Facile Preparation of TiO\textsubscript{2} Nanobranch/Nanoparticle Hybrid Architecture with Enhanced Light Harvesting Properties for Dye-Sensitized Solar Cells

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We report TiO\textsubscript{2} nanobranches/nanoparticles (NBN) hybrid architectures that can be synthesized by a facile solution phase method. The hybrid architecture simultaneously improves light harvesting and charge collection performances for a dye-sensitized solar cell. First, TiO\textsubscript{2} nanorods with a trunk length of 2 \( \mu m \) were grown on a fluorine-doped tin oxide (FTO)/glass substrate, and then nanobranches and nanoparticles were deposited on the nanorods’ trunks through a solution method using an aqueous TiCl\textsubscript{3} solution at 80 \(^\circ\)C. The relative amount of nanobranches and nanoparticles can be controlled by multiplying the number of TiCl\textsubscript{3} treatments to maximize the amount of surface area. We found that the resultant TiO\textsubscript{2} NBN hybrid architecture greatly improves the amount of dye adsorption (five times compared to bare nanorods) due to the enhanced surface area, while maintaining a fast charge collection, leading to a three times higher current density and thus tripling the maximum power conversion efficiency for a dye-sensitized solar cell.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted attention as one of the most promising solar conversion devices due to their low fabrication cost and high conversion efficiency [1–4]. In general, a DSSC consists of four parts: the sensitizer (dye molecule), a semiconductor for electron transport, a redox electrolyte, and charge collecting electrodes. Typically, nanoparticle-based photoanodes using n-type semiconductors (TiO\textsubscript{2}, ZnO, SnO\textsubscript{2}, BaSnO\textsubscript{3}, Zn\textsubscript{2}SnO\textsubscript{4}, etc.) have been investigated for adsorption of dye molecules as a result of their large surface areas [4–10]. However, these nanoparticle-based photoanodes limit charge collection efficiency because they have a large number of transport-limiting trapping/detrapping events on the nanoparticle surface; that is, they show a low charge collection efficiency [11, 12].

One strategy for overcoming this low charge collection efficiency is the use of vertically aligned one-dimensional (1D) nanostructures, which offer a direct electron transport pathway to the electrode, thus enabling low charge recombination. To date, various 1D nanostructured photoanodes have been studied, including nanowires (NWs), nanotubes (NTs), nanoparticle-decorated NWs, dendritic NWs, and core/shell NWs [13–19]. For instance, single-crystal TiO\textsubscript{2} nanowires were found to have a large electron diffusion coefficient compared to TiO\textsubscript{2} nanoparticles, owing to a lower density of surface defects [14]. Additionally, a preferentially oriented anatase TiO\textsubscript{2} nanotube, which has a small quantity of high angle grain boundaries, shows a large electron diffusion coefficient and diffusion length compared to TiO\textsubscript{2} nanoparticles [17]. Moreover, dendritic ZnO NWs with multiple branches demonstrated an enhanced photocurrent...
and internal quantum efficiency over nanoparticle-based cells [19]. Nevertheless, these 1D nanostructured photoanodes frequently display a low light harvesting efficiency due to a lower dye loading capacity, which leads to a low photocurrent density compared to nanoparticle-based DSSCs [14]. Recently, to address this low dye loading problem in 1D nanostructures, a few studies have adopted hierarchical structures based on the 1D nanostructures (e.g., nanoarrays and branched arrays) [20–23]. Even though the hierarchical structures exhibit improved charge collection and light harvesting efficiencies, their preparation methods are somewhat complex and require vacuum equipment, making it difficult to reproduce the synthesis technique and prepare large scale devices.

Here, we report a facile solution phase method to synthesize a TiO2 nanostructured photoanode consisting of nanobranches/nanoparticles on the trunks of the NWs. These hybrid NWs can be synthesized simply by using an aqueous TiCl3 solution at low temperature (80°C). One advantage of our method is that it enables us to control the relative amount of nanobranches and nanoparticles on the TiO2 NW trunks as a result of applying multiple TiCl3 treatments, to maximize dye adsorption (i.e., the light harvesting property). Additionally, this method facilitates a scalable preparation (up to a 4-inch wafer) due to it being a low temperature process. We carefully investigated the effect of the TiCl3 treatment on the morphology progress and dye adsorption capacity, and we demonstrate that the hybrid architecture improves the photocurrent and incident photon-to-current conversion efficiency (IPCE) for DSSCs by a factor of two compared to nanorod-based DSSCs.

