Synthesis of hierarchical TiO$_2$ nanowires with densely-packed and omnidirectional branches

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In this study, a hierarchical TiO$_2$ nanostructure with densely-packed and omnidirectional branches grown by a hydrothermal method is introduced. This morphology is achieved via high-concentration TiCl$_4$ treatment of upright backbone nanowires (NWs) followed by hydrothermal growth. Secondary nanobranches grow in all directions from densely distributed, needle-like seeds on the jagged round surface of the backbone NWs. In addition, hierarchical, flower-like branches grow on the top surface of each NW, greatly increasing the surface area. For dye-sensitized solar cell (DSSC) applications, the TiO$_2$ nanostructure demonstrated a photoconversion efficiency of up to 6.2%. A parametric study of the DSSC efficiency showed that branched TiO$_2$ DSSCs can achieve nearly four times the efficiency of non-branched TiO$_2$ nanowire DSSCs, and up to 170% the efficiency of previously-reported sparsely-branched TiO$_2$ NW DSSCs.

1. Introduction

The development of a photoelectrode composed of various types of nanostructures in order to achieve large surface area, enhanced photocatalytic efficiency, and high crystallinity is one of the main issues in optoelectronic and photocatalysis applications. TiO$_2$ has been extensively studied as a core material for such applications as it is physicochemically stable, non-corrosive, and cost-effective along with a wide band gap. TiO$_2$ nanostructures have garnered significant interest for water-splitting hydrogen generation since the Honda–Fujishima effect was reported. Also, among the nanomaterials, TiO$_2$ still exhibits the highest power conversion efficiency in DSSC applications while ZnO NW DSSCs have shown limited photoconversion efficiencies due to their low stability in the carboxylic anchoring groups of the sensitizer. Nanoparticle (NP) is the most common nanostructure of TiO$_2$ for applications in conventional Grätzel-type solar cells. However, once electrons are generated, they suffer recombination at the NP interfaces where the electron diffusion is retarded. Thus, many efforts have concentrated on overcoming this limitation by using one-dimensional (1D) nanostructures such as nanowires (NWs) and nanotubes (NTs) which provide a direct pathway for electrons to the electrode. 1D TiO$_2$ nanostructures have been actively investigated and several synthesis methods have been reported such as hydrothermal growth, anodizing, electrospinning, and acid vapor oxidation (AVO). As reported in previous studies, TiO$_2$ NWs grown by the hydrothermal method generally have a rutile crystal structure, whereas hydrothermally grown anatase TiO$_2$ structures have been reported very recently. The rutile phase is generally known to exhibit comparable performance to the anatase phase, yet with better chemical stability and a higher refractive index thereby providing suitable properties for applications such as DSSCs. Since Feng et al. and Liu et al. reported hydrothermal synthesis methods of TiO$_2$ NWs directly on transparent conductive substrates, 1D TiO$_2$ nanostructures and their variations expanding the 1D shape into 3D are increasingly being developed for optoelectronic devices. Fewer variations of 3D nanostructures of TiO$_2$ have been demonstrated in contrast to the wide variety of ZnO nanomaterials that include nanoflakes, nanowheels, and nanotetrapods. More recently, to achieve enhanced photocatalytic activity with higher surface-to-volume ratio, several studies have focused on multidimensional and hierarchical TiO$_2$ nanostructures such as nanobranched and nano-tetrapods. However, these structures have either tiny or sparsely distributed branches, hence leaving much room for improvement. In this study, we report on the synthesis of hydrothermally grown, omnidirectional, 3D hierarchically-branched and densely-packed TiO$_2$ nanostructures.
nanowire photoanodes. TiO₂ nanobranches were grown in high density in all directions from chemically-modified, rutile-structure, TiO₂-backbone NW surfaces. Parametric studies comparing the DSSC efficiencies show the effect of these structural differences on the photoanode performance.

