Front. Optoelectron. China 2011, 4(1): 24–44
DOI 10.1007/s12200-011-0207-0

REVIEW ARTICLE

Dye-sensitized solar cells based on ZnO nanotetrapods

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Abstract In this paper, we reviewed recent systematic studies of using ZnO nanotetrapods for photoanodes of dye-sensitized solar cells (DSSCs) in our group. First, the efficiency of power conversion was obtained by more than 3.27% by changes of conditions of dye loading and film thickness of ZnO nanotetrapod. Short-circuit photocurrent densities (J_{sc}) increased with the film thickness, J_{sc} would not be saturation even the film thickness was greater than 35 μm. The photoanode architecture had been charactered by good crystallinity, network forming ability, and limited electron-hopping interjunctions. Next, DSSCs with high efficiency was devised by infiltrating SnO_2 nanoparticles into the ZnO nanotetrapods photoanodes. Due to material advantages of both constituents described as above, the composite photoanodes exhibited extremely large roughness factors (*RF*s), good charge collection, and tunable light scattering properties. By varying the composition of the composite photoanodes, we had achieved an efficiency of 6.31% by striking a balance between high efficiency of charge collection for SnO_2 nanoparticles rich films and high light scattering ability for ZnO nanotetrapods rich films. An ultrathin layer of ZnO was found to form spontaneously on the SnO_2 nanoparticles, which primarily was responsible for enhancing open-circuit photovoltage (V_{oc}). We also identified that recombination in SnO_2/ZnO composite films was mainly determined by ZnO shell condition on SnO_2, whereas electron transport was greatly influenced by the morphologies and sizes of ZnO crystalline additives. Finally, we applied the composite photoanodes of SnO_2 nanoparticles/ZnO nanotetrapods to flexible DSSCs by low temperature technique of "acetic acid gelation-mechanical press-ammonia activation." The efficiency has been achieved by 4.91% on ITO-coated polyethylenenaphtalate substrate. The formation of a thin ZnO shell on SnO_2 nanoparticles, after ammonia activation, was also found to be critical to boosting V_{oc} and to improving inter–particles contacts. Mechanical press, apart from enhancing film durability, also significantly improved charge collection. ZnO nanotetrapods had been demonstrated to be a better additive than ZnO particles for the improvement of charge collection in SnO_2/ZnO composite photoanodes regardless of whether they were calcined.

Keywords dye-sensitized solar cell (DSSC), metal oxides, nanostructure, ZnO nanotetrapod, photoanode, flexible solar cell

1 Introduction

Photoelectrodes of dye sensitized solar cells (DSSCs) are nanostructured by nature for effectively ferrying electrons and holes [1,2]. The rapid advances of nanomaterials and nanotechnology in recent years are therefore propitious in promoting the development of DSSCs [3]. The nanoscale engineering of new photoelectrode architectures should not only enhance our understanding of the inherent working of DSSCs but also help to improve the cell performance, especially in the emerging frontiers such as flexible DSSCs and solid-state DSSCs [4–8]. In a series of recent work, we have demonstrated the viability of new photoanode architectures in DSSCs comprising building blocks of ZnO nanoplates [9], ZnO nanotetrapods [7,10,11] and TiO_2 nanospindles [12]. This article we reviewed our systemic studies on DSSCs based on ZnO nanotetrapods related photoanodes, namely, pure ZnO nanotetrapods based photoanode [7], ZnO nanotetrapods/SnO_2 nanoparticles composite photoanode with [10] and without calcination [11].

Although TiO_2 nanoparticles are still the most efficient photoanode material of DSSC, there are many for improvement in terms of charge transport and recombination suppression by designing new nanostructured photoanodes [2,13,14]. In addition, novel different nanostructures are also important in meeting the challenges of developing flexible DSSCs and solid state DSSCs. Various

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Received October 18, 2010; accepted December 30, 2010

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new nanostructures have been tested for applications in DSSC, especially one-dimensional (1D) nanoarrays, which when used as photoanodes exhibit superiority in electron transport [5,13–15]. However, their DSSC performances have been limited by practical problems such as lack of control over nanostructures during materials fabrication processes.

For TiO_2 based DSSCs on flexible polymer substrates, the best efficiency reported is 7.4% [16], which is still much lower than those based on the traditional high temperature calcined TiO_2 photoanodes [17]. A common problem of the low temperature treated TiO_2 photoanodes consists in the poor electrical contacts between the TiO_2 nanoparticles, which hinder charge collection in the photoanode [18]. In the past few years, many strategies [16,18–21] have been attempted to address this issue but no significant improvement. This status quo raises the question about whether TiO_2 nanoparticles are the best choice for the photoanodes of flexible DSSCs. In fact, ZnO is known to be much more versatile nanostructural former since numerous well-defined nanostructures of ZnO have been generated even under mild conditions [22]. Understandably, ZnO, being chemically more reactive, is more amenable to crystallization and morphological transformations under mild conditions. As has also been demonstrated, low-temperature treated ZnO photoanodes achieved even better DSSC performance than those obtained at high temperature [23,24]. Therefore, replacing TiO_2 with ZnO seems to be a reasonable direction toward flexible DSSCs [8,25].

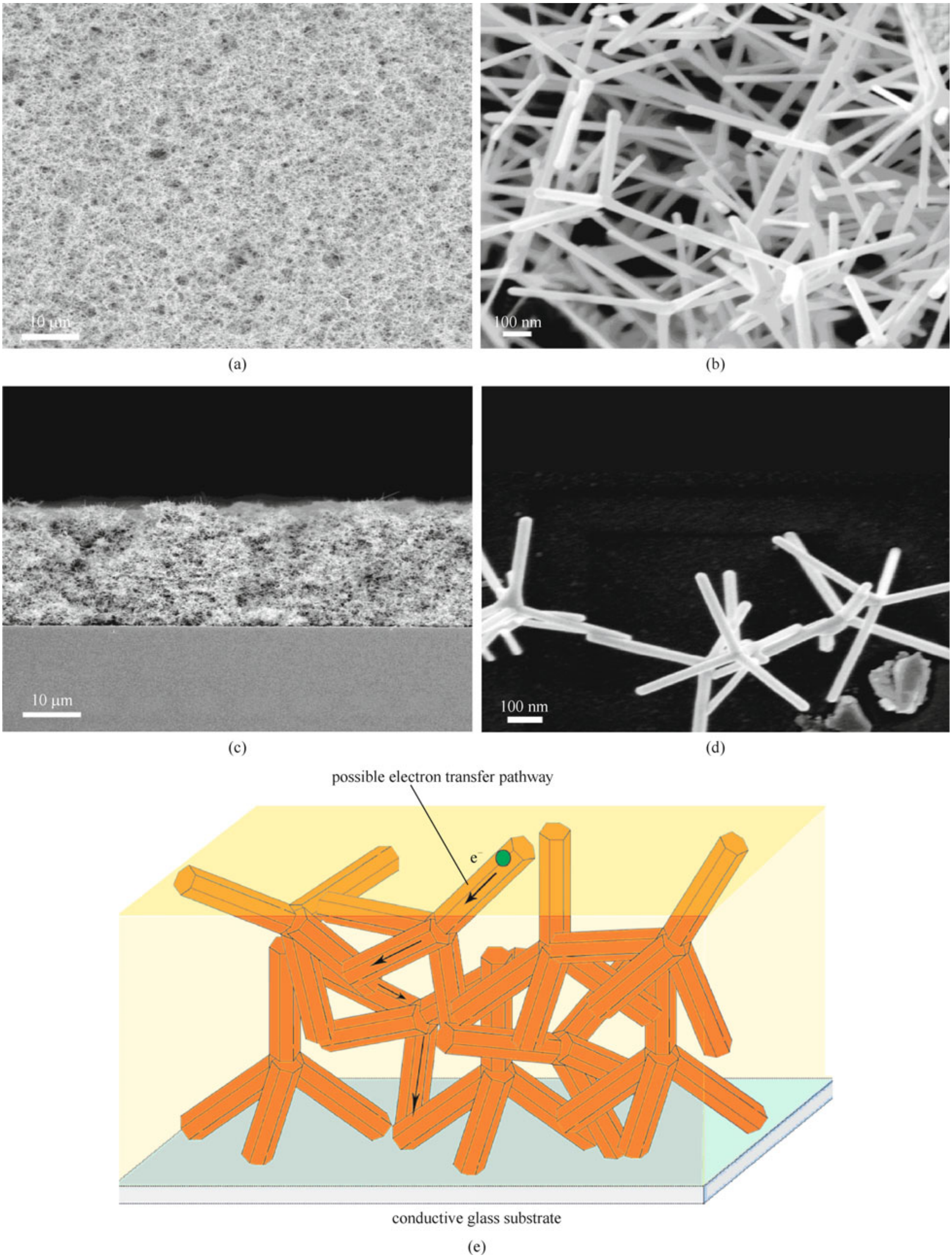
Research results in controlled synthesis of ZnO nanotetrapods achieved by our group [26] prompted us to apply such a novel nanostructure to DSSC [7]. Hsu et al. reported ZnO tetrapods based DSSCs with 1.2% efficiency. The relatively low efficiency is due to the use of large size tetrapods (about 5 μm in arm length and hundreds of nm in arm diameter) and a gelation additive of zinc acetic ($ZnAc_2$) for assisting film formation [26]. Besides, the thermal decomposition of $ZnAc_2$ could introduce undesired impurities. In contrast, we used well-crystallized ZnO nanotetrapods (about 500 nm in arm length and 40 nm in arm diameter) to construct photoanodes [27]. We found that the formation of pure nanotetrapod photoanode film did not need any binder in the film-preparation paste and the calcination step, because the numerous contacts among the tangled nanotetrapods gave the film sufficient mechanical stability. As a result, a decent power conversion efficiency of 3.27% was achieved even when the film was not calcined. This was the first time that DSSC based on pure ZnO nanotetrapod photoanode was demonstrated with a reasonable efficiency; simply by physically contacting the nanotetrapods, the branched nanotetrapods network could effectively transport photoinduced electrons. Later on, Chiu et al. [28] and Bacsa et al. [29] also reported studies on ZnO nanotetrapods based DSSCs with their photoanodes all calcined at high temperatures.

Literally, the ZnO nanotetrapods photoanode for DSSC is noteworthy in the following aspects: 1) ZnO nanotetrapods as a branched 1D nanomaterial with excellent crystallinity can significantly reduce the numerous electron-hopping interjunctions existing in the porous nanoparticle films, and therefore promote charge transport and suppress carrier recombination; 2) The radiating branches of the ZnO nanotetrapods equip them with the ability to form mechanically robust network films; 3) The well-defined nanotetrapods network permits easy blending with other additives such as SnO_2 nanoparticles; 4) The outstanding network forming ability of the well-crystallized ZnO nanotetrapods should also permit low-temperature processing of photoanodes needed for flexible DSSCs; 5) Unlike ZnO nanowire arrays which need be grown in situ and hence are unsuitable for large-scale production, the ZnO nanotetrapods photoanode films should be easily fabricated on flexible substrates in a roll-to-roll fashion. These advantageous features make the ZnO nanotetrapods a preferred photoanode material for DSSCs, particularly flexible DSSCs [25]. Indeed, on the basis of our work in the past few years, the ZnO nanotetrapods have fulfilled our expectation as a novel photoanode material for DSSCs, and added new perspectives on the important roles nanostructures can play in DSSCs.

This review is organized as follows. First, we will summarize our work on pure ZnO nanotetrapods based DSSCs. Second, the work on the composite photoanode of SnO_2 nanoparticles/ZnO nanotetrapods will be discussed. Third, our application study of the nanomaterial system in flexible DSSCs will be reconsidered. Finally, we will present conclusions and prospects about the use of ZnO nanotetrapods in DSSCs.

