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Cellulose nanofiber-templated three-dimension TiO₂ hierarchical nanowire network for photoelectrochemical photoanode

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Abstract
Three dimensional (3D) nanostructures with extremely large porosity possess a great promise for the development of high-performance energy harvesting and storage devices. In this paper, we developed a high-density 3D TiO₂ fiber-nanorod (NR) heterostructure for efficient photoelectrochemical (PEC) water splitting. The hierarchical structure was synthesized on a ZnO-coated cellulose nanofiber (CNF) template using atomic layer deposition (ALD)-based thin film and NR growth procedures. The tubular structure evolution was in good agreement with the recently discovered vapor-phase Kirkendall effect in high-temperature ALD processes. The NR morphology was formed via the surface-reaction-limited pulsed chemical vapor deposition (SPCVD) mechanism. Under Xenon lamp illumination without and with an AM 1.5G filter or a UV cut off filter, the PEC efficiencies of a 3D TiO₂ fiber-NR heterostructure were found to be 22–249% higher than those of the TiO₂-ZnO bilayer tubular nanofibers and TiO₂ nanotube networks that were synthesized as reference samples. Such a 3D TiO₂ fiber-NR heterostructure offers a new route for a cellulose-based nanomanufacturing technique, which can be used for large-area, low-cost, and green fabrication of nanomaterials as well as their utilizations for efficient solar energy harvesting and conversion.

Keywords: atomic layer deposition, cellulose nanofiber, 3D structure

(Some figures may appear in colour only in the online journal)

1. Introduction

Photoelectrochemical (PEC) water splitting has received considerable attention in the development of solar fuel technologies to relieve our dependence on fossil fuels and to reduce greenhouse gas emissions [1–4]. High-performance photoelectrodes of PEC systems demand broad-band and high-percentage light absorption; instantaneous and low-loss charge separation, collection and transportation; and large and clean electrode—electrolyte interfaces [4–11]. Three-dimensional (3D) branched nanowire (NW)/nanorod (NR) architectures are considered to be excellent candidates for PEC photoelectrode development. They are composed of highly conductive core NWs that are fully covered with dense and active NR branches [10, 12–16]. Their high performance is a result of their extremely large surface area density, long optical paths, and the potential to achieve rapid photogenerated electron-hole separation and transport. Our recent
development of a surface-reaction-limited pulsed chemical vapor deposition (SPCVD) technique, as a derivative of atomic layer deposition (ALD), enabled uniform growth of high-density NR branches on ultra-compact NW arrays, which led to significant performance gain in solar energy conversion [10, 12].

Natural cellulose-based nanomaterials such as cellulose nanofibers (CNFs) are another type of widely used large-scale renewable 3D mesoporous structures owing to their great abundance, low cost, bio-compatibility, and degradability [17–20]. They are composed of elementary cellulose fibrils and show comparable mechanical properties (e.g., Young’s modulus and tensile strength) as other fibrous materials (e.g., carbon fibers and glass fibers) [21]. CNFs also exhibit significant absorbability to both hydrophilic and hydrophobic materials [22]. They are therefore a remarkable template for processing functional 3D nanostructures with extremely large porosity and possess great promise for the development of high-performance energy harvesting and storage devices. For example, nanofibrillated cellulose was utilized as a paper substrate to fabricate thin film transistors achieving high transparency and flexibility of the device [20]; nanostructured networks of cellulose-graphite platelet composites were applied as Li-ion battery anodes, demonstrating excellent flexibility and good cycling performance [23, 24]; porous cellulose-templated TiO2 nanostructures were used in photocatalytic and dye-sensitized solar cells, exhibiting significantly enlarged surface area and improved electron transport properties [25, 26]; and cellulose/polyaniline nanocomposites were developed for supercapacitors with enhanced mass-specific capacitance [27]. Combining the successful exploration of CNF-templated nanostructures with branched functional NR configurations would lead to a novel hierarchical nanostructure with further enhanced PEC performance and photoelectrode manufacturability. In this paper, we integrated the SPCVD technique for synthesizing high-density TiO2 NR branches with mesoporous CNF templates. The CNF framework was well preserved under high deposition temperature by introducing ZnO overcoating. The ZnO layer was completely converted into TiO2 during growth, following the Kirkendall effect [28]. To the best of our knowledge, this is the first time that high density NR branches have been grown into mesoporous CNF networks, which further enlarges the surface area as well as introduces new functionality. Compared to other CNF-templated mesoporous nanostructures (i.e., TiO2-ZnO bilayer tubular nanofibers networks and TiO2 nanotubes networks), a 3D TiO2 fiber-NR heterostructure exhibited significantly enhanced photocurrent and PEC efficiency, owing to their large surface area and good electrical conductivity.