2. Experimental details

2.1. Synthesis of TiO₂ nanowires with densely-packed and omnidirectional branches

The omnidirectional, densely-packed, and hierarchically-branched TiO₂ nanowire structures (DB: densely branched) were synthesized by the so-called “2 + 1 method”, which comprises two hydrothermal growth steps with an intermediate high-concentration TiCl₄ treatment. A schematic illustration of the formation of the DB structure is shown in Fig. 1. To begin, upright TiO₂-backbone NWs (LG: lengthwise growth) were grown on a fluorine-doped SnO₂ conductive glass (FTO) substrate by the hydrothermal method. Although TiO₂ NWs can be grown directly on a FTO substrate without any seed layer due to a small lattice mismatch between FTO (a = b = 0.4687 nm) and rutile TiO₂ (a = b = 0.4594 nm),19 Feng et al. observed that TiO₂ nanowires grown directly on FTO glass tend to induce electrical shorting with the electrolyte. In addition, in several studies it has been reported that mixed-phase nanocomposites composed of a thin anatase TiO₂ layer and rutile TiO₂ nanowires show enhanced photocatalytic reactivity.20–24 Thus, a thin anatase TiO₂ layer was deposited by drop casting a diluted anatase paste (Solaronix) onto cleaned FTO glass before the hydrothermal NW growth. As a precursor solution, 30 ml of hydrochloric acid aqueous solution (37%, Sigma Aldrich) and 30 ml of distilled water were mixed in a 150 ml PTFE-lined stainless-steel autoclave and stirred for 5 min, followed by the addition of 1 ml of Ti-butoxide [C₆H₃(O)Ti] (97%, Sigma Aldrich). After stirring the solution for another 5 min, LG NWs were grown by immersing the anatase TiO₂-coated substrate into the solution in a face-down position and heating for 11 h in an oven pre-heated to 180 °C. The possible underlying mechanism of the TiO₂ NW growth from Ti-butoxide or other titanium precursors can be found elsewhere.18,22 After the reaction was complete and the sample had cooled, the TiO₂ NWs grown on the substrate were thoroughly rinsed with distilled water and dried. To obtain a densely-seeded surface (DS: densely seeded), the LG sample was immersed in a high concentration (0.2 M) TiCl₄ aqueous solution at room temperature overnight. The surface treatment of TiO₂ nanostructures via hydrolysis of TiCl₄ (TiCl₄ + 2H₂O → TiO₂ + 4HCl) is one of the well-known routes to produce epitaxial growth of rutile layers on the electrode surface. More details of the reaction mechanism can be found in previous reports.27,45,46 In order to grow the NW branches from the seeds on the surface, another hydrothermal process was performed in the same manner as for the LG NW process, this time for 3.5 h. Finally, hierarchical TiO₂ NWs with densely-packed and omnidirectional branches (DB: densely branched) were achieved.

For a parametric study of the DSSC efficiency, sparsely-branched (SB) TiO₂ NW photoanodes were also synthesized as a benchmark using a seed preparation method previously reported by Liao and Wu.28 For SB NWs, a premixed solution of 1.7 ml of Ti-isopropoxide [C₃H₆(O)Ti] (Sigma Aldrich) and 2 ml of hydrochloric acid (37%) was mixed with 40 ml of distilled water, after which the LG NWs were placed into the solution for 4 h at 95 °C in order to obtain sparse seeds on the surface (SS: sparsely seeded). Then, another hydrothermal process conducted in the same manner as before for 3.5 h resulted in SB NWs. In order to increase the roughness of each NW surface for higher dye loading, LG, DB, and SB NWs were treated with a mild (0.05 M) TiCl₄ aqueous solution at 70 °C for 30 min (tLG, tDB, and tSB, respectively). As a final step in the NW synthesis, all NW samples were annealed in air at 500 °C for 30 min to remove any residual organics.

