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ARTICLE

Fabrication of Metal Oxide Nanobranched on Atomic-layer-deposited TiO₂ Nanotube Arrays and Their Application in Energy Storage

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Due to the chemical stability and easy fabrication by atomic layer deposition (ALD), TiO₂ nanotubes are regarded highly useful in constructing branched nanostructure electrodes for solar conversion and electrochemical energy storage devices. Here we present a facile and scalable fabrication of metal oxide nanobranched on ALD pre-formed TiO₂ nanotubes. The metal oxide branches can be a wide range (nearly any) of desirable materials, such as NiO and Co₃O₄ demonstrated herein. These unique heterostructured core-branch hollow nanowire arrays are ready to be utilized as active electrodes in electrochemical energy storage devices. As one example, the TiO₂/NiO nanoarray battery cathode exhibits a relatively high gravimetric capacity value of ~153 mAh/g and a fairly good stability up to 12,000 cycles with a capacitance of 132 F/g at 2 A/g. Depending on the material of the nanobranched, the core-branch metal oxide nanoarrays can have other applications in lithium-ion or lithium-air batteries, and electrochromatic devices.

Introduction

Over the past decades, there has been great interest in developing and refining new materials for applications in energy and environment related fields. In this context, heterostructured nanomaterials appear highly promising due to the combination of different materials with precise control of their interface contributing to new or enhanced functions.¹ Heterostructured core-branch nanostructures are typically hybrid materials made up of distinct phases with different functions.^{2, 3} One of their important aspects is that coupling between different phases induced by electrical/magnetic/mechanical/optical interactions can result in new functionality that cannot be found in conventional materials.⁴ For this purpose, it is highly desirable to develop suitable strategies for rational synthesis, organization and integration of these nanoscale building blocks.²⁻⁷

One of the challenges in the synthesis of novel core-branch heteronanostructures is to combine one material that provides ideal support properties (such as a high surface area and good mechanical support) with the other having desired functionalities. To date, tremendous efforts have been dedicated to the fabrication of heterostructured core-branch nanowire arrays through either one-step or stepwise synthetic approaches, for example, electrochemical deposition,^{8, 9} chemical bath deposition,¹⁰ hydrothermal synthesis method,¹¹ thermal oxidation,¹² sputtering,^{13, 14} pulsed laser deposition,¹⁵ and atomic layer deposition.¹⁶ These methods either independently operate or cooperate with each other to form different heterostructured core-branch nanowire arrays whose core or shell materials consist of metals,¹⁷ oxides,¹⁰ carbon,¹⁴ hydroxides,¹⁸ semiconductors¹⁹ and

polymers.⁶ Amongst all the synthetic approaches, atomic layer deposition (ALD) appears to be a powerful technique due to its simplicity, reproducibility and the high uniformity of the deposited materials.^{20, 21} ALD is usually combined with other chemical or physical methods in the fabrication of high-quality heterostructured core-branch nanostructures with improved electrochemical and optical properties.^{22, 23}

TiO₂ is known as one of the most promising materials for applications in photocatalysis, solar cells, supercapacitors and lithium ion batteries.²⁴⁻²⁶ The energy storage functionality of TiO₂-based materials is expected to be enhanced by its combination with other transition metal oxides (such as Co₃O₄, NiO and Fe₂O₃). In the application of electrochemical energy storage of these composite materials, TiO₂ provides not only a chemically stable template but also charge storage contributions. Compared with the TiO₂ in previous reported heterostructured materials,²⁷⁻³¹ ALD TiO₂ nanotubes have the merits of excellent thickness control and 3D uniformity, as well as richness in nanoscale structure. Therefore, ALD TiO₂ provides good opportunities to achieve high-performance core-branch nanostructure arrays for energy conversion and storage devices.

