Research Article

Preparation of Vertically Aligned ZnO/TiO₂ Core-Shell Composites for Dye-Sensitized Solar Cells

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Vertically aligned ZnO/TiO₂ (VA-ZnO/TiO₂) core-shell composites deposited on ZnO-seeded indium tin oxide (ITO) glasses have been synthesized by a chemical bath deposition approach for growing one-dimensional ZnO structure followed by a spin procedure for coating TiO₂ on the surface of ZnO structure. The influences of the cycles of spin coating of TiO₂ (CSCT) on the properties of VA-ZnO/TiO₂ and performances of the assembled DSSCs were studied. The power conversion efficiency of the VA-ZnO/TiO₂-based DSSC measured under illumination of 100 mW/cm² and AM 1.5 can reach 0.81%, representing 93% improvement when compared with that of the pristine VA-ZnO electrode (0.42%). The intensity-modulated photocurrent spectroscopy (IMPS) and electrochemical impedance spectroscopy (EIS) were applied to study the kinetics and interfacial transfer of the photogenerated electrons. Both the photocurrent and power conversion efficiency correlate well with the steady state electron density. Enlargement in surface area and dye adsorption, suppression of dissolution of Zn²⁺, diminishment in electron recombination, and fast transfer of injected electrons from excited dyes to TiO₂ conduction bands arising from coating TiO₂ on VA-ZnO are regarded as the predominant causes for this improvement.

1. Introduction

Regarded as a promising alternative to conventional silicon-based solar cells, DSSCs have attracted worldwide attention in both academia and industry because of the inherent characteristics of low production cost, simple processing, less toxic manufacturing, and moderate energy conversion efficiency [1–5]. The common architecture of DSSCs consists of a dye-sensitized semiconductor film deposited on transparent conducting oxide (TCO) glass as a photoanode, the redox couples (usually I[−]/I₃[−]) in organic solvent as electrolyte, and a counter electrode usually made from platinum or carbon materials on TCO [2, 6]. Photoexcitation of the adsorbed-dyes generates photoelectrons, which are then transferred to the conduction bands of semiconductors where they infiltrate to the back contact, and then to the counter electrode through the external circuit. The oxidized dyes are regenerated by capturing electrons from the reducing ions in the electrolyte, accompanying the formation of oxidizing ions which are then reduced by the electrons donated from the counter electrode.

Inevitably, the property and morphology of the semiconductor films must substantially affect the performance of DSSCs.

Lin et al. [3] indicated that strategies to boost the photo-to-electricity conversion efficiency included the enhancement of electron transport within the semiconductor film and reduction of recombination between injected electrons and I₃[−] ions in electrolytes. Up to now, TiO₂ nanoparticles with sizes of 10–20 nm have been widely employed as the materials for fabricating mesoporous photoanodes in DSSCs. Although this construction can feature with high dye loads and light harvesting as a result of high surface area, however, it may create a plenty of grain boundary, which in turn reduces the electron transport efficiency and increases the recombination probability [2, 7, 8]. Vertically aligned (VA) one-dimensional (1D) nanostructures such as nanotubes and nanorods have been considered to provide straight routes to facilitate electron transfer and suppress the recombination rate by reducing the grain boundaries and traveling length of photoelectrons before reaching the back contact [9–11].

The electron diffusion coefficient and electron mobility of ZnO film are reported to be $1.2 \times 10^{-4} \text{ cm}^2/\text{s}$ and 10^{-1} – $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which are both higher than those of $5 \times 10^{-5} \text{ cm}^2/\text{s}$ and 10^{-6} – $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, of TiO_2 [12–18]. These characteristics imply that ZnO can be a potential candidate as the photoanode of DSSC in addition to TiO_2 semiconductor [3]. Although the pristine 1D structure of ZnO can raise the transport rate of electron, however, the DSSC's energy conversion efficiency is low when compared with nanoparticulate TiO_2 . For example, Jung et al. [19] reported a light-harvesting efficiency of 0.26% based on a ZnO nanowire photoanode by optimizing the synthesis parameters, and Gan et al. [20] revealed an overall power conversion efficiency of 0.79% by a ZnO nanowire/ TiO_2 nanoparticle photoanode prepared by the ultrasonic irradiation assisted dip-coating method.

