the Ce concentration in YAG powder and above 550 nm YAG band gap can be seen. Therefore, the use of Ce can support the adsorption of light at certain wavelength and this

adsorbed energy was rearranged with YAG which can continuously emit photons at a certain wavelength to increase probability of interaction of photons with dye molecules. Interaction of photons emitted from Ce added YAG powder with dye molecules is very important in this study to enhance the efficiency of DSSC.

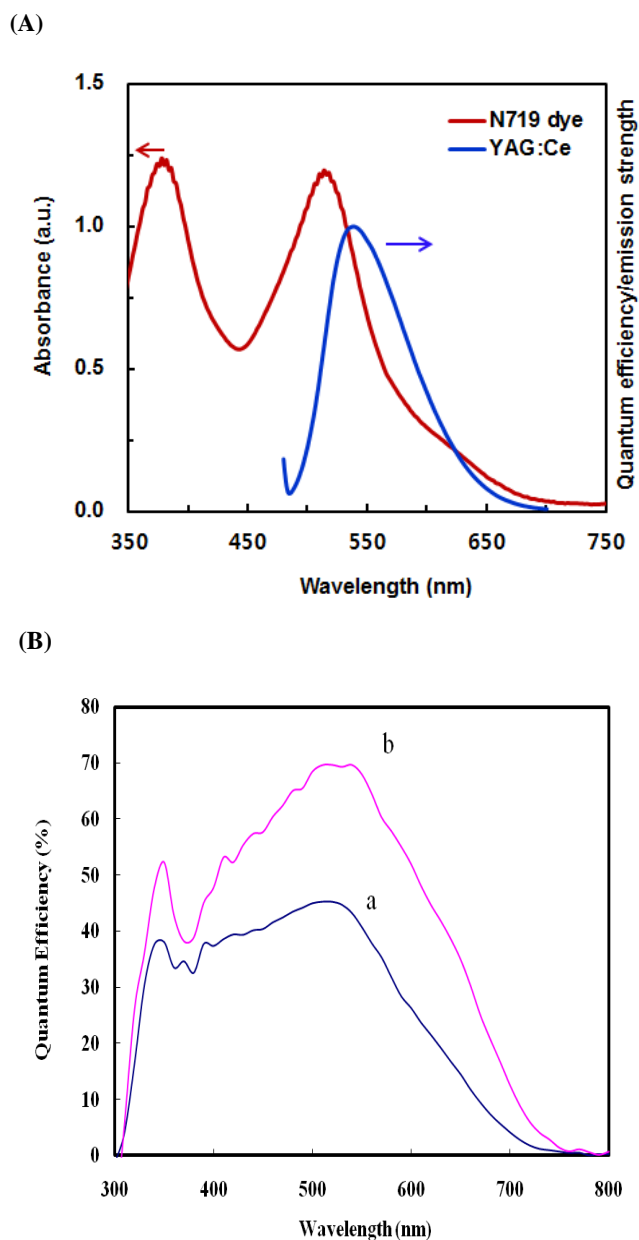


Figure 3. (A) UV/Vis spectrum of N719 dye solution and photoluminescence emission spectrum of YAG:Ce powder; (B) action spectra of DSSCs without (a) and with yttrium aluminum garnet (YAG) doped with cerium ions (b).

Figure 4 shows photocurrent (I_{SC}) versus photovoltage (V_{OC}) characteristics for the cells and photoelectrochemical performance was measured by calculating energy conversion efficiency (η). For only TiO_2 , the efficiency (η) was 5.1% and it was increased to 6.3% for 5 wt.% fluorescence powder added TiO_2 . The effect of different wt.% ratio of fluorescence powder added TiO_2 was also

investigated and shown in figure 4.

When the wt.% ratio was increase the efficiency was decreased therefore 5 wt.% ratio was the optimum condition. DSSC with only TiO₂ has lower J_{SC} and V_{OC} and this is because it has lower proportion of excitons. When fluorescence powder was added, it had increased the number of photons hence higher probability of photon and dye molecules interactions. From these result, it is clear that solar cells constructed with adding fluorescence powder in TiO₂, had increase the surface morphology of electrode and efficiency was increased by a factor of two. Further improvements are expected from the use of a more appropriate fluorescent additive with a better match of absorption band and emission band.

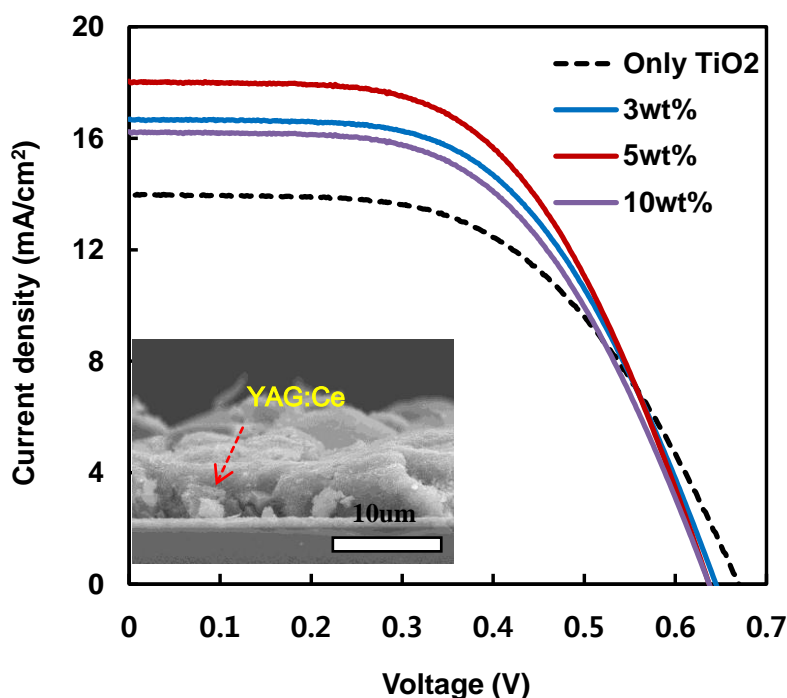


Figure 4. The photocurrent-voltage curves for dye-sensitized solar cell based on only TiO₂ and different wt.% of Ce ion added YAG powder in TiO₂. TiO₂ electrode (black line), 3 wt.% fluorescence powder doped TiO₂ electrode (blue line), 5 wt.% fluorescence powder doped TiO₂ electrode (red line) and (purple line) 10 wt.% fluorescence powder doped TiO₂ electrode. Inlet is cross sectional SEM image of 5 wt.% YAG:Ce powder doped TiO₂ electrode.

Table 1. Photocurrent-voltage characteristics of dye-sensitized solar cells based added amount of YAG:Ce powder

Amount of YAG:Ce (wt. %)	Voc (V)	Isc (mAcm ⁻²)	Fill factor	η (%)
0	0.67	14.0	0.54	5.1
3	0.64	16.7	0.55	5.9
5	0.64	18.1	0.54	6.3
10	0.64	16.2	0.55	5.7

4. CONCLUSION

Electrochemical response in dye sensitized solar cells was enhanced by adding fluorescence powder into TiO₂ photoelectrode. UV-vis spectrum had showed strong possibility of interaction of photons emitted from YAG:Ce powder with dye molecules. This process had generated additional excitons to enhance electrochemical response and ionic conductivity of cell. At optimum conditions (5 wt.% YAG:Ce) energy conversion efficiency of this cell was increased about 24 % higher than the cell developed without fluorescence powder under constant light intensity.

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