2 ZnO nanotetropod photoanode

The crack-free, extremely open porous structure of a 30 μm thick ZnO nanotetrapod film can be appreciated from Figs. 1(a)–1(c), which was prepared by the doctor blade method. Of note, besides butanol solvent, no binder or corrosive additive was contained in the film-preparation paste in preparing the ZnO nanotetrapods film, which made it possible for us to sidestep the calcination procedure by just evaporation away the volatile solvent at about 80°C. A close-up view of the ZnO nanotetrapods' film in Fig. 1(d) catches some details of the inter-tetrapod connections. It can be observed clearly that the nanotetrapods are well connected with at least one stout contact for each neighboring pair. Such inter-tetrapod connections are held responsible for the structural stability of the hollow film and also secure continuous electron transport pathways, as schematically illustrated in Fig. 1(e). Although with such zigzag electron transport pathways instead of the straight-through pathways of well-aligned



(a) (b) (c) (d) (e)

Fig. 1 Structural characteristics of 30 μm thick ZnO nanotetrapod film. SEM images viewed from top (a), at high resolution (b), in cross-section (c), and at detailed inter-tetrapod connections (d); (e) schematic showing a possible electron transport pathway across the ZnO nanotetrapod film. Sample in (d) was from residue left on FTO-glass substrate after scratching away nanotetrapods film. (Ref. [7], published with permission) nanowire arrays, the nanotetrapod's film should still exhibit better charge transport than nanoparticle films, simply because the branched structure of the nanotetrapods ensures that at least one of its four arms roughly points to the direction perpendicular to the conductive glass substrate. As a consequence, the average number of interjunctions across which photoinjected electrons in the nanotetrapods film need to pass along the perpendicular direction in order to be collected at the anode should be over two orders of magnitude lower than that of common nanoparticle photoanodes. This can be appreciated simply from the size ratio of nanotetrapods (500–800 nm in arm length) to nanoparticles (10–20 nm in diameter).

As a most popularly used dye for the research of TiO_2 DSSCs, N719 was also employed in the present study although it is by no means an optimized dye for the ZnO nanotetrapods based DSSCs. The dye loading conditions including the dye concentration in ethanol and the corresponding dye loading time have been optimized for the ZnO nanotetrapods films with different thicknesses by monitoring the adsorbed amount of dye as well as the resulting short-circuit photocurrent densities (J_{sc}) of the corresponding DSSCs. J_{sc} was found to first increase on dye loading time and then gradually decrease; the optimized dye loading time t_{opt} for the J_{sc} peak was not sensitive to film thickness but depended greatly on dye concentration. Increasing dye concentration from 0.3 mM to 0.1 mM raised t_{opt} from 20 to 75 min, and also improved the saturated J_{sc}. Such optimization of dye loading condition is especially important for acidic dye sensitized ZnO photoanodes because one needs to balance the maximum dye adsorbing density on ZnO surface and the minimum corrosion of the ZnO nanostructure; the latter often yields Zn-dye complexes which could hinder electron injection [30,31].

Under the optimized dye loading condition, the optimum performance of the ZnO nanotetrapods based DSSCs was $J_{sc} = 9.71\ \mathrm{mA \cdot cm^{-2}}$, open-circuit photovoltage (V_{oc}) = 614 mV, fill factors (FF) = 0.55, and efficiency = 3.27% at the photoanode thickness of 31.1 μm, as shown in Fig. 2(a). Such performance is a little bit lower than that of the recently reported ZnO nanoparticle photoanode fabricated at room temperature on flexible substrate (efficiency = 3.8%) [23]. However, it represents a significant improvement over the best DSSC based on a well-aligned ZnO nanorod array photoanode: about 60% higher in J_{sc} mainly due to a higher RF of our nanotetrapods film (350 for the about 30 μm thick nanotetrapods film versus 200 for the 20 μm thick nanorod arrays film), about 50% higher in FF, and as a consequence nearly 120% higher in overall efficiency [13]. A higher efficiency was reported subsequently by Chiu et al. on a similar system primarily thanks to their use of an organic D149 dye with higher extinction coefficient, in addition to the necessary calcination procedure [28].

Figure 2(b) plots the amount of dye loading versus the nanotetrapod film thickness and RF, which are related by a proportionality factor. The RF of our nanotetrapod film is calculated to be 11.2 μm^{-1}, by multiplying the BET surface area ($18.56\ \mathrm{m^2 \cdot g^{-1}}$) with the weight of a ZnO nanotetrapod film with a given area and thickness, and then divided by the projected area of the film on the glass substrate. The dependence of cell performance on nanotetrapods' film thickness, and therefore RF and the amount of dye loading as revealed in Fig. 2(b), is shown in Figs. 2(c) and 2(d). First, J_{sc} increases sub-linearly to $10.31\ \mathrm{mA \cdot cm^{-2}}$ with film thickness up to about 36.0 μm (RF = 403.2), while the efficiency has reached the saturation level of 3.27% at a relatively small thickness of about 31.1 μm (RF = 348.3). In most cases of nanoparticle photoanodes, the optimum film thickness, beyond which J_{sc} begins to decrease, is in the range of 10–20 μm [13], mainly limited by the effective electron diffusion length (L_n). A film thicker than L_n will not result in higher J_{sc}, but only increase dark current. Obviously, L_n of our nanotetrapods film is at least > 36.0 μm, highlighting the efficient electron collection of our nanotetrapods photoanode even without calcination. It can be observed from Fig. 2(d) that, V_{oc} decreases from 780 to 596 mV and FF decreases from 0.61 to 0.49 as the film thickness increases from 5.3 to 36.0 μm, such data was maintained at relative high level among that of the reported dye sensitized ZnO solar cells [13,32]. Also included in Figs. 3(c) and 3(d) for comparison are data from some of other nanotetrapods films, which were calcined at 450°C in air for 30 min. It can be seen that there is nearly no performance difference between the solar cells based on calcined and non-calcined nanotetrapods photoanodes. Plausibly, the calcination temperature of 450°C, which is commonly used and effective on TiO_2 and ZnO nanoparticles photoanodes, may be too low to have noticeable effect on the bonding between the nanotetrapods.

Electrochemical impedance spectroscopy (EIS) is a powerful technique to study the kinetics of complex interface processes in DSSCs [33,34]. Under appropriate conditions, electron transport in the active film, electron recombination at the semiconductor-electrolyte interface, charge transfer at the counter electrode, and diffusion of redox species in the electrolyte can be disentangled as a function of frequency by virtue of equivalent circuit models. For our ZnO nanotetrapod's photoanodes, two distinct features need to be clarified: one is the non-necessity of the calcination procedure and the other is the excellent electron collection property. To our surprise, no obvious difference on the EIS spectral features could be detected for the ZnO nanotetrapods' films with and without calcination. As EIS is very sensitive to interface changes, the similar EIS results indicate that the interface structure did not undergo significant change upon calcinations, which is consistent with the little change in cell performance due to calcination described above.

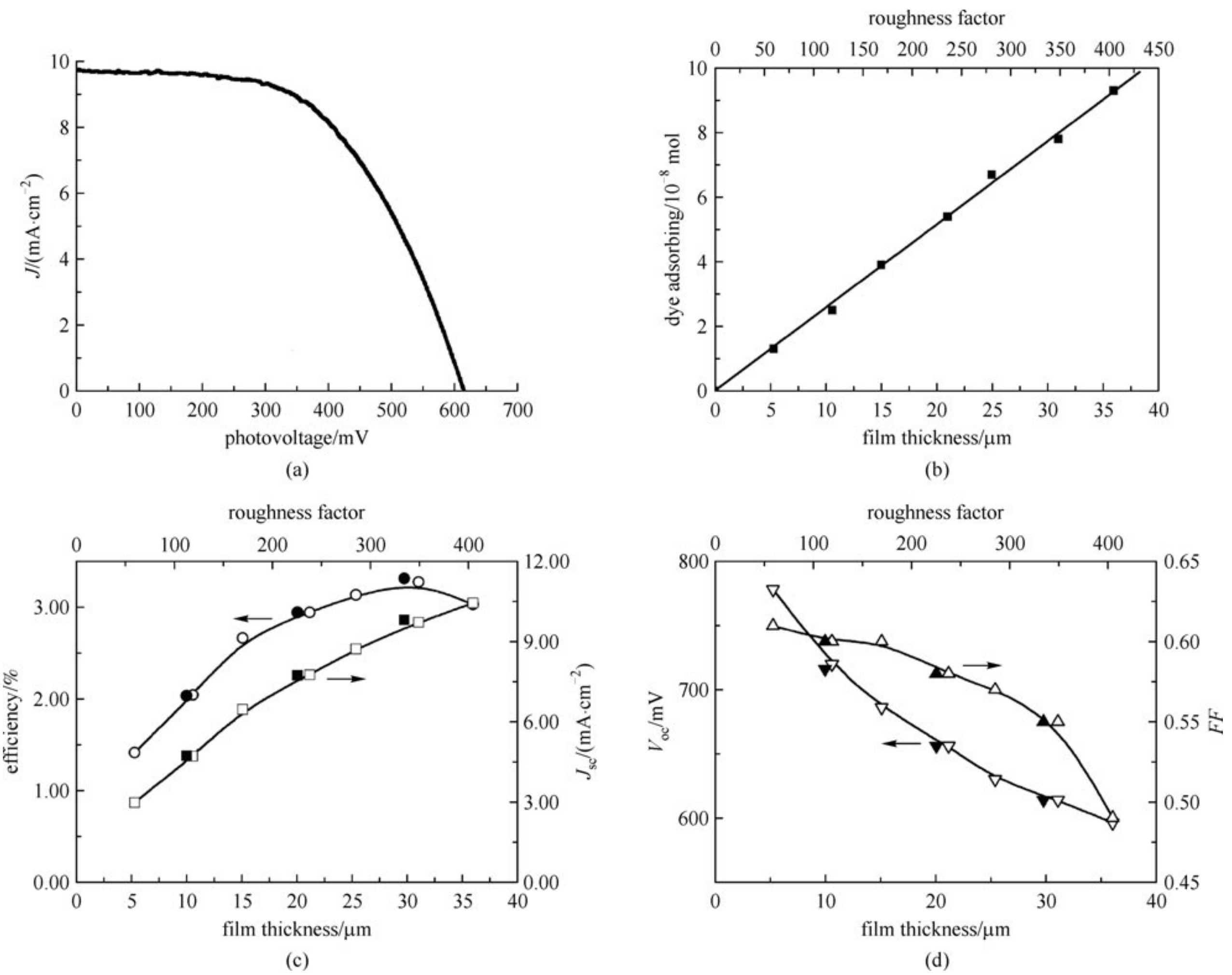


Fig. 2 (a) *J-V* characteristic curve of typical ZnO nanotetrapod cell with film thickness of 31.1 μm; (b) dependence of dye loading amount on film thickness ($\propto RF$); dependence of cell performance on film thickness including overall solar conversion efficiency and short-circuit photocurrent density (c) and open-circuit photovoltage and fill factor (d). Open symbols and solid symbols in (c), (d) correspond to nonclacined and calcined photoanodes, respectively (Ref. [7], published with permission)

As an example, shown in Fig. 3 are the EIS Nyquist plots for two ZnO nanotetrapod photoanodes (with thickness of 10.2 and 21.3 μm, respectively), which were taken at an applied potential of -0.3 V, under 0.1 sun illumination. The spectra exhibit Warburg-like diffusion lines (short straight lines with a slope of approximately 1) in the high frequency region, corresponding to the electron transport process across the photoanode film, followed by big semicircles toward the low frequency region, representing the solid-electrolyte interfacial charge recombination process. According to the well documented diffusion-recombination model [35,36], we can use the following equation to fit impedance spectra in the low frequency region,

$$Z = \frac{1}{3}R_t + \frac{R_r}{1 + i\omega/\omega_r}, \tag{1}$$

where R_t is electron transport resistance, R_r is interfacial recombination resistance, ω_r is characteristic frequency of recombination, and ω is angular frequency of applied AC voltage. From the fitting procedure, R_t and R_r for the 10.2 μm photoanode are estimated to be 300 and 9000 Ω, respectively, and for the 21.3 μm photoanode are 640 and 17300 Ω, respectively. A simple estimate gives the charge collection efficiencies ($\eta_{mL} = 1 - R_t/R_r$ [37]) of about 100%, suggesting that at least for the photoanodes with thicknesses up to 21.3 μm and at the applied potential of -0.3 V, most of the photoinjected electrons can reach the conductive glass substrate by diffusion before recombination. This result demonstrates the long effective electron diffusion length of the ZnO nanotetrapods films and explains why J_{sc} of our nanotetrapods DSSCs is still below the saturation point even when the film thickness has been increased up to > 20 μm. Such a long effective diffusion length has also been verified by Chiu et al. [28].