2. Experimental

2.1. Preparation of the TiO2 Nanowires (NWs). Rutile TiO2 NWs were synthesized on a fluorine-doped tin oxide (FTO)/glass substrate by a hydrothermal method [24]. Before growing the TiO2 nanorods, a TiO2 seed layer was deposited by a spin coating method using a TiO2 polymeric sol [25] and then annealed at 450°C for 1 h. Titanium butoxide (97%, Aldrich) was slowly added to 50 mL of a hydrochloric acid (HCl) aqueous solution (25 mL of deionized (DI) water + 25 mL concentrated HCl solution (38%)) and stirred for 30 min to obtain a transparent solution. This precursor solution was transferred into a sealed Teflon-lined stainless steel autoclave (100 mL volume) and then the TiO2 seed layer-coated FTO/glass substrates were immersed in this solution. The autoclave was placed in an electric oven and heated to 170°C for 4 h without stirring. The resultant TiO2 nanorod samples were washed with DI water several times and finally annealed at 450°C for 1 h in air.

2.2. TiCl3 Treatment. To grow the nanobranches and nanoparticles, the TiO2 nanorod samples were immersed into a solution containing 10 mL of DI water, 0.1 mL of concentrated HCl solution, and 1 mL of TiCl3 solution (Aldrich, 10 wt.% in 20–30 wt.% HCl solution) and held at 80°C for 30 min in an oven. The effect of the TiCl3 treatment time (30 min, 1 h, 2 h, and 4 h) on the morphology was examined first. The relative quantity of nanobranches/nanoparticles was controlled by repeating the TiCl3 treatment. We have labeled the sample names as 30 min-1, 30 min-2, 30 min-3, and 30 min-4 to correspond to the number of additional TiCl3 treatments. Afterward, all samples were washed with DI water and annealed at 450°C for 1 h in air.

2.3. Fabrication of DSSCs. The annealed samples were soaked in a ruthenium dye solution (N719, ruthenium (2,2′ bipyridyl-4,4′ dicarboxylate)2 (NCS)2) at room temperature for 12 h. Platinum-coated FTO substrates prepared by sputtering were used as the counter electrodes. The sandwich-type DSSCs were assembled using the samples as the photoanodes and the Pt-coated FTO glasses as the counter electrodes with a hot-melt film (~60 μm, Surlyn, DuPont) as a spacer. Finally, the electrolyte was an iodide-based liquid electrolyte (SI6 Li535-01, Merck), which was introduced into the cell through a hole in the counter electrode. The active area of all samples was 0.25 cm².

2.4. Material and DSSC Characterization. The crystal structure and phase of the synthesized samples were identified by an X-ray diffractometer (XRD, Bruker, New D8 Advance) with CuKα radiation operated at 40 kV and 40 mA. The morphologies of the prepared samples were observed by a field-emission scanning electron microscope (FESEM, Hitachi, SU70) and a high-resolution transmission electron microscope (HRTEM, JEOL, JEM-3000F). The photovoltaic performance and electron impedance spectroscopy (EIS) of the DSSCs were measured with a potentiostat (CH Instruments, CH1308C) under AM 1.5G simulated solar light (100 mW/cm², Sol3A, Newport). The ultraviolet-visible (UV-Vis) absorption spectra of the dye solutions, collected by desorption from the samples, were investigated with an UV-Vis spectrometer (Agilent Technologies, Cary 5000). The DSSCs’ electron transport properties were characterized by intensity-modulated photovoltage spectroscopy (IMVS) using an electrochemical workstation (Zennium, Zahner) with an attached frequency analyzer and a light-emitting diode (667 nm).

3. Results and Discussion

The morphology of the TiO2 nanorods (NRs) used as the stem for the TiO2 hybrid architecture is shown in Figures S1 and S2 (in Supplementary Material available online at http://dx.doi.org/10.1155/2015/39715). The NRs are grown on the FTO/glass substrate by a hydrothermal method [26]. The NRs have an average diameter of the length of 103 ± 15 nm and 2.0 ± 0.2 μm (Tables S1 and S2), presenting high crystallinity with a preferred growth direction of [001]. Figure 1 shows top-view FESEM images of the TiO2 hybrid architectures’ microscopic morphologies, prepared by repeating the TiCl3 treatment (1–4 times) at 80°C for 30 min. It can be seen that the TiCl3 treatment significantly affects the morphology of the TiO2 NRs. After the first TiCl3 treatment (sample 30 min-1), small nanobranches (~10 nm in diameter and
Figure 1: The effect of the number of TiCl$_3$ treatments on the morphology of the TiO$_2$ NWs. Top-view FESEM images, (a) one 30 min treatment (30 min-1), (b) two-treatment (30 min-2), (c) three-treatment (30 min-3), and (d) four-treatment (30 min-4).