2.2. Dye-sensitized solar cell fabrication

Dye loading was conducted by immersing the TiO₂ photoanodes into a 0.5 mM ethanolic solution of di-tetrabutylammonium cis-bis(isothiocyanato)bis[2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) (N719, Solaronix) dye for 18 h. As counter electrodes, several drops of 0.2 mM ethanolic H₂PtCl₆ solution were spread onto the FTO substrates, which had been pre-drilled with small holes for electrolyte injection, followed by heating at 400 °C for
30 min. Then, the sensitized photoanodes and counter electrodes were sandwiched and bonded together using 60 μm thick hot-melt foil spacers (Meltonix 1170-60, Solaronix). The iodide-based redox electrolyte (AN 50, Solaronix) was introduced into the cell through the holes in the counter electrode, and then covered and sealed using a thin glass cover slip.

3. Results and discussion

The NWs were characterized after each growth step by Scanning Electron Microscopy (SEM). As shown in Fig. 2a, after the first growth step the LG NWs had a diameter of approximately 200 nm and a length of 2.5 μm, with flat, tetragonal crystallographic surfaces. After DS modification by high concentration (0.2 M) TiCl₄ aqueous solution treatment, the surface of the LG NWs was modified to feature a jagged circular cross-section and was decorated by needle-like seeds as shown in Fig. 2b. Successive hydrothermal growth of the DS nanowire for 3.5 h resulted in very dense omnidirectional growth of nanobranches, which were approximately 200 nm in length and 30 nm in diameter (DB, Fig. 3a and b). Notably, the DS process induced growth of dense branches on the tip of each NW resulting in a dandelion-like structure greatly increasing the surface area. Contrary to the DS modification and DB structure, the SS treatment retained the square cross section of the backbone NWs as shown in Fig. 4a such that the bundles of nanobranches for the SB NWs grew only in limited directions from the square rutile-type TiO₂ NW trunks, as displayed in Fig. 4b. The areal densities of the LG, SB and DB structures calculated from the SEM images are around $1.6 \times 10^9$ NWs cm⁻², $4.4 \times 10^{11}$ branch NWs cm⁻² and $6 \times 10^{11}$ branch NWs cm⁻² respectively. Considering the areal density and the dimension of each nanowire (LG: 200 nm (diameter) × 2.5 μm (length), SB and DB branch: 30 nm (diameter) × 200 nm (length)), the roughness factors of the LG, SB and DB structures, defined as the ratio of the total surface area of the NW structure to its projected substrate area, are calculated to be around 32, 83 and 113 respectively. Fig. 5a and b show higher magnification SEM views of the DB and tDB NWs, respectively, demonstrating an obvious difference in surface roughness by the mild TiCl₄ treatment. It is noted that a high-concentration TiCl₄ treatment at this step hinders effective dye loading by filling up all narrow spaces between the branches. Therefore, mild TiCl₄ treatment conditions should be chosen for an appropriate TiO₂ precipitation rate.

The crystal structure of the DB TiO₂ NWs has been characterized by Transmission Electron Microscopy (TEM), Raman spectroscopy (excitation wavelength: 532 nm), and X-ray Diffraction (XRD). TEM characterization of the NW backbone of the DB TiO₂ structures was achieved by removing individual NWs from an LG array. A bright-field TEM image of a single LG

Fig. 2 SEM images of (a) upright backbone TiO₂ NWs (LG: lengthwise growth), and (b) TiO₂ NWs after densely-seeded (DS) surface modification via a high-concentration (0.2 M) TiCl₄ treatment. The insets of (a) and (b) show high-magnification top and side views of each structure.