Herein, on the scaffold of ALD-TiO₂ nanotubes, we fabricated core-branch hollow nanowire arrays (branch materials include NiO, Co₃O₄ and Fe₂O₃) on nickel foam and carbon cloth substrates and demonstrate their potential energy storage applications. The nanoflake branches are obtained using chemical deposition methods (chemical bath deposition and electro-deposition), both are general and scalable. Different from previous TiO₂ rod based heterostructured materials,²⁷⁻³¹ the obtained core-branch hollow nanowire arrays have higher

porosity, large surface area and thus lower weight. For a demonstration, the as-prepared TiO_2/NiO core-branch nanoarrays are investigated as cathode for battery application. As a result of the Faraday reactions on the nanoflake surfaces and the 3D core-branch architecture, the electrode demonstrate high-rate capability and excellent cycle life. It is optimistic that the developed synthetic method can be applied to other heterostructured nanoarrays of different material combinations for their applications in lithium ion battery, electrocatalysts, and photoelectrochemical devices.

Results and discussion

Figure 1a schematically illustrates the core-branch metal oxide nanostructures based on ALD- TiO_2 nanotube core fabricated in three steps. The three steps are as follows. (1) Large-scale hydrothermal synthesis of free-standing $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowire arrays as sacrificial template. (2) TiO_2 nanotube arrays by ALD and template removal. (3) Deposition of the branched nanostructures via various available chemical deposition methods (e.g., chemical bath deposition, electro-deposition and hydrolysis deposition). Photographs of the obtained final sample are shown in Figure 1b. Because of the chemical stability of TiO_2 in both acidic and basic solution, there is in principle no limit to the type of materials for the branch. In our study we have deposited NiO , Co_3O_4 and Fe_2O_3 . Herein the TiO_2/NiO core-branch hollow nanowire array was chosen as a case study for detailed investigation.

In the first step, the hydrothermal-synthesized $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowires grow quasi-vertically on the nickel foam, forming an aligned nanowire array architecture. Results of detailed characterization of the $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowires are shown in Supporting Information (Figure S1). TEM images reveal that the $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowires have a smooth texture and their average diameters is ~ 80 nm (Figure S1c and d). The obtained $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowires are single-crystalline, supported by the pattern of selected area electronic diffraction (SAED) and HRTEM image (Figure S1c and e). Following the first step, TiO_2 layer with a chosen thickness (~ 10 nm herein) is uniformly coated on the surface of the $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowires by ALD, forming core-shell nanowires. After immersing into 0.1 M HCl for 30 min, the $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowires core will be completely dissolved, leaving self-supported TiO_2 nanotube arrays (Figure 1c and Figure S2). This simple etching process does not cause collapse of the array structure. According to the XRD pattern of the nanotube arrays and SEAD pattern of an individual nanotube (Figure S2), the as-deposited TiO_2 nanotubes without annealing are amorphous. This is in consistence with the results in literature.^{20, 21} In order to grow the branch NiO flake material on the TiO_2 nanotube scaffold, CBD, another facile solution method for metal oxide nanostructures, is employed followed by annealing. The CBD-deposited NiO nanoflakes with thicknesses of ~ 15 nm are interconnected with each other, forming a highly porous branch structure on the TiO_2 nanotubes with an overall width of ~ 220 nm (Figure 1d and S3a). Such TiO_2/NiO core-

branch hollow nanowire arrays can also be fabricated on other substrates such as carbon cloth (Figure S3b and c).

The detailed microstructure of the TiO_2/NiO core-branch hollow nanowires is revealed by TEM-HRTEM investigation. Apparently, the heterostructured nanowires consist of core nanotubes and branch nanoflakes, which are intimately intertwined with the core nanotubes (Figure 2a and b). The branch nanoflakes exhibit rough appearance and a polycrystalline SAED pattern corresponding to cubic NiO phase (JCPDS 4-0835) (Figure 2a). Additionally, the lattice fringes with a lattice spacing of about 0.24 nm corresponds to the (111) planes of NiO (Figure 2c). The composition of the core-branch hollow nanowires is clearly distinguished by energy dispersive X-ray spectroscopic (EDS) elemental maps (Figure 2d-g) of Ti, Ni and O from the designated area in Figure 2d. It is worth noting that the pristine amorphous ALD- TiO_2 core nanotubes turn into polycrystalline anatase phase after the annealing treatment (350°C for 2 h). In the XRD pattern of the core-branch hollow nanowires, except for the peaks owing to the nickel foam, the other peaks are consistent with those of the NiO phase (JCPDS 4-0835) and anatase TiO_2 phase (JCPDS 89-4921) (Figure 2h). In addition, the EDS spectrum verifies the composition of the core-branch nanowire to be Ti, Ni and O (Figure 2i), which is in agreement with the EDS mapping result above.