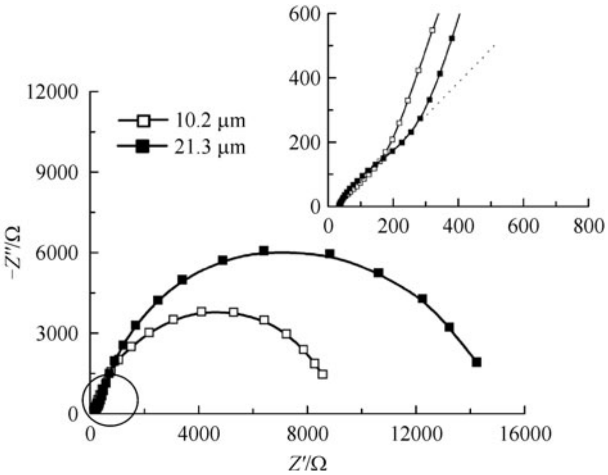


Fig. 3 Impedance spectra of DSSCs based on ZnO nanotetrapods photoanodes with different film thicknesses, at applied potential of –0.3 V under 0.1 sun illumination. Inset shows enlarged portion of circled area, dotted line highlights Warburg-like diffusion lines (Ref. [7], published with permission)

3 SnO_2 nanoparticles/ZnO nanotetrapods composite photoanode

To increase surface areas of the ZnO nanotetrapods based photoanodes to promote light harvesting, a reasonable consideration is to introduce apposite nanoparticles into the nanotetrapod matrix given that there is ample space left between the nanotetrapods. Key to the idea is that the ZnO nanotetrapods' network figures as a global electron transport highway while the encapsulated nanoparticles serve to increase the *RF* and take part in the local charge transport [4,38,39]. Similar scheme has been practiced in nanoparticles/nanowires composite systems [4,6,38,40,41], but in most of these cases, the constituent nanoparticles and nanowires were of the same material [38]. We employed SnO_2 nanoparticles for this purpose largely based on the following considerations: 1) DSSCs based on SnO_2/ZnO nanoparticles composites have been demonstrated and the synergy between the components has been discussed [42,43]; 2) SnO_2, being more stable than TiO_2 and ZnO, is more amenable for film formation via sol-gel reactions at moderate temperatures; 3) Our survey experiments on blending in TiO_2 nanoparticles, albeit with increased V_{oc}, resulted in significantly reduced J_{sc}, which was also revealed in photoanodes consisting of TiO_2 nanoparticles/ZnO nanowire arrays blends [6,40]. On top of these, a proper electronic structure combination of the components, e.g., conduction band edge positions [44], distribution of accepting states in the conduction bands [39], is critical to the performance of the composite photoanodes. In practice, different surface chemistry of the constituents has to be duly considered.

3.1 Nanostructural characterizations

We synthesized the SnO_2 nanoparticles with an average size of about 5–10 nm using a modified hydrothermal recipe [45]. Good monodispersity and suitable size combination of the SnO_2 nanoparticles and the ZnO nanotetrapods allowed ready formation of 3D interpenetrating network films. In our experience, a higher content of ZnO nanotetrapods is more helpful to stabilizing the composite film by releasing any locally accumulated, capillary force induced stress during the film drying process when freshly deposited on a FTO glass substrate, leading to better-adhered composite films to the substrate with minimal micron sized cracks. On the other hand, when more ZnO nanotetrapods were blended, the film became hollower and more optically opaque due to the light scattering effect. This is revealed the diffuse reflectance spectra in Fig. 4. The reflectance spectra appear to abide by the Mie scattering theory, which states that pores with a comparable size to the light wavelength can act as effective light scattering centers [46,47]. Understandably, light scattering in the pure SnO_2 nanoparticles film is nearly negligible because the pores inside the film are too small (<20 nm) to act as effective scattering centers. However, the diffuse reflectance of the composite films increases dramatically and monotonously with the increase of the ZnO content, culminating in the pure ZnO nanotetrapods films. Notably, a substantial fraction of visible light is scattered back. This is not surprising because when more ZnO nanotetrapods are blended with SnO_2 nanoparticles, more pores will be generated with sizes closer to ideal for light scattering, e.g., 50–100 nm, as suggested by Hore et al. [46]. This has been corroborated by our nitrogen adsorption-desorption measurements [10].

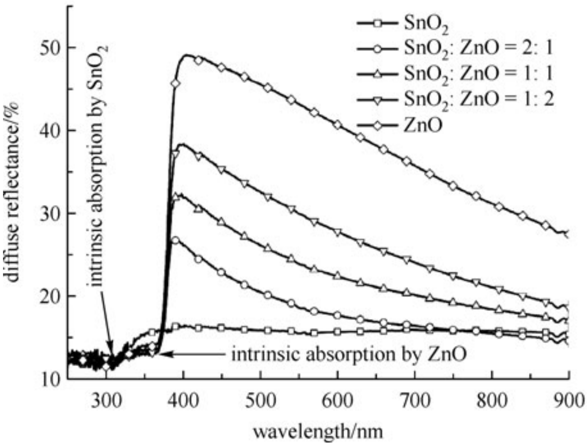


Fig. 4 Diffuse reflectance spectra of pure SnO_2 nanoparticles film, pure ZnO nanotetrapods film and three SnO_2 nanoparticles/ZnO nanotetrapods composite films. All films are prepared with same thicknesses of around 6 μm on glass slides (Ref. [10], published with permission)

To study how the ZnO shell condition on the SnO_2 nanoparticles influences the cell performance, we carried out high resolution TEM-EDX and XPS measurements. Although no evident core-shell structure could be observed by high resolution TEM due to the thinness of the layer, the Zn signal could always be detected by EDX analysis in the region of pure SnO_2 nanoparticles. Using an atomic ratio of 2%–5% for Zn/Sn in the SnO_2 nanoparticles region, and assuming ideal spheres of 8 nm diameter for the SnO_2 nanoparticles, we estimate the ZnO shell to be only 1 to 2 atomic layers thick. More important, the XPS study supports the presence of Sn-O-Zn bonds between the SnO_2 core and the ZnO shell evidently, by the comparison of the Sn $3d_{5/2}$ spectra of the composite films and the pure SnO_2 film, as shown in Fig. 5. The Sn $3d_{5/2}$ peak is shifted to a lower energy for the composite films (486.20 eV) from that of the pure SnO_2 film (486.65 eV). The lower electrophilicity of Zn^{2+} in the shell than that of Sn^{4+} in the core should be responsible for the down-shift of the Sn $3d_{5/2}$ peak upon the formation of the ultrathin ZnO shell. Besides, the peak position at 486.20 eV is independent of the composition for the three composite films, indicating a similar ZnO shell coverage and thickness on SnO_2 under the same treatment conditions. In relation to the origin of the core-shell structure, we suspect that it stem from the chemical instability of ZnO in a polar solvent; the alkaline ZnO tends to be deposited on the relatively acidic surface of SnO_2 [48].

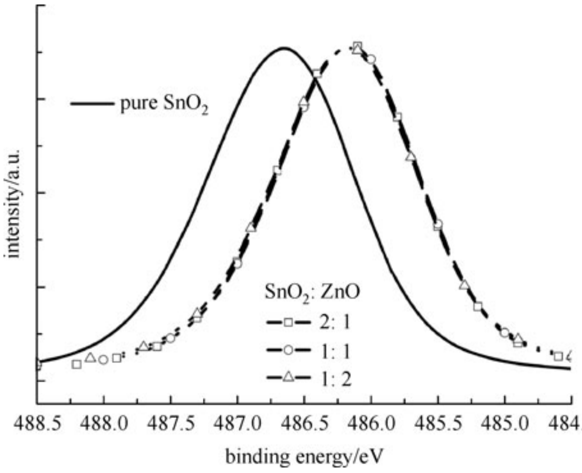


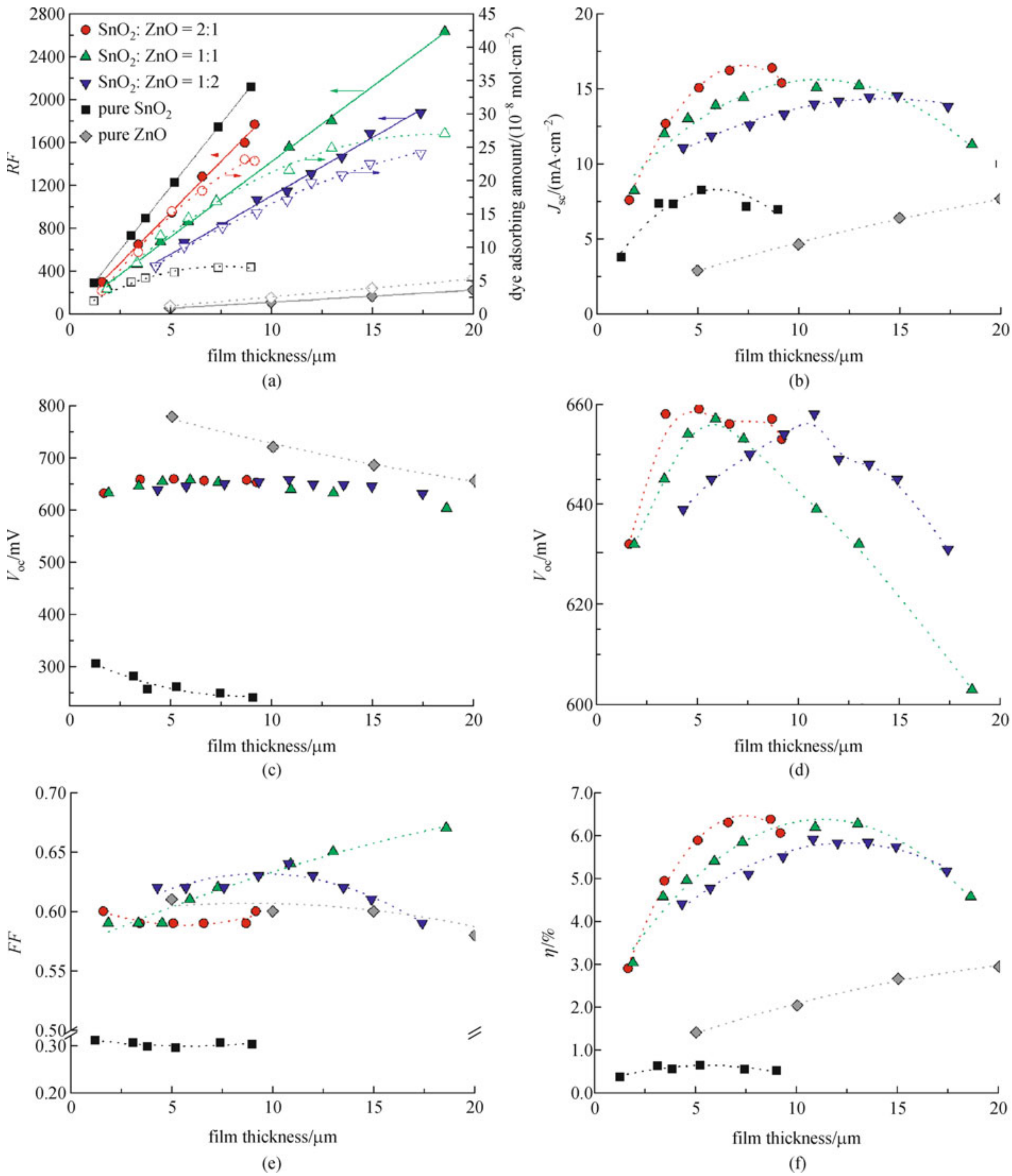
Fig. 5 Sn $3d_{5/2}$ XPS spectra of pure SnO_2 nanoparticles film and the three composite films (Ref. [10], published with permission)

3.2 Performance appraisal of the DSSCs

Presented in Fig. 6 are the performance test results of the DSSCs based on the three series of composite films under 1 Sun AM 1.5G simulated solar light. The corresponding data for the pure SnO_2 nanoparticles film and for the pure ZnO nanotetrapods film [7] are also included for comparison. Significantly, the *RF* values for the three series of composite films can exceed 1600, much higher than that of the pure ZnO nanotetrapods film and also comparable to those of the most efficient TiO_2 nanoparticles photoanodes [49]. It is noticed that the dye adsorbing amount per *RF* for the pure SnO_2 film is obviously lower than those of composite films due probably to the more basic surfaces of the latter, i.e., the ZnO ultrathin layer modified SnO_2 surfaces [48].