Fig. 3 SEM images of omnidirectional, densely-packed, and 3D hierarchically-branched TiO₂ NWs (DB): (a) tilted view, (b) top view. The insets of (a) and (c) show high-magnification images of an individual DB NW.
NW is shown in Fig. 6a with the corresponding selected area electron diffraction (SAED) pattern inset. The diffraction pattern indices to the [110] zone axis of rutile TiO$_2$ indicate that crystal growth occurred in the [001] direction. Fig. 6b shows the tip of an LG NW revealing its constituent nearly-parallel needle-like structures. Fig. 7 shows the TEM results for branches removed from a DB NW array. A single branch is shown in the bright-field TEM image in Fig. 7a. The corresponding SAED pattern for the branch shown in the inset was acquired along the [111] zone axis. Crystal growth in the [001] direction is again concluded. In Fig. 7b a bundle of branches is shown demonstrating the highly dense nature of the branched growth, which prohibited selective imaging of the interface between the NW backbone and a given branch.

Fig. 8a and b show XRD patterns and Raman spectra, respectively, for LG, SB, and DB NWs. The similar appearance of the peaks for the three different TiO$_2$ NW types in both the XRD and the Raman characterization demonstrates the strong similarity between their crystal structures. It is worth noting that the anatase phase could only be detected in the Raman spectra, which is attributed to the larger penetration depth of
the Raman light source into the thin anatase base layer. We believe that the anatase peaks in the LG, SB, and DB spectra are due to the above-mentioned thin anatase paste layer, which was deposited prior to the hydrothermal growth, since only rutile Raman peaks were detected for the NW arrays grown without the paste layer. Thus, we conclude that the NWs exhibit the rutile phase (confirmed by the TEM analysis above) while the thin paste layer retains the anatase phase.

DSSC performance was investigated for LG, DB, SB, tLG, tDB, and tSB TiO₂ photoanodes. The current density–voltage (J–V) characteristics as displayed in Fig. 9 were measured under AM1.5 (100 mW cm⁻²) illumination from a solar simulator with an active area of 0.08 cm² for all cells. Further characteristics are summarized in Table 1. The short circuit current density (Jsc) and the overall light conversion efficiency increased for the NW samples in the order LG < tLG < SB < tSB < DB < tDB. While the DSSCs with LG photoanodes attain a photoconversion efficiency of 1.6%, tDB DSSCs show an efficiency of 6.2%, which demonstrates an increase in efficiency by almost four times. Furthermore, the efficiencies of the DSSCs constructed using DB and tDB photoanodes show 170% and 130% higher efficiencies than those using SB and tSB photoanodes, respectively. The efficiency increase is attributed to several effects. First, the densely-packed branches and the enhanced surface roughness resulting from the TiCl₄ treatment significantly increase the surface area and hence also the amount of dye loading. Second, omnidirectional branches enable effective photon absorption by preventing photons from passing through the vertical NWs without being absorbed. Third, light scattering and trapping enhancement by the high density of branches increases the light harvesting efficiency. The efficiency ratio of LG, SB and DB DSSCs is in quite good agreement with that of the areal densities above mentioned, which indicates that the surface area increase is the main reason of the efficiency enhancement. It is worth noting that our DB structure has an effective thickness of around 2.7 µm (2.5 µm in length for LG backbone and 200 nm in length for the branches), which is much thinner than the NP photoanode having a thickness of ~10 µm in the conventional Grätzel-type DSSCs.

4. Conclusions

We have reported omnidirectional, densely-packed, and 3D hierarchically-branched TiO₂ nanostructures grown by a hydrothermal method. This morphology was achieved using a high-concentration TiCl₄ treatment on upright backbone NWs followed by hydrothermal growth. The branches grew in all directions from a very dense distribution of needle-like seeds on the jagged cylindrical surface of the backbone NWs resulting in a DB structure and increased surface area. The DSSCs fabricated with DB TiO₂ photoanodes showed a light conversion efficiency of up to 6.2%, which is almost four times the efficiency of DSSCs constructed using non-branched upright TiO₂ NWs, and up to 170% higher than the efficiency of previously-reported sparsely-branched TiO₂ NW DSSCs. The densely-branched TiO₂ structure may also have potential applications in water splitting, photocatalysis, and gas sensors.

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