The phases of the core-branch nanowires are further confirmed by the XPS analysis. For the Ni 2p spectra (Figure S4a), two Ni 2p core levels ($2p_{1/2}$ and $2p_{3/2}$) and two satellite peaks are observed. The binding energy separation between core levels Ni $2p_{1/2}$ (871.7 eV) and Ni $2p_{3/2}$ (854.2 eV) is ~ 17.5 eV, which matches with electronic states of NiO .³² For the Ti 2p spectra (Figure S4b), the splitting binding energy between Ti $2p_{1/2}$ (465.5 eV) and Ti $2p_{3/2}$ (459.7 eV) core levels is ~ 5.8 eV, indicating a normal state of Ti^{4+} in the anatase TiO_2 .²⁶ In O1s spectra (Figure S4c), the peaks at 529.9 and 531.5 eV reveal the existence of Ni-O and Ti-O bonds, respectively, which are consistent with Ni 2p and Ti 2p spectra. To further check the phase change of ALD- TiO_2 nanotubes, we conducted the TEM-HRTEM test of single ALD- TiO_2 nanotubes after annealing. The ALD- TiO_2 nanotubes after annealing show typical polycrystalline nature as revealed by SAED pattern (Figure S5a). The measured lattice spacing of 0.35 nm is in good agreement with the (101) interplanar distance of anatase TiO_2 phase (JCPDS 89-4921) (Figure S5b). Importantly, the as-prepared TiO_2/NiO core-branch nanowires show a large specific surface area of ~ 167 m^2/g (Figure S5b), which is important for the application of the porous material. On the basis of the characterization results, it is justified that the TiO_2/NiO core-branch hollow nanowires arrays are successfully prepared via the three-step method.

The developed protocol here is very robust and can be extended to fabricate other core-branch hollow nanowires. Figure 3 shows the example of $\text{TiO}_2/\text{Co}_3\text{O}_4$ following the similar three-step procedure. The hydrothermally-grown single-crystalline $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowires can be used as both physical sacrificial template (non-reactive) for a wide range of hollow nanostructures, and chemical template (reactive) towards ternary 1D nanostructures via solid-state reaction of core-shell nanowires.