The dependence of short-circuit photocurrent density, J_{sc}, on film thickness exhibits obviously nonlinear arc-shaped trends (Fig. 6(b)) for all except the ZnO nanotetrapods films. For the three series of composite films with SnO_2:ZnO = 2:1, 1:1 and 1:2 compositions, J_{sc} become saturated at about 7, 10 and 15 μm, respectively. At the thicknesses of the saturated J_{sc}, the *RF* and dye adsorbing amount are nearly the same, which are about 1600 and in the range of $2.0 \times 10^{-7} - 2.4 \times 10^{-7}$ mol·cm^{-2}, respectively. The nonlinear trends of J_{sc} versus *RF* (dye adsorbing amount) and their saturated positions should be due primarily to the Beer's Law, which is related to the light harvesting efficiency (*LHE*) of a photoanode through the equation $LHE(\lambda) = 1 - 10^{-\varepsilon\Gamma}$ [50], where Γ is the surface coverage of dye (mol·cm^{-2}) and ε is the dye's molar absorption coefficient (mol^{-1} cm^{2}) at wavelength λ. Additionally, light scattering effect as revealed by diffuse reflectance spectra of the three composite films also needs be considered; the light scattering effect could cause deviation from the Beer's law [50] and thus may be partially responsible for different arc shapes of the J_{sc}–thickness plots.

V_{oc} values (600–660 mV) of the three composite films (Fig. 6(c)) are found to lie between those of the pure SnO_2 nanoparticles film and the pure ZnO nanotetrapod's film but much closer to the latter. The origin of the V_{oc} enhancement of SnO_2/ZnO composite photoanodes in comparison to pure SnO_2 has been debated since the first report on this subject [51]. Early on, researchers generally ascribed the V_{oc} enhancement to the functioning of the thin ZnO shell to suppress recombination [48,51]. Our IMVS and XPS results [10] show that the band edge up-shift due to the ZnO shell formation on the SnO_2 surface plays the key role, which can be taken as the new evidences supporting Niinobe et al.'s viewpoint [43]. The V_{oc} dependences for the three composite films on thickness are similar (see Fig. 6(d)): first increase and then decrease, a phenomenon which seems to be at odd with the previously reported monotonically decreasing trend of V_{oc} with film thickness [38,45]. This could be attributed to the uncontrolled dark current loss through the bare FTO substrate (there was no blocking layer in our composite photoanode) which would give rise to nonmonotonical variation of J_{inj}/J_{dark} and therefore V_{oc} according to the equation of $V_{oc} = (k_BT/q)\ln(J_{inj}/J_{dark})$ [2], where k_B, q and T is Boltzmann constant, electron charge and absolute



(a) (b) (c) (d) (e) (f)

Fig. 6 Thickness dependent characteristics of SnO$_2$ nanoparticles/ZnO nanotetrapods composite films as well as pure SnO$_2$ nanoparticles film and pure ZnO nanotetrapods film. (a) *RF* (denoted by solid symbols) and dye adsorbing amount (denoted by open symbols); (b) short-circuit photocurrent density J_{sc}; (c) open-circuit photovoltage V_{oc}; (d) a blown-up region highlights V_{oc} of three composite films; (e) fill factor *FF* and (f) overall energy conversion efficiency η (Ref. [10], published with permission)

temperature, respectively, and J_{inj} is injected photocurrent density from dye to the semiconductor and J_{dark} is dark current due to the recombination at semiconductor/electrolyte interface. *FF* for the three composite films vary within the range of 0.55 to 0.70 (Fig. 6(e)) depending on the thickness, which are generally higher than that of pure SnO$_2$ nanoparticles films and comparable to that of pure ZnO nanotetrapods films. Although the unexpected *FF* dependences on film thickness remain to be explained, complications arising from the peculiar nanostructures and their combinations, uncontrolled dye corrosion on ZnO in the composite films, etc. may play a part.

Maximum cell efficiencies for the three composite films obtained from Fig. 6(f) are listed in Table 1. The efficiencies up to 6.31% are a dramatic improvement over the best SnO_2 based DSSCs (about 2%) [52] and rank among the highest for SnO_2/ZnO composite photoanodes based DSSCs [48,51]. The V_{oc} enhancement over that of the pure SnO_2 film is mainly responsible for the significant improvement in the overall efficiency of the SnO_2/ZnO composite film based DSSCs, since pure SnO_2 photoanode itself can also yield high photocurrent [52]. On the other hand, the difference in maximum efficiency among the three composite films is within 15%, which is mainly ascribed to the difference in J_{sc}. As another noteworthy feature, our composite photoanodes achieve the best performance at the weight ratio of SnO_2 : ZnO = 2 : 1, and this contrasts with the work of Tennakone et al. on ZnO big particles/SnO_2 nanoparticles composite films, which obtained the maximum efficiency strictly at the ZnO: SnO_2 weight ratio of nearly 1 : 1 [42,51]. Such a difference is largely a result from the peculiar structure of our nanotetrapods, which possess three-dimensionally distributed long arms and can be embedded in the SnO_2 nanoparticles matrix without occupying much space in contrast to the space-filling, micron-sized ZnO particles used by Tennakone et al. [42,51].

3.3 Relationship between J_{sc} and IPCE

To elucidate the dependence of the cell performance on the composition of our SnO_2/ZnO composite photoanodes, we analyzed the three determining factors of J_{sc} and IPCE: $LHE(\lambda)$, Φ_{inj} and η_{mL} [53]. Such analysis should be helpful for developing new composite photoanodes.

IPCEs of the three composite photoanodes are shown in Fig. 7. The maximum IPCE values are also selectively listed in Table 1. The maximum IPCE value for the three composite films at about 520 nm decreases from 74.1%, 71.5% to 67.6% with increasing content of ZnO nanotetrapods. As expected, this decreasing trend of IPCE for the composite films is naturally in keeping with the gradual drop of the maximum J_{sc} from 16.3 mA · cm^{-2}, 15.1 mA · cm^{-2} to 14.5 mA · cm^{-2} with increasing ZnO content. It is also important to recognize from Fig. 7 that with the increase of the ZnO content, the IPCE value in the long wavelength tail increases but suffers a comparable or higher decrease in the short wavelength region. A similar observation has also been reported on IPCE of a film in which a light scattering material was directly blended with TiO_2 nanoparticles [54].

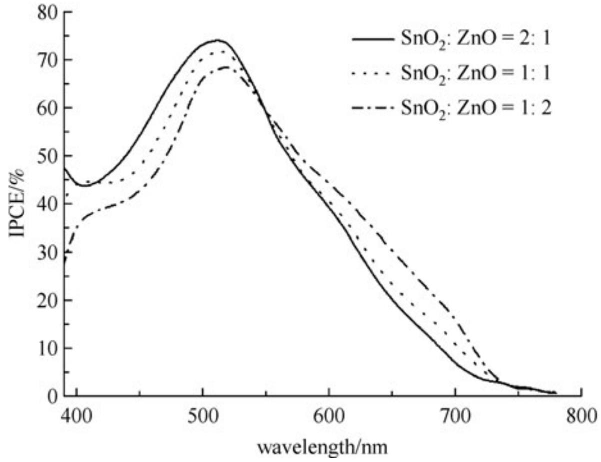


Fig. 7 IPCE of DSSCs based on three typical composite photoanodes with different weight ratios as listed in Table 1 (Ref. [10], published with permission)

The *LHE* of a cell depends mainly on intrinsic properties of the dye, e.g., the wavelength dependent molar absorption coefficient, and its adsorbing density on porous photoanodes, which is governed by the Beer's law [50]. For a practical solar cell such as our ZnO nanotetrapods based DSSCs, the *LHE* equation should accommodate the scattering effect by introducing the concept of effective optical path length within the photoanodes. The effective optical path length can be increased by the addition of relatively large particles to small nanoparticles matrix to induce light scattering of the photoanodes, which is also called the light-trapping effect [49,55]. Such light trapping effect leading to enhancement on IPCE especially in the near-infrared wavelength range is very important for DSSCs, because the widely used Ru-pyridine based dyes absorb light weakly in this region. In our work, the broad pore size distribution resulted in relatively strong light scattering. As reflected in Fig. 4, the optical path length in the three composite films is gradually enhanced in the sequence of SnO_2 : ZnO = 2 : 1, 1 : 1, and 1 : 2. Consequently, IPCE on the red side of the spectra is gradually enhanced in this sequence as revealed in Fig. 7.

To examine the difference in Φ_{inj}, we employed the time-resolved fluorescence decay method [56,57] to probe the N719 dye in the three composite films with nearly the

Table 1 Summary of performance parameters of DSSCs based on SnO_2 nanoparticles/ZnO nanotetrapods composite photoanodes

sample	thickness/μm	V_{oc}/mV	J_{sc}/(mA · cm^{-2})	*FF*/%	$IPCE_{max}$/%	η/%
SnO_2 : ZnO = 2 : 1	6.6	656	16.3	0.59	74.1	6.31
SnO_2 : ZnO = 1 : 1	10.9	639	15.1	0.64	71.5	6.18
SnO_2 : ZnO = 1 : 2	13.5	648	14.5	0.62	67.6	5.83

same adsorbing amount. A pure N719 dye solution was used as a control. We observed that all of the three composite films yielded closely similar decay curves, which could be fitted with a biexponential model. Simply dividing the integral areas of the three fitted decay curves by that of the control, we could estimate the corresponding injection efficiencies, which were found to show negligible variations [10].

We next consider the charge collection efficiency, η_{mL}, determined by IMPS/IMVS measurements through the following equations [15,58,59],

$$\eta_{\mathrm{cc}} = 1 - \frac{\tau_{\mathrm{t}}}{\tau_{\mathrm{r}}}, \tag{2}$$

$$\tau_{\mathrm{t}} = \frac{1}{\omega_{\mathrm{t}}} = \frac{1}{2\pi f_{\mathrm{t}}}, \tag{3}$$

$$\tau_{\mathrm{r}} = \frac{1}{\omega_{\mathrm{r}}} = \frac{1}{2\pi f_{\mathrm{r}}}, \tag{4}$$

where τ_{t}, τ_{r} are electron transport time across the photoanode films and recombination time of electrons with I_3^- ions in the electrolyte, respectively, and f_{t} and f_{r} are the characteristic frequency minimums of the IMPS and IMVS imaginary components, respectively.

Figure 8 plots τ_{t} and τ_{r} as a function of the incident photon flux (light intensity, I_0) for the three composite films. Obviously, the lower the content of ZnO nanotetrapods in a composite film, the larger the gap between τ_{t} and τ_{r}, and thus the higher the change collection efficiency according to Eq. (2). More specifically, the charge collection efficiencies of the three composite films at the highest light intensity ($1.32 \times 10^{16}\ \mathrm{cm^{-2} \cdot s^{-1}}$) are respectively 82.6%, 90.2%, and 95.0%, in the order of decreasing ZnO content. Such distinct differences in the charge collection efficiency is notably parallel to the composition dependent IPCE variations for the three composite films at 515 nm (the wavelength of the LED light source in IMPS/IMVS measurements), suggesting that η_{mL} predominates *LHE* and Φ_{inj} in determining IPCE for the composite films. Such a charge collection limitation naturally explains the monotonic decrease of IPCE in the short wavelength region (< 515 nm) with the increase of ZnO nanotetrapod content (see Fig. 7). On the surface, the gradual decrease in charge collection efficiency with increasing ZnO content (resulting from the increase in charge transport time but the nearly constant recombination time) seems to be contrary to our expectation that more ZnO nanotetrapods should improve charge transport. However, for the same dye adsorbing amount and *RF*, photoinjected electrons need to transport a much longer distance (the film thickness) in the SnO_2:ZnO = 1:2 composite film to reach the conductive glass substrate than in the SnO_2:ZnO = 2:1 composite film.