~60 nm in length) were formed on the surface of the individual TiO$_2$ NRs (Figure 1(a)), which lengthen further (~100 nm long) with an increased density on the NR surface after the second TiCl$_3$ treatment (sample 30 min-2, Figure 1(b)). When the treatment was repeated three times (sample 30 min-3, Figure 1(c)), the length of the nanobranches increased to 200–300 nm, reducing the interspaces between the TiO$_2$ NRs; these interspaces decreased significantly after the fourth treatment (sample 30 min-4, Figure 1(d)). We also investigated the effects of the TiCl$_3$ treatment duration time (Figure S3). An increased duration time provides a similar effect on the morphology; that is, it lengthens the nanobranches and increases their density as the duration time was increased from 30 min to 4 h.

The detailed variation in the TiO$_2$ nanostructure morphology with multiple TiCl$_3$ treatments was investigated further by utilizing cross-sectional FESEM images (Figure 2). For the 30 min-1 and 30 min-2 samples, there were no significant changes in the TiO$_2$ NRs except for the formation of nanobranches. However, for the 30 min-3 sample, the nanobranches grew in length, reducing the space between NRs, especially at their tops (Figure 2(c)). Interestingly, at the bottom of the nanorods, nanoparticles with an average size of ~30 nm formed together with the nanobranches, suggesting that more than three TiCl$_3$ treatments induce a different growth mode, generating nanoparticles at the bottom of the NRs. Finally, after the fourth treatment (30 min-4), the TiO$_2$ nanoparticles completely filled the NR interspaces, up to the top of the film. These two different growth modes, that is, the nanobranch and nanoparticle growth, during the multiple TiCl$_3$ treatments enable the morphology to be tuned, thereby controlling the relative surface area of the 1D nanostructure based on the NRs.

The XRD patterns of the samples discussed above are shown in Figure 3. All diffraction peaks of the TiO$_2$ NRs (30 min-1) are in agreement with tetragonal rutile TiO$_2$ (JCPDS number 21-1276, P4$_2$/mnm, $a = b = 4.593$ Å, $c = 2.959$ Å). In general, rutile TiO$_2$ NRs prepared by a hydrothermal method grow along the (001) plane, as it has the fastest growth rate compared to the other crystal faces [13, 27, 28]. Similar to other reports, our TiO$_2$ NRs have a preferred growth direction of [001], which was
Figure 2: Cross-sectional SEM images of the TiO$_2$ NWs obtained by repeating the TiCl$_3$ treatments, (a) 30 min-1, (b) 30 min-2, (c) 30 min-3, and (d) 30 min-4. After three TiCl$_3$ treatments, nanoparticles start to form and fill the gaps between NWs.

Figure 3: XRD patterns of TiO$_2$ NWs and hybrid architectures obtained by the TiCl$_3$ treatments (0–4 times). Also confirmed by a TEM analysis (Figure S2). For the XRD peaks of the multiple TiCl$_3$ treatment samples, there were no considerable differences from the 30 min-1 sample, suggesting that the nanobranches and nanoparticles are also rutile tetragonal structures. The perceptible development of the (110) diffraction peaks at 27.5° in the 30 min-2, 30 min-3, and 30 min-4 samples implies that the nanobranches have the same preferred [001] growth direction [24].

Based on the above observation, the formation process of the TiO$_2$ nanobranch/nanoparticle (NBN) hybrid architectures is displayed schematically in Figure 4. After the first treatment, short nanobranches are formed on the surface of the NRs, which grow to longer nanobranches with an average length of ∼100 nm after the second TiCl$_3$ treatment. The third TiCl$_3$ treatment induces nanoparticle growth from the bottom of the film, which reduces the interspaces between the NRs at their bases. With a further TiCl$_3$ treatment, however, additional nanoparticles formed, filling the remaining interspaces between the NRs to the top of the film, finally forming a NBN hybrid architecture.
It should be noted that these interesting 1D architectures are obtained by simply repeating the TiCl$_3$ treatment, which enabled the unusual growth (or deposition) behavior during the additional TiCl$_3$ treatments. In general, the pH of the growth solution significantly affects the growth morphology (i.e., the crystal phase and morphology) of TiO$_2$ nanocrystals [29], that is, nanoparticles near pH 7 and elongated nanorods or nanoneedles below pH 4. Therefore, the two different growth modes, of the nanobranches and nanoparticles, might relate to the change in the solution's pH value during the multiple TiCl$_3$ treatments. A detailed analysis of this is under investigation.