To demonstrate the application of the TiO_2/NiO core-branch

hollow nanowires arrays in electrochemical energy storage, battery electrode based on the TiO₂/NiO core-branch hollow nanowires arrays grown on the nickel foam are characterized and their high-rate capability is investigated. The electrochemical performance of TiO₂/NiO core-branch hollow nanowires arrays in alkaline electrolyte is similar to those of pseudocapacitor, which was proposed by Conway in 1975 and learned from battery.^{33, 34} In our case, all capacity values are calculated based on the capacity equation of battery. Figure 4a shows the typical cyclic voltammetry (CV) curve of the TiO₂/NiO core-branch hollow nanowires arrays at different scanning rates. A strong redox couple is noted. The CV curve indicates that the capacity characteristics are mainly governed by faradaic redox reactions. In our experiment, the capacity of the TiO₂/NiO core-branch nanowires arrays mainly comes from NiO, which plays a decisive role in the electrochemical energy storage and conversion. The anodic peak is due to the conversion from NiO to NiOOH, whereas the cathodic peak corresponds to the reverse reaction from NiOOH to NiO. The reactions involved can be simply illustrated as $\text{NiO} + \text{OH}^- - \text{e}^- \leftrightarrow \text{NiOOH}$. According to this reaction, the theoretical capacity of NiO is $\sim 354 \text{ mAh g}^{-1}$. In order to further verify the proposed reaction, XPS, Raman, and electrochemical impedance spectroscopy (EIS) tests at both charge and discharge states were conducted ex-situ. Figure 4b presents the XPS spectra of the Ni 2p at charge and discharge states. Only one Ni 2p_{3/2} peak at 854.2 eV characteristic of NiO is noticed at discharge state. After charge, the Ni 2p_{3/2} peak splits and includes two components, one at 854.2 eV due to Ni–O bonds and the other one at 855.5 eV owing to Ni–OOH bonds, respectively.^{35, 36} The phase change during charge and discharge is also verified by Raman and EIS results. The Raman spectrum recorded from the sample at discharge state shows one broad band at $\sim 570 \text{ cm}^{-1}$ corresponding to the typical Ni–O stretching mode (Figure 4c). After charging, two new remarkable Raman peaks are observed at 475 and 554 cm^{-1} belonging to NiOOH at the charge state (Figure 4c).^{35, 36} Meanwhile, Nyquist plots show that the electrochemical impedance of the cathode at charge state is much smaller than that at the discharge state (Figure 4d). This is due to the fact that the NiOOH formed at charge state is an n-type semiconductor that has a higher electric conductivity than the NiO phase (p-type semiconductor) at discharge state. Taking the results above, the proposed redox reaction mechanism $\text{NiO} + \text{OH}^- - \text{e}^- \leftrightarrow \text{NiOOH}$ is reasonable. In addition, it should be mentioned that the TiO₂ does not exhibit faradaic redox reactions in the KOH electrolyte to store energy, but may have certain electric double-layer capacitance contribution. Even so, it is found that the capacity contribution from the TiO₂ is negligible as compared to the NiO. The TiO₂ mainly acts as a backbone to support the whole core-branch nanowire arrays, so that a higher surface area is achieved than pure NiO nanoflake array directly grown on Ni foam.

To further demonstrate the potential use of the metal oxide core-branch hollow nanowires, batteries were assembled with the TiO₂/NiO core-branch nanowire arrays as the cathode and activated carbon as the anode. One battery device is shown in Figure S6a. The cell voltage can reach up to 1.6 V (Figure 5a), higher than that ($\sim 1 \text{ V}$) of the conventional symmetric active carbon-based electric double-layer capacitors in aqueous

electrolytes.³⁴ Figure 5b shows the typical cyclic voltammetry (CV) curve of the assembled battery in the voltage range of 0–1.6 V at the scanning rate of 10 mV/s. A strong redox couple is noted. The anodic peak A is due to the conversion $\text{NiO} \rightarrow \text{NiOOH}$, whereas the cathodic peak C corresponds to the reverse reaction $\text{NiOOH} \rightarrow \text{NiO}$. The reaction involved in the cathode of the asymmetric supercapacitor can be simply illustrated as follows.

The reaction in the activated carbon anode can be expressed as follows,

where K^+/C^- represents the absorption of K^+ on the surface of activated carbon. Hence, combining the reactions above together, the whole reaction for the battery is illustrated as follows.

The TiO₂/NiO core-branch nanowires electrode exhibits a capacity of 153 mAh/g at 2 A/g and 134 mAh/g at 10 A/g, with a capacity retention of 88 % (Figure 5b). Moreover, the electrode also has a fairly good cycling stability (Figure 5c). After 12,000 cycles at 2 A/g, the capacitance drops slightly to 132 mAh/g with a retention of 87 % (Figure 5d). Note that these capacity values are obtained based on the mass of TiO₂/NiO core-branch nanowires. The working voltage of the assembled battery is between 0.8 and 1.6 V, which is capable to drive modern microelectronics. A tandem cell was constructed by connecting three battery units in series. Each unit cell has the same electrode mass and area. The tandem batteries can work between 3 and 4.8 V and thus easily power the green light-emitting-diodes (LED) (Figure 5d). This demonstration further verifies the high application potential of the TiO₂/NiO core-branch hollow nanowire arrays electrode materials for high-performance batteries with fast recharge ability.