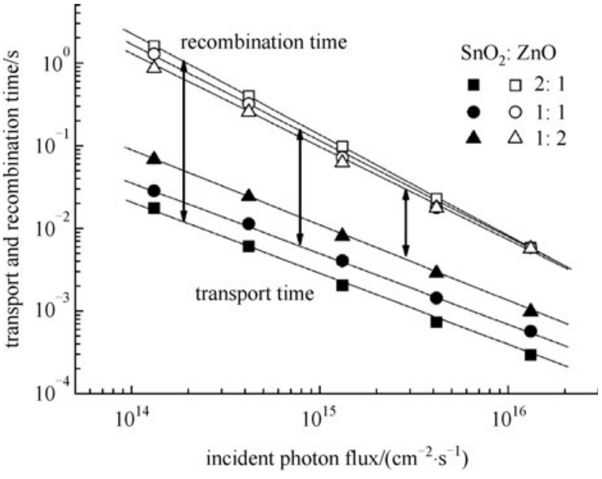


Fig. 8 Incident light intensity dependent transport and recombination time constants for SnO_2 : ZnO nanotetrapods = 2 : 1, 1 : 1 and 1 : 2 composite photoanodes (as listed in Table 1) (Ref. [10], published with permission)

3.4 Role of ZnO naontetrapods on electron transport and recombination in the composite films

In the above, we have established that ZnO in the composite films exists in two forms: one is ZnO nanotetrapods and the other is ultrathin ZnO shells on SnO_2 nanoparticles. To clarify the roles of the ZnO nanotetrapods and the ZnO shells in charge transport and recombination kinetics in the composite films, we purposely dissolved ZnO in the composite films with acidic solutions while monitoring the charge transport and collection properties. For this study, the SnO_2:ZnO = 2:1 and 1:1 composite films were chosen and treated with 1% HAc in EtOH/H_2O (1:2 by volume) for 30 min (denoted as sample HAc30) to totally dissolve ZnO nanotetrapods, resulting in nearly pure SnO_2 nanoparticles films. The structural differences between the original films and the corresponding HAc30 films have been confirmed by SEM and XPS. Corrosion of ZnO nanotetrapods yields new pore channels, leading to deteriorated continuity in the nanoparticles network. Figure 9 compares typical images of the SnO_2:ZnO = 1:1 composite film before and after HAc treatment, highlighting the corrosion induced porosity and the resulting discontinuity of the electron transport network. Such a scenario is definitely maintained in the SnO_2:ZnO = 2:1 composite film albeit to a less extent due to the lower ZnO nanotetrapods content. The differences between HAc treated films and their original films not only lie in the changed nanotetrapods' shape, but also relate to the altered ZnO shell thickness on SnO_2 nanoparticles which was revealed by XPS spectra in the core level region of Sn $3d_{5/2}$ of the original and HAc30 films [43].

It is of interest to pin down the extent to which ZnO nanotetrapods separately impinge on electron transport and recombination kinetics irrespective of the ZnO shell

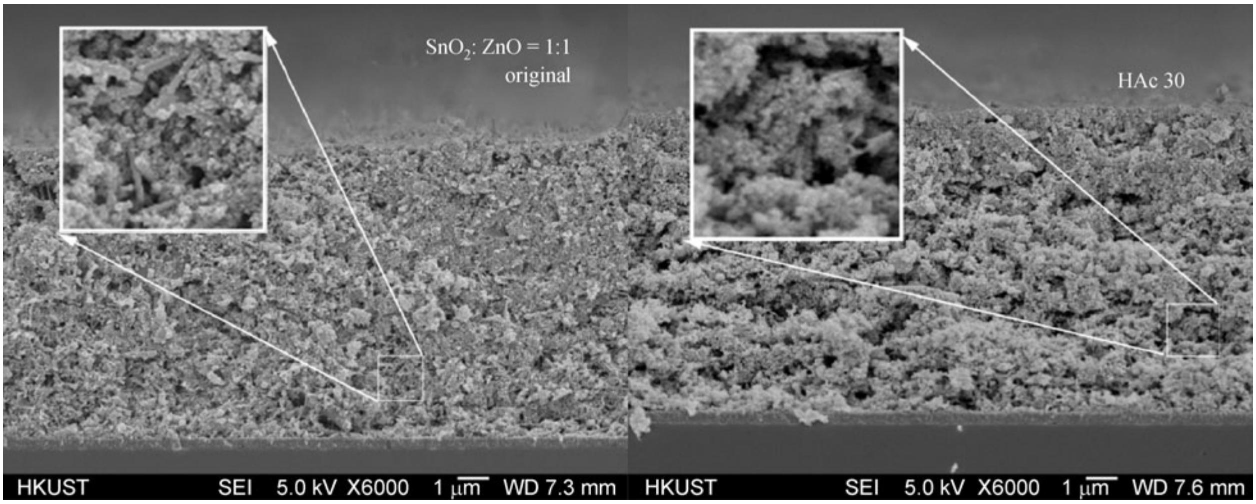


Fig. 9 Cross section view SEM images showing structural differences between original $SnO_2:ZnO = 1:1$ composite film (Original) and corresponding HAc30 film. Note that corrosion of ZnO nanotetrapods leads to more porous structure with less continuity in SnO_2 nanoparticles network (Ref. [10], published with permission)

thickness on SnO_2 nanoparticles, since both the corrosion of ZnO nanotetrapods and the decrease of the ZnO shell thickness occur simultaneously during the HAc treatment. So are the cell performance benefits from the structural advantages of ZnO nanotetrapods over ZnO particles in SnO_2/ZnO composite films [48,51]. Along this line, we opted to study two reference composite films (5.0±0.2 µm thick) prepared by blending our SnO_2 nanoparticles separately with two types of ZnO particles, one with a size of about 40 nm (synthesized according to Ref. [60].) and another with a size of about 500 nm (commercially available). The weight ratios of the two reference films were controlled at $SnO_2:ZnO = 2:1$ for the sake of comparison with the $SnO_2:ZnO$ nanotetrapods = 2:1 composite film on transport and recombination kinetics. The large particles are similar to what were employed in literatures [48,51], while the small particles have a BET surface area of $25.6\ m^2 \cdot g^{-1}$, comparable to that of the ZnO nanotetrapods (BET = $18.9\ m^2 \cdot g^{-1}$), for which a similar dye adsorbing amount can be expected. Advantageously, because the ultrathin ZnO shells on SnO_2 are similar in all these films due to the similar preparation procedures used (this can also be appreciated from their similarly enhanced V_{oc}, all above 600 mV), the variation in transport kinetics can then be exclusively attributed to the changes of the ZnO particles or nanotetrapods in the composite films. To facilitate comparison, diffusion coefficient D_n as an intrinsic material property will be used in place of τ_t. It is calculated by $D_n \approx d^2/2.35\tau_t$ [15,61], where d is the film thickness. According to the relationship between D_n and τ_t, the dependence of D_n on light intensity (I_0) can also be described by a power law expression $D_n \propto (I_0)^{1-\alpha}$ [61].

D_n and τ_r dependences on the incident photon flux (light intensity, I_0) of the composite films are shown in Figs. 10(a) and 10(b). Taken as a whole, Fig. 10(a) highlights the importance of morphologies of the ZnO additives in modulating the transport kinetics given the similar ZnO shelled SnO_2 nanoparticles for all of the composite films, while Fig. 10(b) repudiates any substantial influence of such morphologies on the recombination kinetics, leaving behind the ultrathin ZnO shells on the SnO_2 nanoparticles as the main determinant of recombination kinetics in the composite films. In getting into more details, we attend to a few important features in Fig. 10(a). First, D_n of the ZnO nanotetrapods derived composite film is larger than those of the two reference films, especially that of the small ZnO particles reference film by a factor of 2.18 to 3.72 in the tested light intensity range. Second, the logarithmic slope $(1-\alpha)$ of D_n dependence on I_0 for the ZnO nanotetrapods derived composite film ($\alpha = 0.11$) is much larger than those for the reference composite films ($\alpha = 0.27$ for the small ZnO particles reference film; $\alpha = 0.41$ for the big ZnO particles reference film, $\alpha = 0.41$). Third, D_n for the small ZnO particles reference film is smaller than that of its corresponding HAc30 film, in marked contrast to the fact that D_n for the ZnO nanotetrapods derived composite film is mostly larger than that of its corresponding HAc30 film.

The larger D_n value and the larger logarithmic slope of D_n dependence on light intensity for the ZnO nanotetrapods derived composite film are testament of the more efficient charge collection than for the two ZnO particles reference films, which become even more apparent under closer to 1 sun light illumination (the highest light intensity employed in our IMPS/IMVS study was only about 1/20 sun). This is consistent with our experimental observation that, under similar film fabrication and solar cell test conditions, the cell performance for the ZnO particles derived composite films proved to be inferior to that for our ZnO nanotetrapods/SnO_2 nanoparticles composite films.

The sharp contrast between the HAc-induced increase of

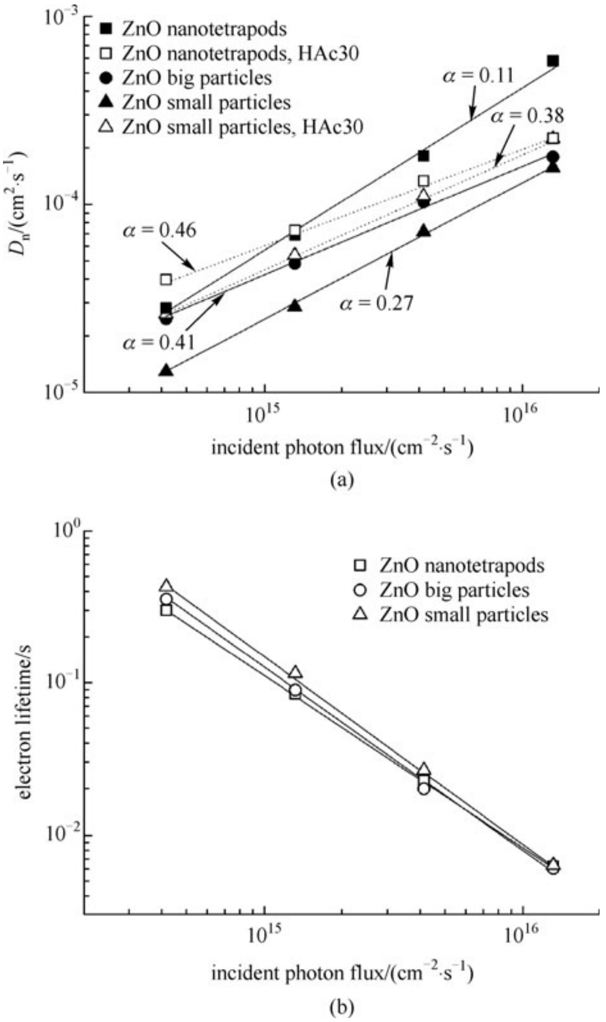


Fig. 10 Incident light intensity dependent electron diffusion coefficient D_n (a) and electron lifetime τ_r (b) of the SnO_2 : ZnO nanotetrapods = 2 : 1 composite film and two reference films with the ZnO nanotetrapods being replaced by ZnO small particles (40 nm) or ZnO big particles (500 nm). Straight lines represent power-law fits. α values are calculated from logarithmic slopes (1-α) by least square fitting (Ref. [10], published with permission)

D_n for the small ZnO particles reference film and the HAc-induced decrease of D_n for the ZnO nanotetrapods derived composite film accentuates the "high-way" role of the nanotetrapods and connotes a "relay transport" mechanism in the composite films. In the "relay transport" scenario, photoinjected electrons are free to move from SnO_2 nanoparticle regions to ZnO additive regions, and vice versa, and finally reach the conductive glass substrate, contributing to the overall J_{sc} of the solar cell. If only the unidirectional electron injection from ZnO part to the SnO_2 nanoparticles matrix were allowed but not the reverse, D_n values of the composite films should not have shifted toward the antithetic directions upon the HAc treatment just because of different morphologies of the ZnO additives. Plausibly, the more numerous grain boundaries between small ZnO particles and SnO_2 nanoparticles would mean more electron traps [39], which would contribute more to the impediment to the inter-particle electron transport. Hence the dissolution of ZnO by HAc should result in increase of D_n as observed. On the other hand, in the ZnO nanotetrapods derived composite film, the ZnO-SnO_2 grain boundaries are much reduced and the ZnO nanotetrapods figure prominently in the electron transport. As a result, the HAc-induced ZnO dissolution led to the decrease of D_n.