2. Experimental section

2.1. Fabrication of CNF template

The CNFs used in our experiments were tetramethylpiperidine-1-oxy (TEMPO) oxidized wood pulp fibers, which were prepared according to the method reported by Saito et al [29, 30]. In particular, the CNFs’ hydrogel solution (0.4 wt%) was obtained by mechanically homogenizing the TEMPO-treated wood pulp fibers on an M-110EH-30 Microfluidizer (Microfluidics, Newton, MA, USA) with a series of 200- and 87 μm chambers via two pass-throughs. After printing the CNFs’ hydrogel on a fluorine doped tin oxide (FTO) glass substrate, the substrate with hydrogel film was frozen in a liquid N2 and ethanol bath. The substrate was then placed into the vacuum chamber of a Labconco 4.5 Freeze Dryer (Labconco, Kansas City, MO, USA) immediately, remaining 12 h at room temperature with a base pressure of ∼35 mTorr, where sublimation of the ice yielded a nanofibrous structure cellulose film, 10 μm thick on the FTO.

2.2. Fabrication of 3D TiO2 fiber-NR heterostructure

The as-prepared CNF nanostructures on FTO substrates were loaded into an ALD chamber for ZnO overcoating at 150 °C. In one growth cycle, H2O and diethyldiazinc vapor precursors were pulsed into the chamber for 1 s each and separated by N2 purging for 60 s. The 150-cycle ALD growth yielded a 30 nm-thick ZnO film covering the CNFs. This CNF-ZnO core-shell structure on FTO substrates was then used for SPCVD TiO2 NR branch growth. Similar to the ALD process, 400 cycles of alternating reactions were conducted at 600 °C. Each cycle consisted of 1 s H2O pulsing + 60 s N2 purging + 1 s titanium tetrachloride (TiCl4) pulsing + 60 s N2 purging. Through this process, TiO2 NRs were uniformly grown on the fibrous backbones.

In order to compare the PEC performance, both CNF-templated TiO2-ZnO bilayer tubular nanofibers and fibrous TiO2 nanotubes networks were prepared. For the TiO2-ZnO samples, 400 cycles of ALD TiO2 films were coated on CNF-ZnO core-shell nanofibers. The deposition was performed at 300 °C with 1 s H2O pulsing + 60 s N2 pulsing + 1 s titanium tetrachloride (TiCl4) pulsing + 60 s N2 pulsing for each cycle. The fibrous TiO2 nanotubes network was synthesized via a 400-cycle ALD TiO2 coating at 150 °C on a CNF template and sintered at 600 °C to crystallize the TiO2 coating and remove CNF templates [4]. The fabrication processes of three kinds of samples are schematically illustrated in figure 1.

2.3. PEC characterization

PEC characterizations were performed in a 1 mol L−1 KOH (pH = 14) aqueous solution using a three-electrode electrochemical cell configuration. The saturated calomel electrode (SCE) was used as the reference electrode, and a Pt wire was used as the counter electrode. All electrodes were connected to a potentiostat system (Metrohm Inc., Riverview, FL) for J–V measurement. Light illumination was provided by a 150 W Xe arc lamp (Newport Corporation, Irvine, CA), and the intensity at the PEC anode position was adjusted to be 100 mW cm−2. An AM 1.5G filter and a UV cutoff filter were also utilized with the lamp for PEC characterizations.
3. Results and discussion