Commercially available ruthenium polypyridine complexes dyes such as N3 and N719 have been widely used in the TiO_2 -based DSSCs and demonstrate superior performance than other dye molecules. However, these Ru-dyes are not suitable to be directly employed in the ZnO-based DSSCs because ZnO crystals may be destroyed by protons releases from dye molecules, causing the formation of Zn^{2+} /dye complexes when they are soaked in an acidic solution containing Ru-dyes over an appropriate soaking time. Furthermore, the formed Zn^{2+} /dyes complexes can agglomerate on the surface of ZnO to generate a thick covering layer instead of a monolayer, and is intrinsically inactive for electron injection [21–23]. Therefore, utilization of core-shell construction to coating a chemically-inert shell layer on ZnO core structure can efficiently avoid dissolution of ZnO crystals and enhance their performance of DSSCs.

Law et al. [24] prepared ZnO nanowires coated with thin shells of Al_2O_3 or TiO_2 by atomic layer deposition and indicated significant improved efficiencies in power conversion of the DSSCs based on the core-shell architectures. In this report, we presented a simpler spin coating method to obtain a shell layer of TiO_2 coated on VA-ZnO arrays, which then acted as photoanodes assembled in DSSCs in an attempt to improve photovoltaic performance by combining the advantages of high surface area and chemical inertness of TiO_2 and high electron transport rate of 1D ZnO nanostructures. The properties of the prepared VA-ZnO/ TiO_2 structures and their influences on the performance of the DSSCs were investigated.

2. Experimental

2.1. Preparation of VA-ZnO/ TiO_2 . A revised version of chemical bath deposition (CBD) established by Ku et al. [25, 26] and a spin coating procedure were employed to prepare VA-ZnO/ TiO_2 grown on indium tin oxide (ITO) ($7 \Omega \text{ sq}^{-1}$, 0.7 mm). The substrates were first deposited with a TiO_2 compact layer; then they were seeded with ZnO layers from a solution of 0.05 M zinc acetate and 0.05 M hexamethylenetetramine (HMTA) by a spin coating technique followed by thermal decomposition at 350°C for 30 min.

An aqueous solution containing 0.02 M zinc acetate and 0.02 M HMTA was applied to grow VA-ZnO structures on the ZnO-seeded ITO substrates by CBD at 95°C for 3 h. The as-prepared VA-ZnO structures were washed with deionized water and ethanol. The CBD procedure was repeated several cycles (1–5) to elucidate its impact on the properties of VA-ZnO/ TiO_2 . Finally, the prepared VA-ZnO samples were calcined at 400°C for 30 min [27].

For the synthesis of VA-ZnO/ TiO_2 core-shell structures, the TiO_2 shell layer was deposited on the surface of ZnO by spin coating a solution containing 0.05 M TTIP and 0.15 M HCl in isopropanol. The spin rate was controlled at 1000 rpm for 30 s. Such procedure was duplicated several times (1–6) to increase the TiO_2 load on VA-ZnO. The prepared VA-ZnO/ TiO_2 composites on ITO substrates were annealed in air at 450°C for 30 min to increase crystallization.

The prepared samples were denoted as ZaTb, where a and b represented the cycles of chemical bath deposition of ZnO (CCBDZ) and spin coating of TiO_2 (CSCT), respectively.

2.2. Characterization of the VA-ZnO/ TiO_2 Composites on ITO Substrates. Crystal phases of the prepared VA-ZnO/ TiO_2 samples were determined by an X-ray diffractometer (XRD) (Rigaku D/MAX 2500) using a grazing incident diffraction model. The morphology of the VA-ZnO/ TiO_2 on ITO substrates was decided by field emission scanning electron microscopy (FESEM, JEOL, JSM-6700F) equipped with an energy dispersive spectrometer (EDS) to quantitatively and qualitatively determine the elements of the prepared samples. The threshold wavelengths and photoabsorbance of the VA-ZnO/ TiO_2 samples were obtained using a UV-Vis spectrophotometer (Jasco, V-550). Photoluminescence (PL) spectra were measured on a spectrofluorophotometer (Jasco, V670) with exciting wavelength of 320 nm.