As regards the recombination kinetics in the composite films, the similar ZnO shells on SnO_2 play the major role instead of the morphology of ZnO crystalline additives since the amount of dye taken up by ZnO crystalline additives is much smaller than that by SnO_2 nanoparticles for all the three composite films. Furthermore, for recombination, photoinjected electrons only need to diffuse to the outer surfaces of nanoparticles (particles) or nanotetrapods, hence the effect of the grain boundaries mentioned above is much less consequential as evidenced by the similar recombination kinetics in Fig. 10(b) for the different ZnO-SnO_2 composite films.

4 ZnO nanotetrapod based flexible DSSCs

In view of the prima facia advantages of ZnO nanotetrapods such as fast electron transport and network-forming ability, we have explored their use in flexible DSSCs. An effective low temperature fabrication technique of "acetic acid gelation-mechanical press-ammonia activation" (hereafter denoted as "AG-MP-NA") has been developed to deposit the SnO_2 nanoparticles/ZnO nanotetrapods composite film on a conductive plastic substrate, scoring a cell efficiency of 4.91%. Several novel features of the method can be summarized here: 1) The in situ formation of ZnO shell on SnO_2 nanoparticles in a composite film plus the key HAc gelation and NH_3 activation steps cannot only raise open-circuit photovoltage ($V_{oc} \approx 700$ mV) with respect to pure SnO_2 based DSSCs (no more than 400 mV [43]) but also consolidate physical and electrical contacts between SnO_2 nanoparticles; 2) the 1D arms of ZnO nanotetrapods dispersed in the SnO_2 nanoparticles matrix can minimize grain boundaries, facilitate directed charge transport and improve charge collection just as we have demonstrated above in high temperature calcined SnO_2 nanoparticles/ZnO nanotetrapods composite photoanodes [10,11]; 3) the branching structure of the nanotetrapods makes it apt to form network structures on flexible substrate with good mechanical durability, which can be processed further by mechanical press.

We start by illustrating the "AG-MP-NA" method in Fig. 11. The corresponding composite film morphologies at different stages of the operation are revealed by the SEM images in Fig. 12. Associated with step 1 is the initial

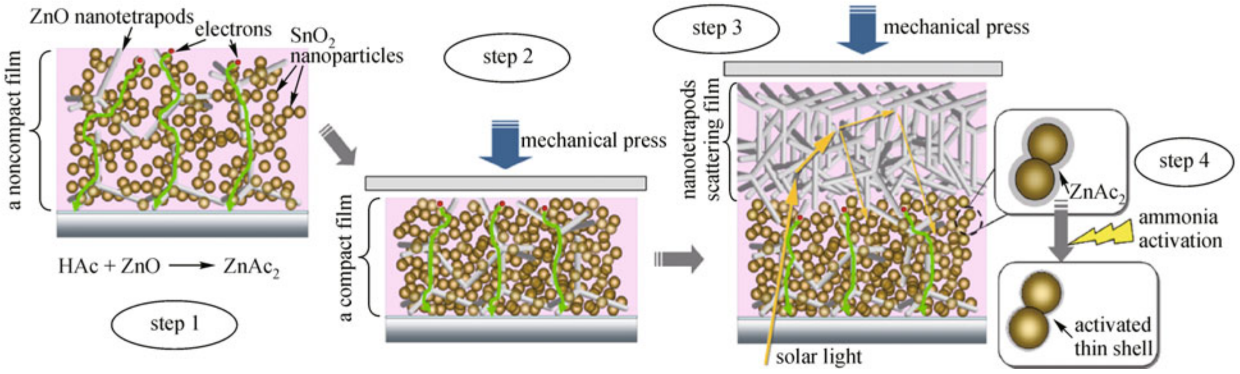


Fig. 11 Schematic showing low temperature technique of "AG-MP-NA" and its effects on films' morphology, surface condition, as well as resulting electron transport and light scattering properties (Ref. [11], published with permission)

spreading of a SnO$_2$ nanoparticles/ZnO nanotetrapods paste onto an FTO-coated glass or ITO/PEN flexible substrate (Figs. 12(a)–12(c)). Diluted HAc was included in the paste to partially corrode the ZnO nanotetrapods, promoting the formation of a zinc acetate (ZnAc$_2$) shell layer on the SnO$_2$ nanoparticles. The as-deposited film from random stacking of the binary nanomaterials contains interspaces between nanotetrapods not fully filled by nanoparticles, making the freshly deposited film look rather hollow with low connectivity (Figs. 12(b), 12(c)). In step 2, an 80–100 MPa hydraulic pressure was applied to the freshly deposited film. As a result, the film thickness is decreased by nearly half (Figs. 12(a), 12(d)), and the SnO$_2$ nanoparticles and ZnO nanotetrapods in the film become much more densely stacked (Figs. 12(e), 12(f)). Conceivably, the transport pathways of photoinjected electrons in the pressed film should be much shorter than those in the unpressed ones as denoted by the green arrow-lines in Fig. 11. More to the point, close packing may imply better contacts between nanostructures in the composite film as well as between the active film and the conductive substrate. For example, the large pores (interspaces) seen in the unpressed film have been filled and/or eliminated by pressing. Step 3 begins with the deposition of another layer but made of pure ZnO nanotetrapods on top of the SnO$_2$/ZnO composite film (Fig. 12(h)). After mechanical press, a dense, robust network is formed (Fig. 12(i)). The compression ratio for this layer is about 4, namely, from 12 to 13 to 3.3 μm (Fig. 12(g)). Its *RF* (total inner pore surface area dived by active film area) is about 150–200, according to our previous work [7], which is about 1/8–1/6 that of the under-layer composite film (*RF* $\approx$ 1200 by multiplying BET surface area of 65.3 $\mathrm{m^2 \cdot g^{-1}}$ to the weight of 1 $\mathrm{cm^2}$ area film). The main function of this layer, aside from the light absorption, lies in the light scattering in the near-infrared region. Its light scattering capability is derived from the sub-micron level pores formed of the nanotetrapods [29]. The inimitable branching structure of our nanotetrapods has imparted this light scattering a certain extent of toughness to endure curvature bending on flexible substrates, a distinct advantage over other kinds of light-scattering materials such as large TiO$_2$ particle assemblies and SiO$_2$ sphere photonic-crystals previously applied to DSSCs [62]. In the last step, the pressed film is immersed in 0.3 M NH$_3$ solution for 20 min and then kept at 150°C for 30 min. This procedure is intended to wash away the unwanted zinc acetate (ZnAc$_2$) on SnO$_2$ and promote the formation of an ultrathin ZnO shell firmly attached to SnO$_2$, the effectiveness of which has been demonstrated by infrared spectra of the films before and after NH$_3$ treatment. Such a shell is important not only for better inter-particles connections, but also for boosting V_{oc} of the SnO$_2$/ZnO composite film based DSSCs by elevating the conductive band edge of SnO$_2$ toward that of ZnO, as revealed in previous works [10,43].

Diffuse reflectance spectroscopy was used to track the changes of light scattering property due to the treatment-induced changes in pore structure [11]. For low temperature treaded films, owing to the no use of binder in the film-preparation paste normally added for releasing the capillary force between nano-constituents, the structural incompatibility between the nanotetrapods and the nanoparticles was more serious. Therefore the as–deposited thick film before mechanical press was loosely stacked. Its open pore structure rendered a large fraction of visible light being multiply scattered. After mechanical press, however, the film becomes translucent because the large pores as the light scattering centers are mostly eliminated. This is in keeping with the diffuse reflectance spectrum of the film with significantly reduced multiple light scattering in the visible region. By overlaying a top layer of pure ZnO nanotetrapods, the film becomes totally opaque. The corresponding diffuse reflectance spectrum confirms that multiple light scattering in this film is the strongest of the three.

Shown in Fig. 13(a) are photocurrent density-voltage (*J*-*V*) characteristic curves of representative DSSCs based on the single layer composite film (Fig. 12(d)) and double-layer-structured film (Fig. 12(g)) on FTO-coated glass and on ITO/PEN substrates. The insets in Fig. 13(a) are optical

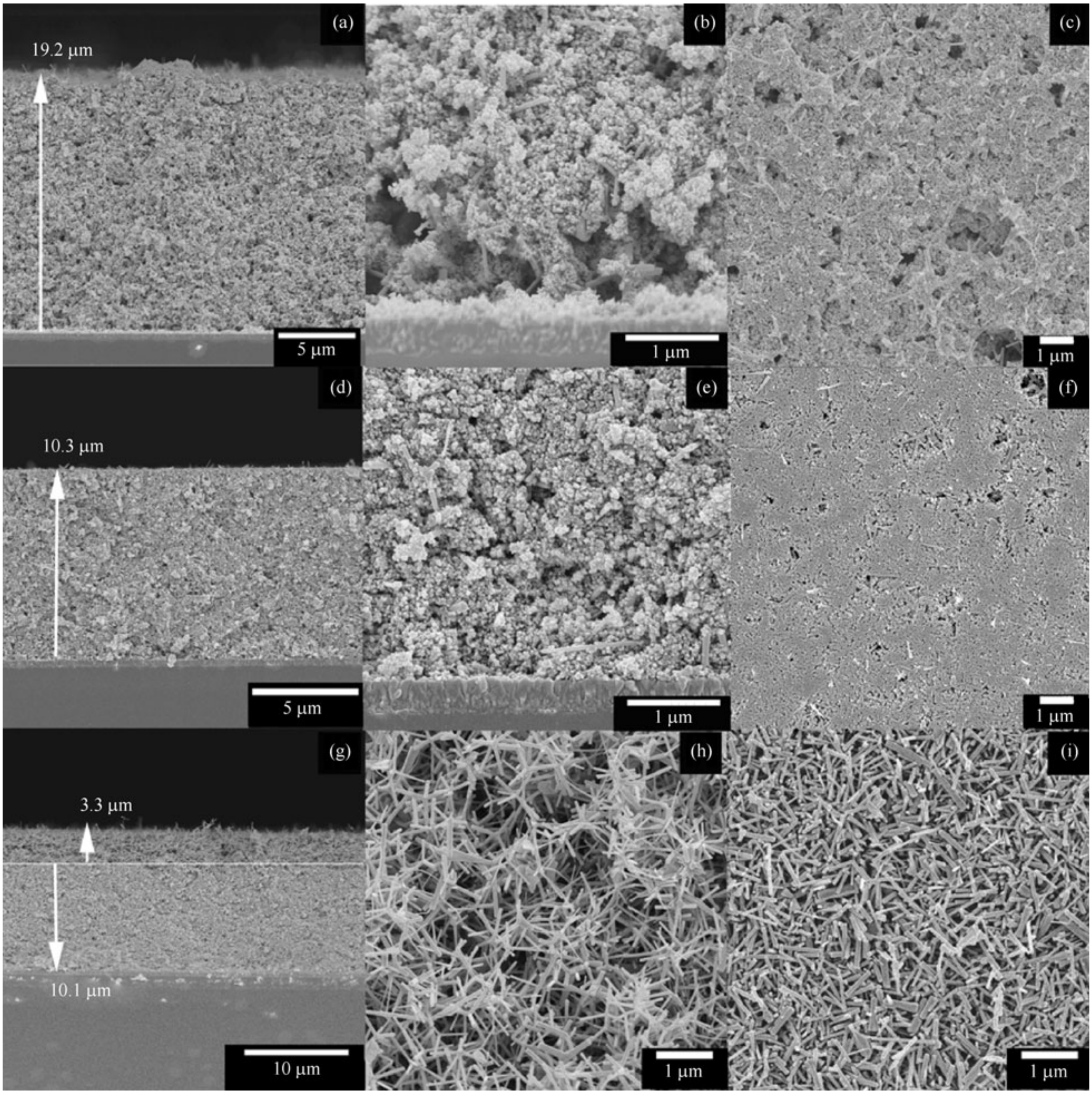


Fig. 12 SEM images of single-layer composite film before (a)–(c), after pressing procedure (d)–(f), and a double-layer-structured film (g)–(i). (a), (d) cross-section view: film thickness is decreased from 19.2 to 10.3 μm due to pressing procedure; (b), (e) cross-section view highlighting difference at active film/FTO-coated glass interface; (c), (f) top view showing different porosities; (g) cross-section view: top light scattering layer is 3.3 μm thick ZnO nanotetrapods network; (h), (i) top view showing the different packing densities of nanotetrapods before (h) and after pressing procedure (i) (Ref. [11], published with permission)

images of the corresponding dye sensitized films. The dark red color reflects sufficient dye adsorbing amount which was detected to be 1.47×10^{-7} mol·cm^{-2} at the roughness of about 1200 for the single layer film on FTO-coated glass. Double layer film possesses 1.72×10^{-7} mol·cm^{-2} dye adsorbing amount at the total *RF* of about 1400 on FTO-coated glass. High bending curvature images of the two films on flexible substrates indicate good mechanical adhesion, another benefit of the pressing procedure and the branching structure of nanotetrapods. This is rather similar to the case of material strengthening arising from fibrous reinforcement. The performance parameters of the DSSCs are listed in Table 2. Notably, our 4.91% efficiency at 1 sun on TCP substrate is among the highest of low temperature processed flexible photoanodes [16,23,63–65] and the V_{oc} is even about 50 mV higher than that of the calcined SnO_2 nanoparticles/ZnO nanotetrapods composite photoanode we reported previously [10]. The improved V_{oc} is mainly