We now discuss the role of the TiO₂/NiO core-branch hollow nanowire arrays played in their high-rate battery performance. The core-branch design allows an effective utilization of both the core and branch components. First, the interface and chemical distribution are homogeneous along the thickness of the forest-like film. Therefore an efficient contact of electrolyte ions with the active surface is maintained, which is expected to contribute to the high power density. Second, the core-branch nanowire arrays grow directly on conductive substrates to form integrated electrode, which reduces the “dead volume” and resistance possibly caused by the polymer binder. Finally, this core-branch architecture is robust in mechanical stability, which can accommodate structural strains and favor an enhanced calendar life. After a long-term cycling of 12,000 times, the nanowire array structure is basically maintained with little structural deformation (Figure S7a and b), and the branch nanoflakes are still tightly connected with the core nanotube (Figure S7c and d).

Conclusions

In summary, we have achieved the fabrication of rational-designed ALD-TiO₂ nanotube based core-branch hollow nanowire arrays directly on current collectors and demonstrated their high-rate battery properties. Our approach exploits the template function of the $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowire arrays with the

help of ALD. The constructed core-branch nanowires consist of a robust TiO₂ nanotube surrounded by branch nanoflakes, as well as a high porosity. Battery cathodes constructed from the TiO₂/NiO core-branch hollow nanowires displays high rate specific capacity and good cycling stability, essentially due to the surface-dominating Faradic reactions on the nanoflakes and the architecture of the core-branch hollow nanowires. In view of the noticeable high-rate capability, our metal oxide nanoarray-based batteries may find application in advanced energy storage devices.

Experiments

Preparation of Co₂(OH)₂CO₃ nanowire arrays: Self-supported Co₂(OH)₂CO₃ nanowire arrays were prepared by a facile hydrothermal synthesis method. The solution was prepared by dissolving 2 mmol of Co(NO₃)₂, 4 mmol NH₄F and 10 mmol of CO(NH₂)₂ in 70 mL of distilled water. Then this resulting solution was transferred into Teflon-lined stainless steel autoclave liners. Nickel foam or carbon cloth substrates (5×7 cm² in sizes) were immersed into the reaction solution. Top sides of the substrates were uniformly coated with a polytetrafluoroethylene tape to prevent the solution contamination. The liner was sealed in a stainless steel autoclave and maintained at 110 °C for 5 h, and then cooled down to room temperature. The samples were collected and rinsed with distilled water. The chemical reactions can be illustrated as follows:

Preparation of TiO₂ nanotube arrays: The as-fabricated Co₂(OH)₂CO₃ nanowire arrays above were coated with a layer of TiO₂ (thickness ~10 nm) by atomic layer deposition (ALD Beneq TFS 200) with TiCl₄ and H₂O as the Ti and O precursors, respectively. Then the sample was immerse into 0.1 M HCl for 30 min to remove the Co₂(OH)₂CO₃ nanowires to leave TiO₂ nanotube arrays.

Preparation of TiO₂/NiO core-branch hollow nanowire arrays: The TiO₂ nanotube arrays were used as the scaffold for NiO branch nanoflakes growth by a simple chemical bath deposition. The TiO₂ nanotube arrays grown on nickel foam substrates (masked with polyimide tape to prevent deposition on the back sides) were placed vertically in a 250 ml pyrex beaker. Solution for chemical bath deposition (CBD) was prepared by adding 5 ml of aqueous ammonia (25–28 %) to the mixture of 10 g nickel sulfate and 2g potassium persulfate. The chemical reactions for chemical bath deposition are represented as follows:

The samples were taken out after reacting for 10 min. Finally, the free-standing TiO₂/NiO core-branch hollow nanowire arrays were formed by annealing at 350 °C for 2 h in argon.