Next, in order to check the usefulness of the NBN hybrid architectures for a solar energy conversion device, we fabricated dye-sensitized solar cells (DSSCs) with them. First, the light harvesting behavior, that is, the dye adsorption property, was investigated by UV/Vis absorption spectroscopy (Figure 5). The absorption spectra were obtained of dye solutions after collecting the dye by a desorption process in a basic solution. The peak at 510 nm in the absorption spectra is a characteristic peak of these dye molecules (N719), and this can be used to estimate the amount of dye molecules adsorbed onto the TiO$_2$ surface. As shown in the inset of Figure 5, the amount of adsorbed dye of the 30 min-4 sample increased nearly by a factor of four compared to the 30 min-0 sample, indicating that the NBN hybrid architecture (30 min-4 sample) has a larger surface area, thus improving the light harvesting efficiency for the DSSCs.

Figure 6(a) shows the photocurrent density-voltage curves of the DSSCs fabricated using the above four samples, which were measured under AM 1.5G simulated solar light (1 sun, 100 mW/cm$^2$) and their representative solar cell parameters are shown in Figures 6(b) and 6(c) (with the other parameters summarized in Table 1). Initially, the short circuit photocurrent density ($J_{sc}$) values increased linearly until the third treatment and eventually reaching a maximum $J_{sc}$ value of 13.4 mA/cm$^2$ for the fourth treatment. This result strongly correlates with the absorbance spectra of the desorbed dye shown in the inset of Figure 5, indicating that the NBN hybrid architecture has an improved light harvesting property, thus increasing the $J_{sc}$ for DSSCs. The open circuit voltage ($V_{oc}$) of the TiO$_2$ NR-based DSSC was 0.82 V. This $V_{oc}$ value decreased slightly with an increasing number of TiCl$_3$ treatments to 0.77, 0.72, 0.71, and 0.69 V for the 30 min-1, 30 min-2, 30 min-3, and 30 min-4 samples, respectively. In the case of the fill factor (FF) values, there were no notable differences (Table 1). As a result, the power conversion efficiency was enhanced from 2.6% (for the NR-based DSSC) to...
Table 1: The photocurrent density-voltage characteristics and dye loading of the NBN-TiO$_2$-based DSSCs with various TiCl$_3$ treatment times.

<table>
<thead>
<tr>
<th>Photoelectrode</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$V_{oc}$ [V]</th>
<th>FF [%]</th>
<th>$\eta$ [%]</th>
<th>Dye loading [$\times 10^{-9}$ mole/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanorod</td>
<td>5.62</td>
<td>0.82</td>
<td>57</td>
<td>2.6</td>
<td>0.34</td>
</tr>
<tr>
<td>30 min-1</td>
<td>7.86</td>
<td>0.77</td>
<td>58</td>
<td>3.5</td>
<td>0.43</td>
</tr>
<tr>
<td>30 min-2</td>
<td>11.26</td>
<td>0.72</td>
<td>58</td>
<td>4.7</td>
<td>0.92</td>
</tr>
<tr>
<td>30 min-3</td>
<td>12.95</td>
<td>0.71</td>
<td>57</td>
<td>5.2</td>
<td>1.50</td>
</tr>
<tr>
<td>30 min-4</td>
<td>13.35</td>
<td>0.69</td>
<td>58</td>
<td>5.3</td>
<td>1.65</td>
</tr>
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Figure 5: The UV-Vis absorption spectra of the dye (N719) detached from the TiO$_2$ films prepared under a varied number of TiCl$_3$ treatments. To measure the UV-Vis absorption spectra of the dye (N719), it was first desorbed by an ammonium (NH$_4$OH) solution in water and ethanol (50:50, v/v).

5.3% (for the NBN hybrid architecture- (30 min-4-) based DSSC), demonstrating that the NBN hybrid architecture is advantageous to improve $J_{sc}$ in DSSCs.

To understand the effect of the multiple TiCl$_3$ treatments on the electron dynamics, an intensity-modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS) was used to measure the samples (Figure S4). All samples show a typical power-law dependence of their transport time constants on the $J_{sc}$ value (Figure S4a). This indicates an exclusive random walk of photoelectrons between trap sites having a power-law distribution of waiting (release) times in the form of $t^{-1-\alpha}$, where the parameter $\alpha$ can be related to the shape of the trap distribution [30, 31]. Initially, the charge transport time increased with the additional TiCl$_3$ treatments, indicating that the route photoelectrons travel to the FTO substrate became longer and more complicated due to the nanobranches and nanoparticles. This reduction in the transport time constant competes with the effect of the increased dye adsorption. The transport time constant and the dye adsorption correlate to the charge collection efficiency and light harvesting efficiency, respectively, which determine the power conversion efficiency.