2.3. Device Fabrication and Measurements. After being heated at 80°C for 1 h, the prepared VA-ZnO/ TiO_2 electrodes were immersed into an 0.5 mM ruthenium (II) 535 bis-TBA (N-719, Solaronix) dye solution in ethanol for 24 h at room temperature under dark condition. The as-obtained dye-sensitized electrodes were rinsed with absolute ethanol and dried in a vacuum oven at 40°C . Afterwards, they were assembled with a Pt counter electrode using a 60 μm thick hot melt ring as the spacer (Surlyn, Solaronix) and sealed by heating to form a sandwich structure. The cell internal space was filled with a I_3^-/I^- liquid electrolyte comprised of 0.05 M I_2 , 0.5 M 4-tert-butylpyridine (TBP), and 0.1 M LiI in 3-methoxypropionitrile (MPN), through a predrilled hole using a vacuum pump.

The photoelectrochemical performances of DSSCs were measured using a source meter (Keithley 2400) and a 300 W xenon lamp (PerkinElmer, PS300BUV). The incident light intensity (AM 1.5 , $100 \text{ mW}/\text{cm}^2$) was calibrated using a power meter (Oriel, 70310) equipped with a photodiode detector (Newport 818UV). Electrochemical impedance spectra (EIS) were measured using an impedance analyzer (PGSTAT 302N, Autolab) equipped with an FRA2 module at an open-circuit potential under illumination intensity

FIGURE 1: Top view FESEM images of (a) VA-ZnO and VA-TiO₂/ZnO samples with CSCTs of (b) 1, (c) 3, and (d) 5.

of 100 mW/cm². The AC amplitude was 10 mV and the frequency evaluated was in the range of 0.1 to 10⁵ Hz. The impedance spectroscopy was fitted with an equivalent circuit using Z-view software. Intensity-modulated photocurrent spectroscopy (IMPS) was operated under short-circuit status using the above-mentioned impedance analyzer with a light emitting diode (LED, 625 nm).

3. Results and Discussion

The morphologies of the prepared VA-ZnO and VA-ZnO/TiO₂ were observed by FESEM. Figure 1 displays the top view FESEM images of the VA-ZnO and VA-ZnO/TiO₂ structures. The results indicate that both ZnO and ZnO/TiO₂ composites grow in the vertically aligned direction forming array structure with hexagonal faces and diameters roughly ranging from 50 to 350 nm. The thickness of the TiO₂ layer cannot be significantly observed to increase with spin coating cycles of TiO₂, which seems to indicate that the TiO₂ layer is much thinner than ZnO nanorod. However, the surface of VA-ZnO is smoother than that of VA-ZnO/TiO₂ by the high resolution image (not shown here), which can be attributed to the adherence of TiO₂ on ZnO surface, supporting the formation of TiO₂ shell layer [27]. Figure 2 demonstrates cross-sectional FESEM image of the VA-ZnO and VA-ZnO/TiO₂ films, confirming one-dimensional array structures. The thickness of VA-ZnO and VA-ZnO/TiO₂ films

with spin coating cycles of 1, 3, and 5 are 7.2, 5.2, 5.1, and 5.5 μ m, respectively. The shortness of the VA-ZnO length with initial coating TiO₂ can be accounted by the dissolution of ZnO by hydrogen chloride acid present in the TiO₂ sol. The TiO₂ coating layer on ZnO can avoid this dissolution with further TiO₂ deposition and slightly lengthen the film thickness. According to the energy dispersion spectroscopy (EDS) measurement, the Ti/Zn atomic ratio of the VA-ZnO/TiO₂ increases from 0.022 to 0.23 as the CSCT increases from 1 to 5. This result verifies the formation of TiO₂ on VA-ZnO, and its content increases with CSCT.