Preparation of TiO₂/Co₃O₄ core-branch hollow nanowire arrays. The self-supported TiO₂ nanotube arrays were used as the

scaffold for Co₃O₄ branch flakes growth through a simple cathodic electrodeposition method. The electrodeposition was performed in a standard three-electrode glass cell at 25 °C, the above self-supported TiO₂ nanotube arrays electrode as the working electrode, saturated calomel electrode (SCE) as the reference electrode and a Pt foil as the counter-electrode. Electrolyte for electrodeposition was obtained by dissolving 8.5 g Co(NO₃)₂ into 100 ml of distilled water. The branch flake was deposited by cyclic voltammetry (CV) as follows: The CV deposition was conducted in the potential range of –0.5– –1.1 V with a sweep rate of 10 mV s^{–1} for 4 cycles. The electrochemical reactions for the precursor were illustrated as follows,

The substrates were taken off and rinsed with distilled water. The samples were annealed at 350 °C in air for 2 h to form TiO₂/Co₃O₄ core-branch hollow nanowire arrays.

Materials characterization and electrochemical measurements: The samples were characterized by X-ray diffraction (XRD, RIGAKU D/Max-2550 with Cu Kα radiation), field emission scanning electron microscopy (FESEM, FEI SIRION), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F), X-ray photoelectron spectroscopy (XPS, PHI 5700) and Raman spectroscopy (LABRAM HR-800). The surface area of the film that scratched from the substrate was determined by BET measurements using a NOVA-1000e surface area analyzer.

The electrochemical measurements of the TiO₂/NiO core-branch hollow nanowire arrays were carried out in a three electrode electrochemical cell with 2 M KOH aqueous solution as the electrolyte. Cyclic voltammetry (CV) measurements were carried out at different scanning rates between 0 V and 0.6 V at 25 °C, Hg/HgO as reference electrode and a Pt foil as counter-electrode. The galvanostatic charge/discharge tests were conducted on a LAND battery program-control test system. The as-prepared electrodes, together with a Pt foil counter electrode and an Hg/HgO reference electrode were tested in a three-compartment system. The film electrodes with 0.5×1.0 cm² in sizes were used for electrochemical impedance spectroscopy (EIS) measurements, which were made with a superimposed 5 mV sinusoidal voltage in the frequency range of 100 kHz–0.01 Hz.

Fabrication of batteries and electrochemical measurements: The batteries were assembled based on the TiO₂/NiO core-branch nanowire arrays as cathode (active area≈ 4.1×4.1 cm², the total mass of active materials is ~25 mg, equal to 1.5 mg cm^{–2}. TiO₂ accounts for ~15 % in this core-branch nanowires) and an active carbon (AC)-based as anode (5.5×5.5 cm², total mass of ~800 mg, the capacity of anode is much larger than the cathode to ensure the cathode performing best). The AC-based anode was fabricated by mixing active carbon (YP-1, Kuraray, Japan) with a certain proportion of carbon black (10 wt.%) and binders (poly(vinyl difluoride) (PVDF) 15 wt. %) to form a slurry. Then, the slurry was filled into a foam nickel substrate (1.5 mm thick) and dried at 90 °C for 5 h. Then, the AC-based anode was rolled to a thickness of 0.5 mm. Afterwards, the cathode and anode electrodes were separated by a porous non-woven cloth separator and assembled into an battery, in which the capacities were

determined by the cathode. The capacities are obtained based on the mass of TiO₂/NiO core-branch nanowire arrays, not the whole weight of electrode. A series of electrochemical tests including cyclic voltammetry (CV) and galvanostatic charge/discharge measurement were performed on CHI660c electrochemical workstation (Chenhua, Shanghai) and Xinwei battery program-control test system.