The as-fabricated CNF networks on FTO substrates are shown by scanning electron microscopy (SEM) in figure 2(a). The higher-magnification inset reveals a 3D fibrous structure of CNFs with an average fiber diameter of ∼0.1 μm. This high-porous nanostructure was well preserved after 150 °C ALD of ZnO thin film conformal coating (figure 2(b)). The surface of the ZnO-coated CNF was relatively rough, which is a result of the polycrystalline nature of the ZnO coating (Inset of figure 2(b)). Figures 2(c) and (d) show the morphologies of the TiO2-ZnO bilayer tubular nanofibers and the TiO2 nanotube fibrous networks, respectively, as two reference samples. Both structures present a well-preserved nanofibrous structure. The 300 °C TiO2 ALD coating yielded a polycrystalline TiO2 shell over the CNF-ZnO core–shell fibers and burned away the CNF templates (inset of figure 2(c)) [4, 31]. The fiber diameter was slightly increased (∼190 nm). The rough surface of the final fibrous structure was replicated from the polycrystalline ZnO and became more notable. The TiO2 nanotubes shown in figure 2(d) and inset demonstrated a smooth surface with a mean diameter similar to those of the fibrous CNF-ZnO core–shell network. It is noteworthy in figure 2 that the fibrous 3D network configuration was very stable during both low-temperature ALD and high-temperature heat treatment processes, and no morphology change could be observed.

Branched TiO2 NR SPCVD growth was conducted on the ZnO-coated CNF templates shown in figure 2(b). The 3D fibrous network morphology was also well preserved after 14 h of the 600 °C SPCVD process (figure 3(a)). From higher magnification SEM images, the uniform and dense coverage of TiO2 NRs can be clearly observed along the entire fiber length (figure 3(b)). The fibers’ trunks were ∼220 nm in diameter, which was ∼22% more than that of the ZnO-CNF template. All TiO2 NRs were rooted on the walls of nanofibers and pointed out divergently. The NRs exhibited an average length of ∼170 nm and a diameter of ∼30 nm (aspect ratio is ∼5.7) (figure 3(c)). The cross-sectional image of a single fiber (figure 3(d)) shows the hollow center of the branched structure and evidences the removal of fiber templates during high-temperature deposition. The diameter of the orifice was close to 1.80 nm, which was larger than the size of the cellulose fiber but comparable to that of the CNF-ZnO core-shell template. The continuous wall thickness was only ∼10 nm.

The crystal structures of these three CNF-templated TiO2 fibrous networks were further investigated by transmission electron microscopy (TEM) (figure 4). All the tubular nanofibers exhibited a uniform wall thickness along the entire channel, which is consistent with the SEM results. TiO2 NR-
branched nanoﬁbers are shown in ﬁgure 4(a), where a uniform ∼10 nm wall can be clearly observed, and the inner diameter is as large as that of the CNF-ZnO core-shell template. The NRs exhibited a uniform contrast, indicating their single crystal structure. These observations are consistent with our recent discovery of the Kirkendall effect during high-temperature TiO2 ALD. When ZnO NW arrays were used as the initial template, the 400-cycle SPCVD of TiO2 at 600 °C yielded high-density branched TiO2 NRs on TiO2 nanotubes that were converted from the ZnO NWs via cation diffusion and exchange. In this process, the ZnO surface was exposed to TiCl4 vapor and quickly converted to TiO2, yielding ZnCl2 vapor byproduct. The subsequent TiCl4 vapor diffused inward, while the Zn2+ and O2− ions diffused outward through the polycrystalline TiO2 shell on the ZnO surface. Upon the reaction between TiCl4 and ZnO, the ZnO was gradually consumed from the TiO2/ZnO interface, eventually generating a hollow TiO2 nanotube [28]. We believe such an effect also applied to our CNF-ZnO core-shell templates, where the ZnO shell was fully converted into the thin TiO2 walls during the initial growth stage.

The TiO2-ZnO bilayer tubular nanoﬁbers were fabricated via 150 cycles of ZnO and 400 cycles of TiO2 ALD at 150 °C and at 300 °C, respectively. The wall thickness of this hierarchical tubular structure was found to be ∼50–60 nm (ﬁgure 4(b)), which is consistent with the typical ALD growth rate of ZnO and TiO2. Unlike the 600 °C growth, the lower temperature (300 °C) inhibited cation diffusion and exchange reactions that are required by the implementation of the Kirkendall effect. Thus, crystalline TiO2 was simply overcoated on the ZnO surfaces and created a TiO2-ZnO bilayer tubular structure by only burning off CNF cores. Direct TiO2 ALD on CNF templates yielded a much smoother tubular structure, as shown in ﬁgure 4(c). The wall of TiO2 nanotubes was fairly uniform with a thickness of ∼40 nm, which is accordant with the typical TiO2 ALD growth rate. The polycrystalline shell exhibited a much larger grain size (>100 nm) formed from the subsequent high-temperature treatment (600 °C), where the CNF templates were also completely removed. Although CNFs have amorphous and crystalline regions, above microscopic observations they reveal no differences in morphology and crystallinity of either TiO2 NRs or ZnO or TiO2 overcoatings along the entire CNF surfaces. The preparation methods and representative morphologies of the three types of samples are summarized in table 1.