Figure 3 depicts the XRD patterns of the VA-ZnO and VA-ZnO/TiO₂ with CSCT under a grazing incident diffraction model. Obviously, the ITO substrate exhibits significant diffraction peaks at 30.4°(222), 35.3°(400), and 50.6°(440) (JCPDS #89-4598). In addition, XRD peaks at 2θ = 31.8°(100), 34.4°(002), 36.2°(101), 47.5°(102), and 56.5°(110) occurs, representing a wurtzite structure of ZnO (JCPDS #89-1397). The strongest peak of ZnO at 34.4° indicates that the (002) direction is the most preferential crystal plane for the aligned ZnO array to grow with good crystallinity along *c*-axis, which is perpendicular to the surface of the ITO substrate. On the other hand, the crystal peaks of TiO₂ are all absent after calcination at 450°C even when the CSCT increases to 6 (sample Z3T6). In general, calcination at 450°C can cause crystallization of TiO₂. Hence, it is some reasons, rather than calcination temperature, that give rise to this

FIGURE 2: Cross-sectional FESEM images of (a) VA-ZnO and VA-TiO₂/ZnO samples with CSCTs of (b) 1, (c) 3, and (d) 5.

FIGURE 3: XRD patterns of VA-ZnO and VA-TiO₂/ZnO samples with CSCTs of 1 and 5.

result. Law et al. [24] mentioned that a TiO₂ shell film with thickness less than 5 nm appeared amorphous. Therefore, the thickness of the TiO₂ layer may be a cause for the XRD results.

Figure 4 represents the effect of CSCT on the optical absorption spectra of VA-ZnO/TiO₂ samples. In the visible light region, the optical absorption exhibits insignificant increase with the cycles of spin coating, which is probable due to the remained trace carbon species in the ZnO/TiO₂ samples after calcination at 450°C for 30 min. In the ultraviolet region, on the contrary, CSCT exerts distinct influence on the optical absorption intensity, which increases in order of Z3T6 < Z3T5 < Z3T4 < Z3T1 < Z3T0 < Z3T3 < Z3T2. Apparently, the changing tendency of photoabsorbance in the ultraviolet region does not coincide with CSCT; conversely, the moderate CSCT (Z3T2) provides the highest absorbance. This phenomenon is suspected to result from the competitive absorption of the UV light between TiO₂ and ZnO, and/or morphology variation with CSCT.

Figure 5 illustrates the photoluminescence spectra (PL) of the VA-ZnO/TiO₂ samples with CSCT. In general, PL is composed of two types of electron transitions. The one, originated from direct transition of electron from conduction band to valence band, is band PL, while the other one, resulted from the indirect transition of electron to the surface state, oxygen vacancy, or crystal defect state, and then to valence band, is excitonic PL [27–30]. Therefore, the band PL can be estimated as the band gap energy of semiconductor, and the excitonic PL can be used to evaluate the density of oxygen vacancy, surface state, crystal defects, and so forth. Figure 5 demonstrates that the predominant PL peaks of

FIGURE 4: Optical absorbances of VA-ZnO and VA-TiO₂/ZnO samples with CSCTs of 1, 2, 3, 4, 5, and 6.

FIGURE 5: PL intensities of Z3T1, Z3T3, and Z3T5 samples with an incident irradiation of wavelength 320 nm.

the VA-ZnO/TiO₂ located at 394, 432, 454, 472, 486, and 496 nm. The peak at 395 nm is considered as the band PL, indicating a band gap energy of about 3.1 eV, which is consistent with the band gap energy of TiO₂ and/or ZnO [27]. In addition, the peak at 430 nm is likely due to the emission of free excitons near conduction band, while the PL peaks in the range of 470–550 nm are probably from the emission of bound excitons [27, 28]. It is inferred that increasing CSCT can increase the thickness of TiO₂ shell layer, and then increases the penetration length of electrons travelling to the ZnO core region, enhancing the probability of electron recombination, leading to the result that increasing CSCT increases both the band and excitonic PLs. In addition, the

TABLE 1: Photovoltaic parameters of the DSSCs based on VA-TiO₂/ZnO as photoanodes with CCBZ under illumination of 100 mW/cm² and AM 1.5.