The light harvesting efficiency is generally affected by the dye loading capacity [34]. As mentioned in Figure 5, the dye loading capacity of the TiO$_2$ photoanodes increased significantly with multiple TiCl$_3$ treatments, implying that the light harvesting efficiency increased with additional TiCl$_3$ treatments. On the other hand, the IMPS and IMVS data (Figure S4) demonstrate that the charge collection efficiency decreased monotonically with the multiple TiCl$_3$ treatments. The effects of the dye adsorption are dominant, the power conversion efficiency of the TiO$_2$ NBN hybrid architecture DSSC increased with repeated TiCl$_3$ treatments.

Second, the charge recombination time constant consistently decreased with an increasing number of TiCl$_3$ treatments. The infiltrated TiO$_2$ nanobranches and nanoparticles decreased the diffusion efficiency of the I$_3^-$ ions in the electrolyte. The relation between the recombination time and $V_{oc}$ can be described by the following equation [32, 33]:

$$V_{oc} = \frac{RT}{\beta F} \ln \left( \frac{AI}{n_0 k_1 [I_3^-] + n_0 k_2 [D^+]^\beta} \right).$$

where $R$ is the molar gas constant, $T$ is the temperature, $\beta$ is the reaction order for the electrons, $F$ is the Faraday constant, $A$ is the electrode area, $I$ is the incident photon flux, $n_0$ is the concentration of accessible electronic states in the conduction band, and $k_1$ and $k_2$ are the kinetic constants of the injected electron with triiodide (I$_3^-$) back reaction and the recombination of these electrons with oxidized dye (D$_n^+$) molecules, respectively. Neglecting the recombination of the injected electrons with oxidized dye molecules, the $V_{oc}$ value is logarithmically dependent on the back reaction of these electrons with the triiodide ($k_1$). Therefore, the rate of the electron recombination from the TiO$_2$ photoanode to the I$_3^-$ ions in the electrolyte increased with an increasing number of TiCl$_3$ treatments.

Figure 7 shows the incident photon-to-current efficiency (IPCE) spectra of the TiO$_2$ photoanode-based DSSCs. All of the DSSCs show the typical spectral response of N719-based DSSCs with a peak at approximately 530 nm. However, the maximum IPCE (or external quantum efficiency, EQE) varies with the number of TiCl$_3$ treatments. The 30 min-4 sample exhibited the maximum IPCE and the NR sample displayed the minimum IPCE. The IPCE of DSSCs is determined by the light harvesting efficiency ($\eta_{lh}$), the charge injection efficiency ($\eta_{inj}$), and the charge collection efficiency ($\eta_{cc}$). The IPCE value can be expressed by the following equation:

$$\text{IPCE} \ (%) = \eta_{lh} \times \eta_{inj} \times \eta_{cc}.$$
Even though the NBN hybrid architecture reduced the electron transport property slightly, it can be concluded that the enhancement seen in the light harvesting efficiency was greater than the decrease in the charge collection efficiency. Interestingly, the IPCE values of the samples after multiple TiCl₃ treatments show a shoulder at a longer wavelength (>680 nm), indicating that the NBN hybrid architecture has additional enhancement effects for DSSCs, that is, improving the light scattering effect. This light scattering effect also enhances the light harvesting efficiency in combination with the increased dye loading capacity.

4. Conclusions

In summary, we report on a TiO₂ hybrid architecture composed of TiO₂ nanobranches and nanoparticles, easily synthesized by a solution phase method. A TiCl₃ aqueous solution treatment at 80°C enables a controlled morphology of the TiO₂ nanorods. By repeating this TiCl₃ treatment, nanobranches and/or nanoparticles are deposited on the trunks of the TiO₂ nanorods, giving hybrid architecture with an enhanced surface area. We found that the resultant TiO₂ nanobranch/nanoparticle hybrid architecture greatly improved the dye adsorption (five times compared to bare nanorods) due to the enhanced surface area, albeit a slight decrease in a charge collection property. Additionally, the complex architecture produces a large light scattering effect, eventually leading to a three times greater current density and thus tripling the maximum power conversion efficiency for a dye-sensitized solar cell. We believe that the synthesized TiO₂ hybrid architecture, after further structural optimization, has the potential for use in other energy harvesting devices.
such as quantum-dot dye-sensitized solar cells (QD-DSSCs), photoelectrochemical (PEC) water-splitting, and solid-state solar cells, which require both high light harvesting and charge collection efficiencies.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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