Specific capacity could be calculated from the galvanostatic discharge curves using the following equation:

$$C_{\text{specific}} = \frac{Q}{M} = \frac{I\Delta t/3600}{M} = \frac{I\Delta t}{3600M} \quad (13)$$

where C (mAh/g) was specific capacity, Q was the quantity of charge, I (mA) represented discharge current, and M (mg), Δt (sec) designated mass of active materials, and total discharge time, respectively

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Notes and references

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[†] Electronic Supplementary Information (ESI) available: More SEM and TEM images of the pristine Co₂(OH)₂CO₃ nanowire arrays and TiO₂ nanotubes, BET and XPS of the core-branch nanowires. See DOI: 10.1039/b000000x/

1. P. Gomez-Romero, *Adv Mater*, 2001, **13**, 163-174.
2. R. Agarwal, *Small*, 2008, **4**, 1872-1893.
3. M. Law, J. Goldberger and P. D. Yang, *Annu Rev Mater Res*, 2004, **34**, 83-122.
4. J. van Embden, J. Jasieniak, D. E. Gomez, P. Mulvaney and M. Giersig, *Aust J Chem*, 2007, **60**, 457-471.
5. C. Liu, F. Li, L. P. Ma and H. M. Cheng, *Adv Mater*, 2010, **22**, E28-E62.
6. R. Liu and S. B. Lee, *J Am Chem Soc*, 2008, **130**, 2942-2943.
7. K. Wang, J. Chen, W. Zhou, Y. Zhang, Y. Yan, J. Pern and A. Mascarenhas, *Adv Mater*, 2008, **20**, 3248-3253.
8. Y. B. He, G. R. Li, Z. L. Wang, C. Y. Su and Y. X. Tong, *Energ Environ Sci*, 2011, **4**, 1288-1292.
9. G. R. Li, Z. L. Wang, F. L. Zheng, Y. N. Ou and Y. X. Tong, *J Mater Chem*, 2011, **21**, 4217-4221.
10. X. H. Xia, J. P. Tu, Y. Q. Zhang, X. L. Wang, C. D. Gu, X. B. Zhao and H. J. Fan, *ACS Nano*, 2012, **6**, 5531-5538.
11. J. P. Liu, J. Jiang, C. W. Cheng, H. X. Li, J. X. Zhang, H. Gong and H. J. Fan, *Adv Mater*, 2011, **23**, 2076-2081.
12. X. H. Zhao, P. Wang and B. J. Li, *Chem Commun*, 2010, **46**, 6768-6770.
13. Y. L. Chueh, C. H. Hsieh, M. T. Chang, L. J. Chou, C. S. Lao, J. H. Song, J. Y. Gan and Z. L. Wang, *Adv Mater*, 2007, **19**, 143-+.
14. J. Chen, X.-h. Xia, J.-p. Tu, Q.-q. Xiong, Y.-X. Yu, X.-l. Wang and C.-d. Gu, *J Mater Chem*, 2012, **22**, 15056-15061.
15. A. Marcu, T. Yanagida, K. Nagashima, K. Oka, H. Tanaka and T. Kawai, *Appl Phys Lett*, 2008, **92**.
16. M. A. Thomas and J. B. Cui, *Journal of Vacuum Science & Technology A*, 2012, **30**.
17. L.-X. Ding, G.-R. Li, Z.-L. Wang, Z.-Q. Liu, H. Liu and Y.-X. Tong, *Chemistry – A European Journal*, 2012, **18**, 8386-8391.
18. X. H. Xia, J. P. Tu, Y. Q. Zhang, J. Chen, X. L. Wang, C. D. Gu, C. Guan, J. S. Luo and H. J. Fan, *Chem. Mater.*, 2012, **24**, 3793-3799.
19. L. Li, Y. W. Yang, G. H. Li and L. D. Zhang, *Small*, 2006, **2**, 548-553.
20. J. R. Bakke, K. L. Pickrahn, T. P. Brennan and S. F. Bent, *Nanoscale*, 2011, **3**, 3482-3508.
21. C. Marichy, M. Bechelany and N. Pinna, *Adv Mater*, 2012, **24**, 1017-1032.
22. C. Detavernier, J. Dendooven, S. P. Sree, K. F. Ludwig and J. A. Martens, *Chem Soc Rev*, 2011, **40**, 5242-5253.
23. Y. Qin, A. L. Pan, L. F. Liu, O. Moutanabbir, R. Bin Yang and M. Knez, *ACS Nano*, 2011, **5**, 788-794.
24. I. Paramasivam, H. Jha, N. Liu and P. Schmuki, *Small*, 2012, **8**, 3073-3103.
25. P. Szymanski and M. A. El-Sayed, *Theoretical Chemistry Accounts*, 2012, **131**.
26. X. H. Lu, G. M. Wang, T. Zhai, M. H. Yu, J. Y. Gan, Y. X. Tong and Y. Li, *Nano Lett*, 2012, **12**, 1690-1696.
27. W. Li and D. Y. Zhao, *Adv Mater*, 2013, **25**, 142-149.
28. X. H. Lu, M. H. Yu, G. M. Wang, T. Zhai, S. L. Xie, Y. C. Ling, Y. X. Tong and Y. Li, *Adv Mater*, 2013, **25**, 267-272.
29. A. M. Nie, J. B. Liu, Q. Q. Li, Y. C. Cheng, C. Z. Dong, W. Zhou, P. Wang, Q. X. Wang, Y. Yang, Y. H. Zhu, Y. W. Zeng and H. T. Wang, *J Mater Chem*, 2012, **22**, 10665-10671.
30. M. Salari, S. H. Aboutalebi, K. Konstantinov and H. K. Liu, *Phys Chem Chem Phys*, 2011, **13**, 5038-5041.
31. W. Q. Wang, J. Yang, Y. P. Gong and H. L. Hong, *Materials Research Bulletin*, 2013, **48**, 21-24.
32. M. M. Natile and A. Glisenti, *Chem. Mater.*, 2002, **14**, 4895-4903.
33. P. Simon and Y. Gogotsi, *Nat Mater*, 2008, **7**, 845-854.
34. B. E. Conway, ed., *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Kluwer Academic/Plenum, New York 1999.
35. S. I. Cordobatorresi, C. Gabrielli, A. Hugotlegoff and R. Torresi, *J Electrochem Soc*, 1991, **138**, 1548-1553.
36. S. I. Cordobatorresi, A. Hugotlegoff and S. Joiret, *J Electrochem Soc*, 1991, **138**, 1554-1559.