Sample	CCBDZ	V_{OC} (V)	J_{sc} (mA/cm ²)	FF	η (%)
BIS4Z1T1	1	0.64	2.85	0.25	0.47
BIS4Z2T1	2	0.64	3.42	0.29	0.65
BIS4Z3T1	3	0.66	4.00	0.3	0.81

TABLE 2: Photovoltaic parameters of the DSSCs based on VA-TiO₂/ZnO samples with CSCT under illumination of 100 mW/cm² and AM 1.5.

Samples	V_{OC} (V)	J_{sc} (mA/cm ²)	FF	η (%)	R_2 (Ω)	W_1 (Ω)
Z3T0	0.61	2.46	0.27	0.42	401.7	19.2
Z3T1	0.66	4.00	0.3	0.81	303.4	22.8
Z3T3	0.64	3.06	0.29	0.58	360.4	35.2
Z3T5	0.62	2.53	0.27	0.43	369.4	42.7

amorphous structure and heterogeneous dispersion of TiO₂ over ZnO may also raise PL emission. These PL behaviors are similar to those that appeared in our previous report concerning the etched VA-TiO₂/ZnO [27].

The CCBZ can affect the property and length of VA-ZnO/TiO₂, which in turn makes a great impact on the DSSC's performance. Figure 6(a) shows the *I*-*V* curves of the DSSCs fabricated with various CCBZ under a constant CSCT of 1, and their photovoltaic parameters are summarized in Table 1. Both the short circuit current (J_{sc}) and fill factor (FF) increase from 2.85 to 4.0 mA/cm² and 0.25 to 0.30, respectively; in contrast, open circuit voltage (V_{oc}) varies little and is in the region of 0.64 V to 0.66 V, as the CCBZ increases from 1 to 3 (the corresponding length of VA-ZnO increased from 3.1 to 7.2 μ m). The power conversion efficiency (PCE) exhibits an enhancement from 0.47 to 0.81% as the CCBZ increased from 1 to 3, primarily due to the increment in J_{sc} and secondarily from the FF. The J_{sc} enhancement arising from the increase of CCBZ is suspected to strongly depend on the increase of length and diameter and on the decrease of crystal defect of VA-ZnO structures, which allow a high dye-loading and facilitate the transport of injected electrons, respectively. These two factors are also expected to account for the alteration of FF. Figure 6(b) displays the onset potentials of the dark current with CCBZ. The dark current is indicative of the level of recombination between electrons in the semiconductor films and the oxidized I_3^- ions in electrolyte. A higher onset potential usually correlates to a lower dark current and a higher efficiency. In this study, the onset potential of the dark current decreases in order of Z3T1 > Z2T1 > Z1T1, which is consistent with the photovoltaic efficiency.

Figure 7 depicts the characteristic of photocurrent versus voltage of DSSCs made with different CSCT, and Table 2 summaries the corresponding photovoltaic parameters. It can be seen that J_{sc} , V_{oc} , FF, and PCE increase firstly as CSCT increases from 0 to 1 and then decrease as CSCT further increases. The sample Z3T0 (i.e., without coating TiO₂) demonstrates the least activity, while the sample with

FIGURE 6: Influences of CCBDZ on the current-voltage characteristics of VA-TiO₂/ZnO (a) under illumination of 100 mW/cm² (AM 1.5) and (b) in the dark.

FIGURE 7: The current-voltage characteristics of DSSCs based on VA-TiO₂/ZnO samples with various CSCTs as photoanodes under illumination of 100 mW/cm² (AM 1.5).

CSCT of 1 explores the highest efficiency. Coating TiO₂ onto ZnO can create high surface area and inhibit the dissolution of ZnO, which then suppress the formation of Zn²⁺/dye complex. In addition, a faster electron-injection efficiency can be expected for the TiO₂-coated ZnO nanorods when compared with bared ZnO nanorods, because the ZnO conduction bands are largely composed of empty s and p orbitals from Zn²⁺, while those of TiO₂ consist predominantly of empty 3d orbitals of Ti⁴⁺ [22, 31]. These factors are suggested

