Enhancement of Photovoltaic Properties of Ti-modified Nanocrystalline ZnO Electrode for Dye-sensitized Solar Cell

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Nano-porous semiconducting materials have been an intensive research field for many photovoltaic (PV) applications. The Grätzel-type dye-sensitized solar cell (DSSC)[1] is one of the important devices of those applications. Using TiO_2 nanocrystalline electrode, it achieved recently the best energy conversion efficiency (η) as high as 11%.[2] ZnO has similar electronic properties with TiO_2 including conduction band (CB) position and band gap,[3] so it has been also regarded as a good candidate for DSSC. Moreover, various simple and effective synthetic routes have been developed for nanocrystalline ZnO materials,[4] while the optimized nanocrystalline TiO_2 colloid can be prepared only through the hydrothermal method until now.[5] Nevertheless, ZnO-based DSSCs showed PV properties much inferior to TiO_2-based devices,[6-9] though some systems using big particles exhibit slightly improved properties.[9] For instance, Fitzmaurice *et al.*[6] showed that 0.8 μm-thick ZnO electrode composed of 15 nm ZnO particles exhibited a low η of 0.4% at AM 1.5 illumination with about one sun light intensity of 119 mW/cm^{2} with small IPCE (incident photon-to-current conversion efficiency) value of 13% at 520 nm.

The low performance of ZnO may be attributed to two major reasons. The one is the chemical instability of ZnO against acidic dye molecules, resulting in partial dissolution of Zn^{2+} ions from ZnO surface.[8] The other is the slow electron injection kinetics to ZnO matrix,[7] though it seems that the kinetics slightly depends on sensitizing condition.[9] Such disadvantageous aspects of ZnO surface have been frequently pointed out, however, as far as we know, no effort to overcome this problem has been reported up to the present, apart from some other applications such as blending ZnO with SnO_2[10] or ZnO-coating on TiO_2 nanoparticle.[11] For this reason, we are now trying various coating methods for improving both the surface chemistry of ZnO and the surface electronic dynamics. As one of those efforts, we briefly report in this communication on the surface modification of ZnO electrode with about 1 w% of TiO_2 using Ti(OBu)₄ as precursor and its improved photovoltaic characteristics.

Ethanolic mono-dispersed ZnO colloid was prepared at 0 °C using zinc acetate by a modified procedure from Spanhel and Anderson method.[4] Ethanol solvent was then partially evaporated until ZnO content reaches to 10.3 w% and then 4 w% of hydroxypropyl cellulose (M.W.=80,000) was added

and agitated for 24h. Compared with conventional TiO_2 paste, as-obtained ZnO paste exhibited slightly lower viscosity. Bare ZnO electrode was prepared by casting the paste using a doctor blade on fluorinated SnO_2 conducting glass (TEC8, Pilkington). The thickness of wet film was controlled by using two layers of adhesive tape as a guide between the blade and ZnO pigment. The films were heated at 450 °C under convection for 30 min. and cut into square pieces of 1.5×1.5 cm[2] for further uses.

Ti-modification was carried out using titanium alkoxide as coating agent: Two droplets of 10 mM Ti(OBu)₄ solution in 2-propanol (approx. 0.5 μmol) were mildly put on the surface of bare ZnO electrode. The weight ratio of added TiO_2 was estimated lower than 1 w% with respect to ZnO. Ti-modified film was obtained by heating at 400 °C for 20 min. Both bare- and Ti-modified ZnO electrodes had thickness of 1.0 μm, being comparable with the previous work,[6] and contained only ZnO crystalline phase. It implies that Ti-modification took place just on the surface of ZnO electrode in amorphous phase. Both electrodes were sensitized with 0.5 mM ethanolic solution of ruthenium dye Ru[dcbpy-(TBA)₂]₂(NCS)₂ [N719] for 24 h at room temperature. DSSC's were fabricated by a conventional procedure described elsewhere.[12]

FE-SEM micrographs were shown in Figure 1. Raw ZnO particles show a narrow size distribution of 5-10 nm in diameter and are aggregated together. The electrodes show a good interconnection of particles of 15-20 nm. When Ti-modified, ZnO grains looked shrunk a little. The reason for this shrinkage of ZnO grain is not clearly understood yet, but
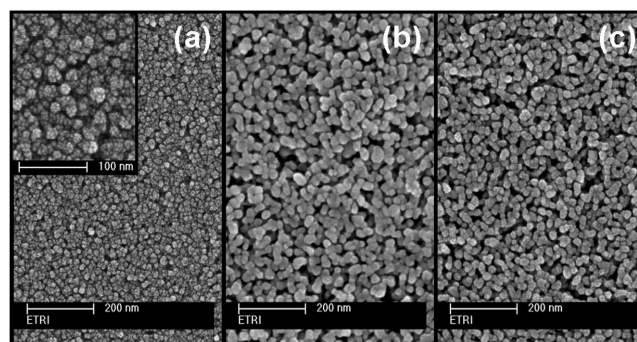