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Figure 1. (a) Schematics of the metal oxide core-branch nanowires grown on Ni foam. The inner core is TiO₂ nanotube obtained by atomic layer deposition (ALD) on sacrificial template. The outer branch can be a wide range of metal oxides obtained by chemical bath deposition or electrochemical deposition. (b) Photographs of Ni foams that are coated with (left) TiO₂ nanotubes and (right) TiO₂/NiO core-branch hollow nanowires. (c) SEM image of TiO₂ nanotubes. (d) SEM image of TiO₂/NiO core-branch nanowires. Insets are the magnified views.

Figure 2. Detailed characterizations of the TiO₂/NiO core-branch hollow nanowires. (a, b) TEM images (SAED pattern in inset). (c) HRTEM image of one branch NiO nanoflake. (d-g) EDS mapping of Ti, Ni and O from the Figure 2d. (h) XRD pattern. (i) EDS spectrum of the nanowire power _s scratched from the substrate.

Figure 3. $\text{TiO}_2/\text{Co}_3\text{O}_4$ core-branch hollow nanowires. (a, b) SEM images at different magnifications. (c, d) TEM images (SAED pattern and HRTEM image in inset).

Figure 4. (a) CV curve of TiO_2/NiO core-branch hollow nanowire electrode in the voltage range of 0–0.6 V at different scanning rates. (b) XPS spectra, (c) Raman spectra, and (d) Nyquist plots of the TiO_2/NiO core-branch nanowire electrode at charge and discharge states.

Figure 5. Electrochemical characterization of TiO_2/NiO core-branch hollow nanowire electrode. (a) Discharge curves at different current densities. (b) CV curve of the assembled battery in the voltage range of 0–1.6 V at the scanning rate of 10 mV s^{-1} . (c) Specific capacities of the nanostructured array electrode at different current densities. (d) Cycling performance at 2 A/g . Photograph of eight green LEDs powered by the tandem battery device.