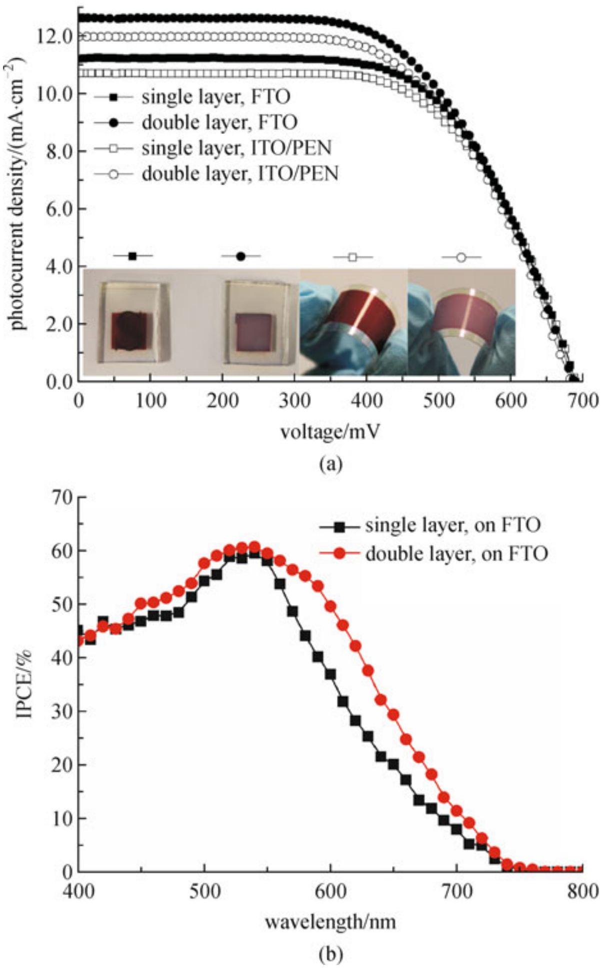


Fig. 13 (a) *J-V* characteristic curves of DSSCs based on "AG-MP-NA" processed films on FTO-coated glasses (solid symbols) and ITO/PEN flexible substrates (open symbols) (inset show photographs of dye sensitized films used to record *J-V* curves, from left to right, single-layer composite film (■) and double-layer-structured film (●) on FTO-coated glasses, and single-layer composite film (□) and double-layer-structured film (○) on flexible substrates); (b) IPCE spectra of DSSCs based on single-layer composite film and double-layer structured film on FTO-coated glasses in (a) (Ref. [11], published with permission)

Table 2 Performance parameters of best performance DSSCs on FTO-coated glasses (S1: single layer, D1: double layer) or ITO/PEN flexible substrates (S2: single layer, D2: double layer), corresponding to *J-V* characteristic curves in Fig. 13(a)

samples	V_{oc}/mV	J_{sc}/(mA·cm^{-2})	*FF*/%	efficiency/%
S1	692	11.2	0.63	4.87
D1	688	12.6	0.59	5.16
S2	690	10.7	0.63	4.65
D2	684	12.0	0.60	4.91

ascribed to the employment of ammonium iodide (NH_4I) based electrolyte instead of imidazolium iodide. While the imidazolium iodide based electrolyte is traditionally optimized with respect to TiO_2 photoanodes, the NH_4I based electrolyte appears to be more compatible with ZnO based DSSCs [32,66], presumably due to the favorable adsorption of NH_3/NH_4^+ on ZnO surfaces and therefore the suppression of recombination kinetics. This can be appreciated from our electrochemical impedance results on SnO_2 nanoparticles/ZnO nanotetrapods composite films with the two different electrolytes: the recombination time is 40% longer in the NH_4I based electrolyte. In comparison to the record TiO_2 nanoparticles photoanode on TCP substrate (with 7.4% efficiency), the relatively low efficiency of our composite photoanode is mainly due to the lower short-circuit photocurrent density (J_{sc}, 12.0 versus 13.4 mA·cm^{-2}) and fill factor (*FF*, 0.60 versus 0.74) [16]. These performance gaps could be further narrow down by optimizing the nanostructures of our composite photoanode and employing better quality plastic conductive films. It is clear that double-layer-structured films possess notably higher J_{sc} but slightly decreased V_{oc} and *FF* in comparison with their corresponding single layer SnO_2 nanoparticles/ZnO nanotetrapods composite films. Plausibly, the higher J_{sc} is mostly due to light scattering enhanced IPCE in the near-infrared region, which has been confirmed in Fig. 13(b). The slight decrease of V_{oc} and *FF* is likely due to the addition of the ZnO nanotetrapods scattering layer, which could modify series resistance and shunt resistance as well as their relationship in the whole film. A larger series resistance and lower shunt resistance for the double layer film than the single layer film can be clearly revealed by their different impedance spectra. According to the well documented one–diode model for DSSCs [3,53,67,68], such changes will lead to smaller V_{oc} and *FF*, a result we have presented above. The relatively better performance of FTO-coated glass than that of ITO/PEN flexible substrate based DSSC is primarily due to the lower transmittance of the ITO/PEN substrate than the FTO-coated glass used in our experiment.

Figure 14 compares typical *J-V* curves (Fig. 14(a)), EIS (Fig. 14(b)) and charge collection kinetics (Fig. 14(c), studied by IMPS/IMVS) of a composite film at different steps of the "AG-MP-NA" technique. Clearly identified are effects of the mechanical press and NH_3 activation steps on the electrical and charge collection properties of the film tied up with the cell performance (Table 3). Here we use "HAc, unpressed film" and "HAc-NH_3, unpressed film" to denote the as-deposited unpressed composite films (about 12 μm thick) with and without NH_3 treatment, respectively. "HAc-NH_3, pressed film" represents the film that has been through the complete procedure including both mechanical press and NH_3 activation treatment. After pressing, the "HAc-NH_3, pressed film" is thinned to about 6.5 μm. We first compare the "HAc-NH_3, unpressed film" with the "HAc-NH_3, pressed film" to establish the effect of the

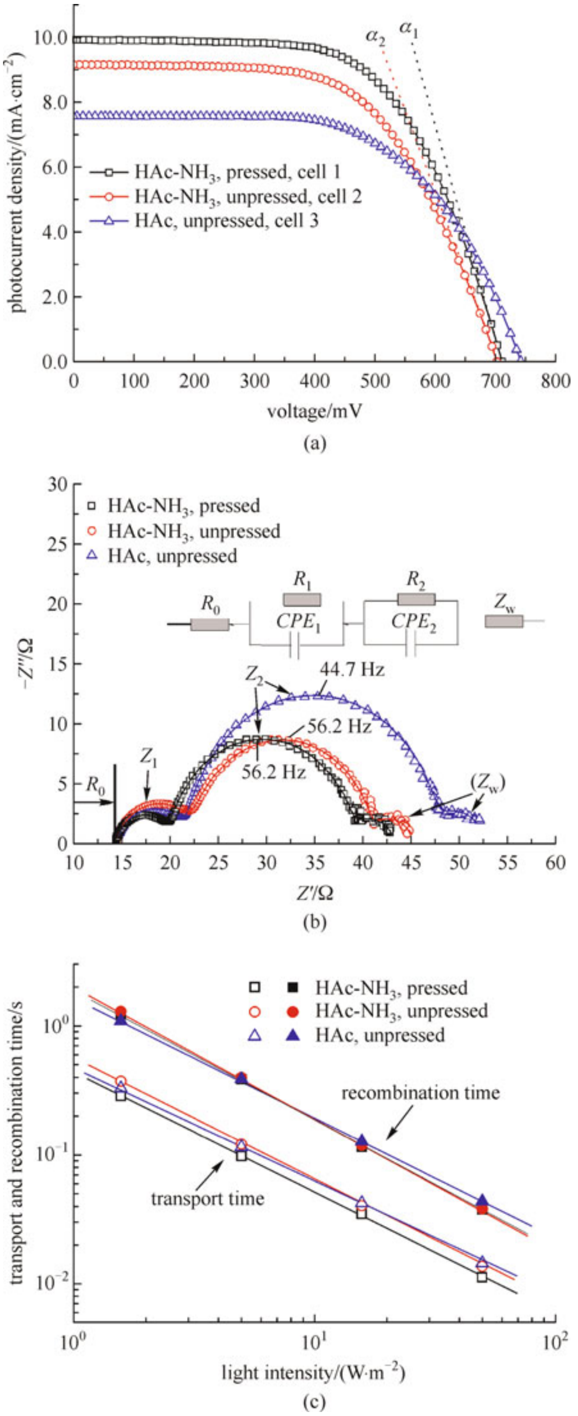


Fig. 14 (a) *J-V* characteristic curves of composite films: black square, film treated by pressing and NH_3 activation (film thickness $\approx$ 6.5 μm, cell 1); red circle, film treated by NH_3 activation but without pressing (film thickness $\approx$ 12 μm, cell 2); blue up-triangle, as-deposited film without further treatment (cell 3). α_1 and α_2 highlight different slopes of the tangents at the open-circuit voltage; (b) EIS Nyquist plots from impedance spectra of the films together with the fitted results (solid line) based on the equivalent circuit model as shown in inset; (c) electron transport and recombination times of the films from IMPS/IMVS measurements. Straight lines are fitted results (Ref. [11], published with permission)

pressing procedure. From Fig. 14(a), it can be observed that in comparison to the "HAc-NH_3, unpressed film," all parameters including J_{sc}, V_{oc} and *FF* of the "HAc-NH_3, pressed film" have been improved, and the efficiency has been steadily improved by about 13%, from 3.85% to 4.35%.

It should be noticed that the impedance spectra in Fig. 14(b) were recorded under 1 sun illumination and at open circuit potential, a condition which is quite different from that in Fig. 3. Correspondingly, a different equivalent circuit model should be applied. We employed a model (see the top inset in Fig. 14(b)) similar to those used previously by other researchers [34,35] to fit our EIS results. It can be seen that the left arc in the high frequency range (10^4-10^2 Hz) shrivels evidently due to mechanical press. This arc, denoted as impedance Z_1, is associated with charge transport at FTO/active film, Pt/electrolyte, as well as inter-nanostructure interfaces. No matter which of these interfaces is tied to such mechanical press induced arc-shrinking, the mechanical press generally reduces the total series resistance (R_s) of the cell. According to the one-diode model of solar cell [33], a smaller R_s commonly gives rise to a higher *FF* [53,68], which is also echoed by the tangential slopes (denoted as α_1 and α_2) at the open-circuit voltages of the *J-V* curves. The scenario is in concurrence with the results in Fig. 14(a) and in Table 3. The middle arcs in Fig. 14(b) (denoted as Z_2, recombination resistance R_2 in parallel with CPE_2, on the frequency scale of about 10^1 Hz), which arise from charge recombination at the active film/electrolyte interface, appear to have no direct causality with the pressing procedure; their fitted R_2 and characteristic frequency f_2 changed little. Charge collection efficiencies (η_{mL}) of the films before and after mechanical press were investigated by measuring the characteristic frequencies (f_t and f_r) using IMPS and IMVS, respectively, and then calculated by using Eqs. (2)–(4). As one can see from Fig. 14(c), there are obvious gaps in τ_t between films with and without mechanical press, whereas their τ_r are very similar, in agreement with the result of EIS presented above. The faster electron transport in a thinner pressed film, due mainly to a shorter electron transport pathway as illustrated in Fig. 11, has led to an enhanced charge collection efficiency, from 64% to 70%, determined by using the data (at the light intensity of 50 W·m^{-2}) in Fig. 14(c). Such decent improvement of η_{mL} appears to be main cause for the increase of J_{sc} as described in Fig. 14(a) resulting from the pressing procedure.