to be responsible for the increase in efficiency with coating TiO₂ layer on ZnO. The results also indicate that all the V_{oc} , J_{sc} , and FF decrease with further increasing the coating of TiO₂ over 1 layer, and thereby causing the decrease of PCE. Upon increasing the coating layer of TiO₂, the thickness of the shell layer became excessively thick, which raises the resistance to transfer injected electrons from the shell layer of TiO₂ to core region of ZnO nanorods because both the electron mobility and diffusivity within TiO₂ are much lower than those of ZnO. The insignificant crystalline characteristic of the coated TiO₂, as indicated by XRD, may develop a high recombination probability of the injected electrons during transportation within the TiO₂ layer. As indicated by PL measurement, increasing CSCT can promote electron quenching within the semiconductor film, which is also an important reason for the decrease of PCE with increasing CSCT. In addition, TiO₂ features a lower conduction band energy (-4.2 eV versus vacuum) than ZnO (-4.0 eV versus vacuum) [22], which is considered to reduce the efficiency for the injected electrons transferred from TiO₂ to ZnO. It is also possible that TiO₂ may agglomerate on the surface or within the interstitial space due to incomplete dispersion of TiO₂ precursor by a spin method, which reduces the PCE by hampering transport of electrolyte.

Electrochemical impedance spectra (EIS) can be adopted to investigate the electron kinetics in DSSCs. Usually three semicircles can be observed as the frequency starts from 100 k to 0.01 Hz. The high-frequency semicircle (1 k–100 k Hz) is related to the capacitance (CPE1) and charge transfer resistance (R_1) between counter electrode and electrolyte, while the low-frequency semicircle (in the mHz range) corresponded to the Warburg diffusion of electrolyte (W_1). The impedance in the middle frequency region is associated

TABLE 3: The parameters of electron kinetics of DSSCs based on the VA-ZnO/TiO₂ samples as photoanodes.

Samples	τ_T (ms)	τ_R (ms)	D (cm ² /s)	L (μ M)	n_s (cm ⁻³)
Z3T0	0.179	118.3	1.23×10^{-3}	120.6	6.6×10^{16}
Z3T1	0.179	118.3	6.41×10^{-4}	87.1	1.2×10^{17}
Z3T3	0.225	100.9	4.92×10^{-4}	70.5	8.8×10^{16}
Z3T5	0.282	86.2	4.57×10^{-4}	62.7	6.8×10^{16}

with the capacitance (CPE2) and interfacial charge transfer resistance (R_2) between TiO₂/dyes and electrolyte. Figure 8 provides the impedance spectra of the DSSCs with Z3T0, Z3T1, Z3T3, and Z3T5. The corresponding R_2 and W_1 values by fitting the impedance spectra based on the equivalent circuit shown in the inset of Figure 8 are listed in Table 3. The interfacial charge transfer resistance (R_2) increases in the order of Z3T1 < Z3T3 < Z3T5 < Z3T0. This result is in good agreement with the changing trends of PCE and the amount of dye loading as shown in Figure 9, which is demonstrated by the optical absorbance with wavelength by dissolving out the adsorbed dye molecules from the photoanode in 10 mL NaOH. The probable reason is that low dye loading on the VA-ZnO/TiO₂ may generate low electron density and interfacial charge transfer rate, causing a high R_2 value. With appropriate coating of TiO₂ on ZnO, the amount of adsorbed dye increases and significantly reduced the R_2 value. In contrast, coating TiO₂ over 3 times increased the R_2 values. This fact may be partly attributed to the penetration limitation of dye molecules due to the blocking effect induced by the coated TiO₂. The EIS results also indicate that increasing TiO₂ coating cycles increases the Warburg diffusion resistance (W_1) which reflects that over coating and/or improperly dispersion of TiO₂ may block the penetration channels of electrolytes.