Figure 1. FE-SEM images of nanocrystalline ZnO powder (a) bare ZnO film (b) and Ti-modified ZnO film (c).
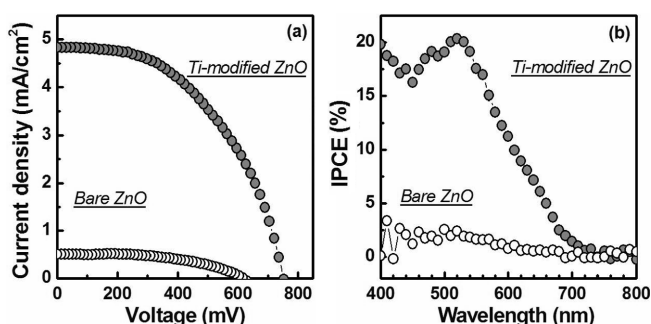
Figure 2. *J-V* curves (a) and IPCE spectra (b) of bare and Ti-modified ZnO DSSCs.

Table 1. Some important photovoltaic properties of bare and Ti-modified ZnO DSSCs

Samples	J_{sc} (mA/cm^2)	V_{oc} (mV)	fill factor	η (%)	Cell Area (cm^2)
Bare ZnO	0.51	619	0.52	0.16	0.214
Ti-modified	4.83	750	0.49	1.78	0.226

it may be attributed to the enhanced interactions of (Zn^{2+}, Ti^{4+})-O on the surface, rendering the texture of surface much denser than before.

J-V curves and IPCE (λ) spectra of the bare- and Ti-modified ZnO DSSC's were represented in Figure 2. Some important PV properties are list in Table 1. The bare ZnO device shows a small η of 0.16%, being comparable with η <0.6% found in previous works.[6-8] In contrast, Ti-modified device shows a remarkable enhancement of *J-V* characteristics with η=1.78%. This value is more than 10 times larger than the bare ZnO device. The observed increase of η can be attributed mainly to the striking increase of J_{sc}, rather than to the moderate increase of V_{oc}, as reflected in the IPCE (λ) results. IPCE spectrum of Ti-modified device exhibits the characteristic profile with the values 8.5 times (at 520 nm)
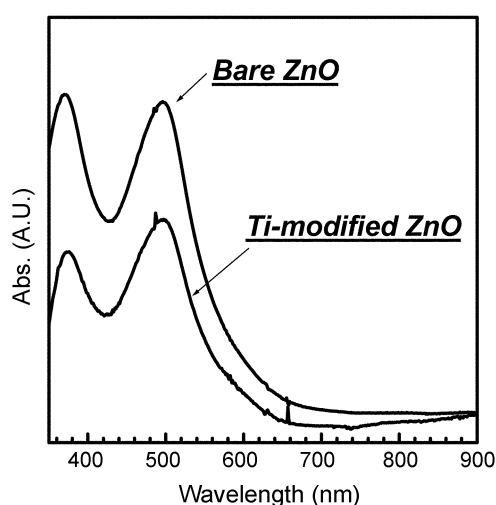

Figure 3. UV-Vis absorption spectra of desorbed dye from the bare ZnO electrode and Ti-modified ZnO electrode.

larger than the bare ZnO device.

Figure 3 shows UV-Vis absorption spectra of dye desorbed from two electrodes. The adsorption of dye on ZnO electrode was found to decrease greatly with Ti-modification, indicating that the formation of undesirable Zn^{2+}-dye aggregate in meso-porous space of the electrode is highly suppressed in Ti-modified electrode.

Considering that dye molecules of Zn^{2+}-dye aggregates should screen the sun light so as to decrease the light harvest efficiency of adequately adsorbed dye molecules, the presence of Zn^{2+}-dye aggregates in bare ZnO electrode can be regarded as the main reason for its low PV properties. For instance, the number of dye molecules effectively adsorbed on ZnO electrode surface is much smaller than the total number detected in absorption spectrum. Moreover the light-sensitization of the effectively adsorbed dye molecules should be highly perturbed by the Zn^{2+}-dye aggregates which screen the photons, resulting in the small IPCE and J_{sc} values. When ZnO surface are modified with TiO_2, Ti-O clusters covering ZnO surface should protect the surface Zn atoms from dissolution so that the unwanted Zn^{2+}-dye aggregates could be avoided, as reflected in the decrease of absorption spectrum. The enhanced covalency in (Ti^{4+}/ Zn^{2+})-O also makes the surface more inert against acidic dye molecules. Like that, the surface chemistry of electrode becomes stable with dye molecules, giving rise to a large increase of J_{sc}.

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