Table 3 Performance parameters of DSSCs corresponding to *J-V* characteristic curves in Fig. 13(a)

samples	V_{oc}/mV	J_{sc}/(mA·cm^{-2})	*FF*/%	efficiency/%
cell 1	712	9.9	0.62	4.35
cell 2	703	9.1	0.60	3.85
cell 3	743	7.6	0.60	3.38

The role of NH_3 treatment is mainly to activate the nanostructured surface, which is important in balancing the transport/recombination kinetics, but more critical appears to be to modulate the injection quantum efficiency for enhancing the cell performance. This point is supported by our new evidence obtained from EIS and IMPS/IMVS. In comparing the impedance spectrum (Nyquist plot) of "HAc, unpressed film" with those of the other two films treated by NH_3 (Fig. 14(b)), one notices a significant larger middle arc associated with electron recombination at the active film/electrolyte interface. The characteristic frequency (f_2, frequency corresponding to the maximum $|Z'|$ point of the middle arc) equals to 44.7 Hz, which is evidently lower than those of the other two films (56.2 Hz). This implies that under the test conditions for impedance spectroscopy, i.e., at 1 sun light intensity, the recombination time of "HAc, unpressed film" is much longer than those of the other two films, simply judging from $\tau_r = 1/(2\pi f_2)$. This result tallies with the corresponding IMVS data shown in Fig. 14(c): at higher light intensity in the tested range (from 1.58 to $50\,W \cdot m^{-2}$), τ_r of "HAc, unpressed film" becomes gradually longer than those of the other two films. The larger recombination resistance (R_2) and longer recombination time (τ_r) strongly suggest different surface properties of the film without NH_3 treatment. In principle, such changes can be ascribed to the unwanted ZnO precursors in the non-NH_3-treated film. The unwanted ZnO precursors could promote the formation of Zn-dye complexes during the dye-adsorbing process, which could hang on the surfaces of the nanostructures and act as an insulating layer, blocking the back reaction pathway of photoinjected electrons from semiconductors to electrolyte. That could be the reason why V_{oc} of such non-NH_3-treated film (V_{oc} = 743 mV) is even higher than those of the other two films (V_{oc} = 712 – 703 mV, Table 3). Another noteworthy aspect for the "HAc, unpressed film" is that, its calculated charge collection efficiency (η_{mL}) equals to 67% at $50\,W \cdot m^{-2}$, which is even higher than that of "HAc-NH_3, unpressed film" (η_{mL} = 64%), whereas its J_{sc} is much lower. Such abnormality implies that there should be other limiting factors responsible for such low J_{sc}. *LHE* is determined by dye adsorbing amount and light-scattering-corrected optical length of a photoanode film. We suggest that *LHE* should not be influenced much by the NH_3 treatment and thus cannot be responsible for the J_{sc} gap mentioned above, because of no detectable difference in the dye adsorbing amount and light scattering property. The only remaining factor is Φ_{inj} of the non-NH_3-treated film, which can be low due to the presence of the Zn-dye complexes as discussed in the last section and in Ref. [30].

Figure 15 examines the effect of ZnO nanostructural morphologies (nanotetrapods and big particles about 500 nm in size) on charge collection efficiencies of the SnO_2/ZnO nanocomposite photoanodes and the resulting cell performance of the corresponding DSSCs. For comparison on the same footing, we used the same weight ratios of SnO_2/ZnO and treatments throughout the experiments. Apparently from Fig. 15, the improvements of η_{mL} by > 10% for the ZnO nanotetrapods over the ZnO big particles should be mostly ascribed to the enhancement of J_{sc}, due to the structural superiority of the ZnO nanotetrapods to the ZnO big particles. Referring to the high temperature calcined SnO_2/ZnO composite films based DSSCs we studied previously [10], the ZnO crystalline additives in the composite films should similarly play two functional roles in the "AG-MP-NA" treated films because similar features of electron transport and recombination kinetics have been found: a) they act as a Zn source for forming a ZnO shell on SnO_2 nanoparticles; b) depending on their morphologies, they impact greatly on the electron transport kinetics in composite films. Namely, ZnO additives can locally gather electrons from the neighboring SnO_2 nanoparticles and promote fast electron transport due to ZnO's higher electron mobility (see the green arrow-lines in Fig. 11). Fundamentally, the fact that ZnO nanotetrapods support faster electron transport in composite films than ZnO big particles can be ascribed to their structural difference: the big ZnO particles are a space-filling object, whereas the ZnO nanotetrapods are a branched one dimensional (1D) material: its 1D arms ensure facile directional charge transport and its symmetric branching structure guarantees good network forming ability and optimized contacts between the binary constituents in composite films. From the SEM images shown in Fig. 16, we can easily estimate the average distance for photogenerated electrons in SnO_2 nanoparticles to migrate and make their way into the nearest neighboring ZnO crystalline additives for the

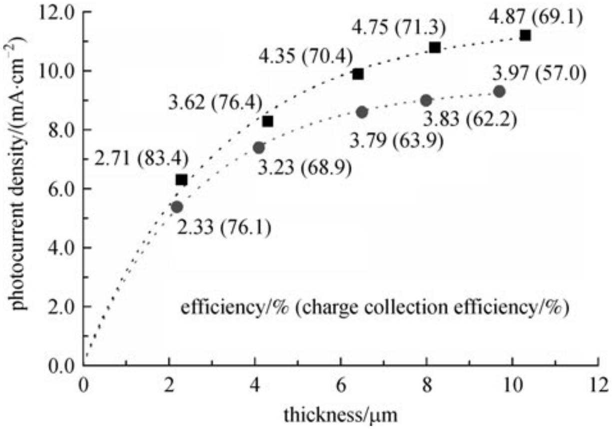


Fig. 15 Dependences of J_{sc} and efficiency (charge collection efficiency) on film thickness for two kinds of nanocomposite films on FTO-coated glasses: black square, SnO_2 nanoparticles/ZnO nanotetrapods; red circle, SnO_2 nanoparticles/ZnO big particles. Charge collection efficiencies were calculated from data measured by IMPS/IMVS at $70\,W \cdot m^{-2}$ (Ref. [11], published with permission)

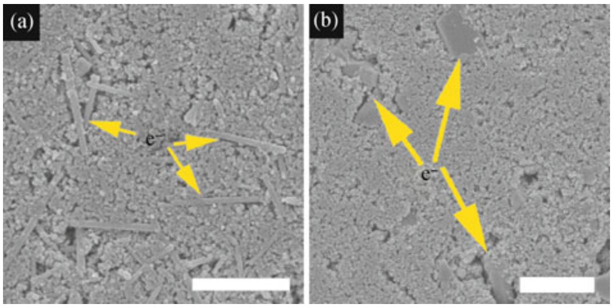


Fig. 16 SEM images of composite films containing ZnO nanotetrapods (a) and ZnO big particles (b) as additives. Scale bar = 1 μm. Yellow arrow-lines highlight different lengths the localized electrons have to migrate from SnO_2 nanoparticles to neighboring ZnO sites (Ref. [11], published with permission)

subsequent accelerated transport in ZnO. For ZnO nanotetrapods, such distance is a few hundred nanometers; whereas it is dramatically increased to several microns for ZnO big particles, as highlighted by the yellow arrows.

5 Conclusions

In the work reviewed here, we have systematically studied the use of ZnO nanotetrapods for DSSC photoanodes, More specifically, we have realized a novel photoanode architecture based on pure ZnO nanotetrapods and demonstrated its outstanding charge collection property. For such ZnO nanotetrapod photoanodes with film thickness up to > 30 μm, the corresponding DSSCs exhibit high V_{oc} and high FF even without calcination. J_{sc} increases to 10.31 mA·cm^{-2}, and the efficiency has reached 3.27%. The unique features of thick photoanode and no calcination make our ZnO nanotetrapod photoanodes especially distinct from most of the nanoparticle photoanodes reported to date.

In another significant stride, we were able to boost the efficiency to 6.31% by blending the ZnO nanotetrapods with SnO_2 nanoparticles. For composite films with higher ZnO nanotetrapods contents, due to the requirement of higher film thicknesses, charge collection losses appear to be a main limiting factor which compromises the benefit from their favorable light scattering ability. We have shown that a ZnO source, be it from particles or nanotetrapods, tends to form a generally similar ultrathin ZnO shell on SnO_2 nanoparticles. By comparison studies using the IMPS/IMVS technique, the functional roles of the ultrathin ZnO shell and the ZnO nanotetrapods in the SnO_2/ZnO composite film have been further elucidated: 1) The ultrathin ZnO shell mainly determines the recombination kinetics rather than the transport rate in the composite films; 2) ZnO nanotetrapods contribute to electron transport in composite photoanodes most probably in a “relay transport” manner, and due to the minimal to moderate hetero-particle grain boundaries, electron transport kinetics is facilitated in the ZnO nanotetrapods derived composite film, accentuating the structural and thus transport supremacy of our branched nanostructure over particles additives in the SnO_2/ZnO composite photoanodes.

The next march was the demonstration of applying the ZnO nanotetrapods to flexible DSSCs for the first time. A 4.91% efficiency has been achieved with a SnO_2 nanoparticles/ZnO nanotetrapods composite photoanode on a plastic substrate. The use of these special nanostructures led to the development of a low temperature technique of “AG-MP-NA,” which has proved effective for activating nanostructured surfaces (better electron injection), shortening electron transport pathways (better charge collection), and ultimately improving cell performance. Two unique characteristics of this nanocomposite photoanode design have rendered it applicable to flexible DSSCs. First, the ZnO shell on SnO_2, conducive to good contacts between nanoparticles and V_{oc} enhancement, is easily activated under a mild condition of NH_3 treatment. Second, the ZnO nanotetrapods with a symmetrically branching 1D structure not only ensures facile network formation on flexible substrate with good mechanical durability, further enhanced by mechanical press, but also has positive bearing on electron transport resulting in an improved charge collection efficiency when compared with ZnO big particles. To sum up, this work points to a promising alternative direction for the development of flexible solar cells by exploiting the core-shell, branching and composite nanostructures.

As often happens, our studies also left many questions unanswered. For example, it is unclear why the FF increases with film thickness. Does the nanotetrapod network need a different charge transport modeling approach? Moreover, we need a more detailed understanding about how the photoexcited electrons are injected from SnO_2 to ZnO. How do the material combination and the interface structure influence the interfacial charge transfer? Therefore it goes without saying that more work is needed to further understand the transport and optical properties of the ZnO nanotetrapods networks. In terms of DSSC device, although we have achieved reasonable efficiencies, there are still problems of charge collection, especially for the composite system on flexible substrates, for which low temperature treatments are the rule. In particular, the electron transport in low-temperature treated photoanodes is slower than in calcined ones. The solution to this problem will rely on the further development of the bottom-up nanotechnology.

Looking ahead, further improvements on the cell performance of the composite photoanodes can be anticipated by taking on several lines of investigation. First, the ZnO nanotetrapods should be grown with thinner diameters and longer arms so as to enhance surface area and improve the connectivity of the network. Second, new film deposition methods need be developed to improve the electrical contacts between the nanotetrapods and the conformity between the nanotetrapods and the embedded nanoparticles. One way is to first build a firmly connected ZnO nanotetrapods network as the electron transport highway, and then deposit the small SnO_2 nanoparticles or ZnO nanoparticles penetrating into and fully filling the remaining spaces. The latter can be accomplished by electrophoretic deposition, which has been widely applied in photoanode film deposition in flexible DSSCs [69,70]. Third, a thin uniform coating of, e.g., TiO_2, onto the ZnO nanotetrapods should mitigate interfacial charge recombination as well as bolster the stability of the film. Finally, other dyes and electrolytes can be tested for the ZnO nanotetarpods based photoanodes and could yield unexpected good results. The reason for this is simple, the dyes and electrolytes used so far are commonly optimized for TiO_2 but not necessarily for ZnO. In concluding this review, we strongly believe that there is a good potential for applications of branched semiconductor nanostructures in mesoscopic solar cells.

Acknowledgements This work was supported by the Research Grants Council of Hong Kong under the General Research Funds (No. 604809). We wish to thank all those who contributed to the work reviewed here.

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