Intensity-modulated photocurrent spectroscopy (IMPS) was used to calculate the charge-transport time (τ_T) according to the formula of $\tau_T = 1/(2\pi f_{\text{IMPS}})$, where the f_{IMPS} represent the frequency of the minimum current of the imaginary part of IMPS [32–34]. Figure 10 provides the IMPS of the DSSCs based on ZnO/TiO₂ photoanodes. The electron diffusion coefficient (D) can be obtained from the expression of $\chi^2/2.35\tau_T$, with χ indicating the film thickness. The electron recombination lifetime (τ_R) can be estimated from the reciprocal of the peak frequency of the central semicircle in the Nyquist plot of the EIS spectroscopy [35]. Following these parameters, the electron diffusion length (L) can be determined by the expression of $(D\chi)^{1/2}$. Furthermore, the steady state electron density (n_s) in the conduction band of VA-ZnO/TiO₂ can be calculated by the term of $k_B T \tau_R / (q^2 A R_2 \chi)$, where k_B , T , q , and A are the Boltzmann constant, absolute temperature, elementary charge, and surface area of the anode film [35]. Table 3 summarizes the parameters of τ_T , τ_R , D , L , and n_s for Z3T0, Z3T1, Z3T3, and Z3T5. The dependence of τ_T on CSCT can be expressed as Z3T0 = Z3T1 < Z3T3 < Z3T5, while the relation of τ_R can be noted as Z3T0 = Z3T1 > Z3T3 > Z3T5. The samples of Z3T0 and Z3T1 exhibit the smallest and largest τ_T

FIGURE 8: Nyquist plots of DSSCs based on Z3T0, Z3T1, Z3T3, and Z3T5 samples as the photoanodes under illumination of 100 mW/cm² (AM 1.5) and AC amplitude of 10 mV. The data points are from experiments, and the solid lines are the fitting results according to the equivalent circuit shown in the inset.

FIGURE 9: Optical absorbances of the dissolved-out dyes of the Z3T0, Z3T1, Z3T3, and Z3T5 samples in 10 mL NaOH solution (0.1 M).

and τ_R . Increasing spin coating cycles of TiO₂ increases τ_T , and decreases τ_R , electron diffusion coefficient, and electron diffusion length, which can be originated from the fact that ZnO possesses higher electron diffusion coefficient and electron mobility than that of TiO₂. In addition, coating TiO₂ shell layers over ZnO nanorods would increase the lateral diffusion of electrons and then increase the transport time and recombination probability of electron captured by redox species in electrolyte, causing a short recombination lifetime. Furthermore, ZnO nanostructures feature less population of

FIGURE 10: Intensity-modulated photocurrent spectroscopy (IMPS) of the DSSCs based on the Z3T0, Z3T1, Z3T3, and Z3T5 as the photoanodes.

deep traps and are then expected to possess a longer electron lifetime when compared with TiO_2 [23]. The results also exhibit that the changing tendency of n_s with CSCT is similar to that of the amount of adsorbed dye on VA-ZnO/ TiO_2 . Enhancing n_s is likely to reduce both the interfacial charge resistance (R_2) and transport resistance of electrons within the photoanode films, which coincides with the results of EIS and IMPS. Similar results have also been reported previously [35]. Overall, the obtained n_s in this work is significantly lower than the averaged one reported in the literature for the DSSCs with TiO_2 nanoparticle-based anodes [35, 36]. It indicates that increasing the surface area of VA-ZnO/ TiO_2 with appropriate pore structure is crucial to further raise the power conversion efficiency.

4. Conclusions

VA-ZnO/ TiO_2 core-shell structure can be successfully deposited on ITO glasses acting as photoanodes in DDSCs by a chemical bath deposition for growing ZnO and a spin method for coating TiO_2 in sequence. Increasing CCBDZ can increase the length of 1D ZnO on ITO substrates, and thereby increase the energy conversion efficiency. The Ti/Zn atomic ratio of VA-ZnO/ TiO_2 raises with increasing CSCT, however, XRD results indicate that TiO_2 on VA-ZnO appears as amorphous. Increasing CSCT over 1 can extend PL intensity and then boosts the electron recombination rate, causing reduced energy conversion efficiency. Coating 1 layer of TiO_2 on VA-ZnO can significantly enhance the energy conversion efficiency, mainly due to the suppression of dissolution of ZnO, the enlargement of surface area, and fast transfer of injected electrons from excited dye to TiO_2 conduction band. However, the energy conversion efficiency gradually decreases with increasing CSCT over 1. The Z3T1 and Z3T0 samples exhibit the less interfacial charge transfer resistance between TiO_2 /dyes and electrolyte, and the smaller transport time than the other samples.

The changing tendency of power conversion efficiency is similar to that of the steady state electron density in the conduction band.

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