Surface area is an important parameter to understand the performance enhancement. Considering that the TiO2 and
TiO$_2$/ZnO tubular structures are ALD replicates of the CNF network, they should offer the same surface area as the CNF template (ignoring the small surface reduction due to thickness increase). With NR branches on the TiO$_2$ shells, the total surface area of such 3D TiO$_2$ NRs should be higher. Based on the average size and density of the NRs, statistical calculation shows that the surface area of TiO$_2$ NR-fiber heterostructure is ∼950% larger than that of other two samples without NR branches. This surface area enlargement is about the same ratio as growing TiO$_2$ NRs inside anodized aluminum oxide templates [32].

Elemental and phase information of the three types of fibrous nanostructures were characterized to further confirm the conclusions of structure evolution drawn from the microscopy analyses. From the 3D TiO$_2$ fiber-NR heterostructure, no Zn signal was detected from the energy-dispersive X-ray spectroscopy (EDS) spectrum (figure 5(a)), nor can the ZnO phase be identified by the X-ray diffraction (XRD) pattern (figure 5(b)). This verifies the fact that all ZnO shells were consumed and replaced by TiO$_2$ nanotube backbones during NR integration via the Kirkendall effect. From the XRD profile, rutile TiO$_2$ was identified, which was believed to be a result of the lower anatase phase stability when a foreign element (e.g., Zn) was involved during the growth [33]. As expected, the TiO$_2$-ZnO bilayer tubular nanofibers showed a strong Zn signal in the EDS spectrum, and the ZnO phase can be clearly identified in the XRD pattern. Due to the existence of Zn elements, the rutile phase also appeared rather than the pure anatase phase from the 300 °C ALD TiO$_2$ in our earlier publication [10]. The EDS and XRD results of the TiO$_2$ nanotube network were identical to typical ALD results as shown in our previous work [4], where only anatase TiO$_2$ was observed. Notably, the EDS analysis showed a distinct C signal from each sample. The amount of carbon preserved in the final products of the TiO$_2$ fiber-NR heterostructure, TiO$_2$-ZnO bilayer tubular nanofibers, and TiO$_2$ nanotube network was identified to be ∼6.2%, 7.9%, and 14.4%, respectively. Exposures of H$_2$O vapor during the 600 °C TiO$_2$ NR and 300 °C TiO$_2$ film growth might provide an oxidation environment and lessen the amount of reserved carbon from CNF calcination.

Due to the long optical paths and possible high quality transport channels for rapid charge separation and conduction, as well as the prominent electrolyte—semiconductor interface areas, the 3D TiO$_2$ fiber-NR heterostructure could be a promising mesoporous configuration for high-performance PEC photoanodes [4, 10, 12, 14, 34, 35]. Such potential merits were explored by conducting PEC water splitting measurements. For performance comparison, the other two samples (TiO$_2$-ZnO bilayer tubular nanofibers and TiO$_2$ nanotube networks) were applied as PEC photoanodes as well. The photocurrent density ($J_{ph}$) versus bias potential characteristics.
Figure 4. TEM characterizations for different CNF-templated 3D architectures. (a) TiO$_2$ fiber-NR heterostructure, the nanotubular structure, and TiO$_2$ NRs with average size of $\sim$170 nm in length and $\sim$30 nm in diameter. (b) TiO$_2$-ZnO bilayer tubular nanofibers and polycrystalline feature on the surface. (c) Fibrous TiO$_2$ nanotube structure with uniform wall thickness of TiO$_2$ and large crystalline domain area.
of these three kinds of samples was measured under the same conditions. All the samples were very stable during the PEC test, and no mechanical damages could be observed after the test. The nanostructures can be reused for the measurement without noticeable performance degradation. Corresponding PEC efficiencies were estimated using the following equation [4]:

\[
\eta \% = \left[ J_{ph} \left( E_{rev}^0 - E_{bias} - E_{acc} \right) \right] \frac{100}{I_0}
\]

where \( E_{bias} \) is the bias potential; \( E_{rev}^0 = 1.23 \text{ V} \) is the standard state reversible potential for the water-splitting reaction; and \( E_{acc} = V_{acc} \) is the open circuit voltage (versus SCE).

The representative \( J_{ph} \)– \( V \) curves are shown in figure 6(a) under the illumination of a 100 W cm\(^{-2}\) Xe lamp source without and with AM 1.5G or UV cutoff filters. The dark current densities of each PEC test remained at fairly small values (<10\(^{-4}\) mA cm\(^{-2}\)) within the bias potential range scanned between ~0.9 V–0.5 V (versus SCE), indicating high quality crystal surfaces of the as-synthesized fibrous networks. In general, the 3D TiO\(_2\) fiber-NR heterostructure exhibited high \( J_{ph} \) and efficiency under all wavelength conditions, where the highest values were obtained from the Xe lamp illumination and the lowest values when a UV cutoff filter was applied. Under the Xe lamp, the maximum efficiency was calculated to be 1.13% at ~−0.31 V. The maximum efficiency dropped to 0.76% at ~−0.26 V for the AM 1.5G filter and 0.17% at ~−0.35 V for the UV cutoff filter (figure 6(b)). This phenomenon evidences that the performance of TiO\(_2\) nanostructure-based photoanodes was mainly governed by UV absorption. Nevertheless, appreciable PEC performance was achieved when only visible light was
illuminated. The photoactivity in the visible light region can be attributed to the presence of carbon elements as discovered in our recent study [4].

Compared to the other two reference samples, the $J_{ph}$ of 3D TiO$_2$ fiber-NR heterostructures exhibited obviously higher values under all illumination wavelength ranges. When illuminated directly under the Xe lamp, maximum efficiency (1.13% at $\sim -0.31$ V) is 45% and 22% higher than that of the TiO$_2$-ZnO bilayer tubular nanofibers (0.78% at $\sim -0.26$ V) and TiO$_2$ nanotube networks (0.93% at $\sim -0.6$ V), respectively (figure 6(b)). When the AM1.5G and UV cut-off filters were applied, the TiO$_2$ fiber-NR heterostructure exhibited even higher advantages compared to the other two. Under AM1.5G illumination, its maximum efficiency was 38% and 97% higher than that of the TiO$_2$-ZnO bilayer tubular nanofibers and TiO$_2$ nanotube networks, respectively. Under only visible light, the enhancement was raised to 195% and 249% as compared to the TiO$_2$-ZnO bilayer tubular nanofibers and TiO$_2$ nanotube networks, respectively. The largest surface area is generally believed to be the main reason for the enhanced performance. However, the much more significant enhancement in the visible light region suggests that the charge transport might be the bottleneck when a higher flux photogenerated charge was induced. This argument can also be supported by the shapes of $J_{ph}$-$V$ characteristics. As shown in figure 6(a), the saturation regions of both the TiO$_2$ fiber-NRs heterostructure and the TiO$_2$-ZnO bilayer tubular nanofiber samples were less obvious, indicating the existence of a larger number of defects and grain boundaries in these two samples acting as the recombination sites, which jeopardizes the separation and transport of photogenerated charges [36, 37].

4. Conclusion

In this work, we developed a high-density 3D TiO$_2$ fiber-NR heterostructure for efficient PEC photoanodes. A 3D CNF network with ZnO shells was used as a template for SPCVD growth of TiO$_2$ NR branches. The ZnO layer interacted with TiCl$_4$ vapor and was quickly converted into polycrystalline TiO$_2$ thin films, seeding the growth of TiO$_2$ NRs. The template dimension and 3D morphology were well preserved. The structure evolution was in good agreement with the vapor-phase Kirkendall effect in ALD system that we discovered recently. The 3D fiber-NR heterostructure offers large porosities and tremendous surface areas for PEC water splitting. Its PEC efficiency was found to be 22%–249% higher than those of the TiO$_2$-ZnO bilayer tubular nanofibers and TiO$_2$ nanotube networks that were synthesized as reference samples. The much more conspicuous photoactivity in longer wavelength regions, together with the $J_{ph}$-$V$
characteristics, suggest that charge transport might be the issue for the 3D fiber-NR heterostructure to further enhance its PEC performance. This technique opens a new avenue toward a cellulose-based nanomanufacturing technique, which holds great promise for large-area, low-cost, and green fabrication of functional nanomaterials, as well as their applications in solar energy harvesting and conversion areas.

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