Highly-ordered Single Crystalline Nanowire Array Assembled Three-dimensional Nb₃O₇(OH) and Nb₂O₅ Superstructures for Energy Storage and Conversion Applications

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KEYWORDS: Nb₃O₇(OH); Nb₂O₅; 3D Nanowire Superstructures; Lithium-ion Batteries;
DSSCs

ABSTRACT

Three-dimensional (3D) metal oxide superstructures have demonstrated great potential for structure-dependent energy storage and conversion applications. Here, we reported a facile hydrothermal method for direct growth of highly-ordered single crystalline nanowire array assembled 3D orthorhombic $\text{Nb}_3\text{O}_7(\text{OH})$ superstructures and subsequently thermal transformation into monoclinic Nb_2O_5 with well-preserved 3D nanowire superstructures. The performance of the resultant 3D $\text{Nb}_3\text{O}_7(\text{OH})$ and Nb_2O_5 superstructures differed remarkably when used for energy conversion and storage applications. The thermally converted Nb_2O_5 superstructures as anode material of lithium-ion batteries (LiBs) showed higher capacity and excellent cycling stability compared to the $\text{Nb}_3\text{O}_7(\text{OH})$ superstructures, while directly hydrothermal grown $\text{Nb}_3\text{O}_7(\text{OH})$ nanostructure film onto FTO substrate as photoanode of dye-sensitized solar cells (DSSCs) without need for further calcination exhibited an overall light conversion efficiency of 6.38%, higher than that of DSSCs (5.87%) made from the thermally converted Nb_2O_5 film. The high energy application performance of the niobium-based nanowire superstructures with different chemical compositions can be due to their large surface area, superior electron transport property and high light utilization efficiency owing to 3D superstructure, high crystallinity and large sizes. The formation process of 3D nanowire superstructures before and after thermal treatment was also investigated and discussed based on our theoretical and experimental results.

Three-dimensional (3D) metal oxide superstructures have aroused great attention in the areas of clean environment and energy because of their large surface area and unique photonic, electronic and optical properties, significantly different from individual constructed entities at the nanoscale of superstructures, thus resulting in outstanding structure-dependent application performance.¹⁻⁴ To full utilization of the complex structures' properties, varieties of metal oxides with different 3D structures, such as multishelled ZnO and Co₃O₄ hollow microspheres,^{4, 5} V₂O₅ hollow microspheres,⁶ manganese oxide superstructures,⁷ **quintuple-shelled SnO₂ hollow spheres,**⁸ **α -Fe₂O₃ multi-shelled hollow microspheres,**⁹ and TiO₂ superstructures,¹⁰⁻¹² have been extensively investigated for energy applications,¹³ exhibiting significantly improved structure-related energy storage and conversion performance. However, these developed materials are still far from practical applications. Therefore, exploring more metal oxide materials with 3D complex structures is still highly needed for practical energy technology applications.

In comparison with currently widely investigated energy materials (*e.g.*, TiO₂), niobium oxides including NbO, NbO₂, Nb₂O₃, Nb₂O₅ and Nb₃O₇X (X=OH, F) have exhibited competitive performance in catalysis, photocatalysis, lithium-ion battery, sensing, and solar cells.¹⁴⁻²¹ Studies demonstrated that monoclinic Nb₂O₅ is a promising energy material for improving the open-circuit voltage of dye-sensitized solar cells (DSSCs) owing to its more negative conduction band edge position compared to TiO₂ and high performance lithium-ion batteries (LiBs) due to its large lithium ion insertion number of 2.5 ($x = 2.5$ for Li_xNb₂O₅).^{17, 22} However, the reported Nb₂O₅ nanostructures (*e.g.*, nanoparticles, nanobelts) obtained by traditional sol-gel and electrospinning methods (need high temperature calcination at 1000 °C) usually possess low surface area, resulting in unsatisfactory application performance.^{17, 18, 23} Recently, orthorhombic Nb₃O₇(OH) nanostructures exhibit an increasing research interest owing to their facile

fabrication process, self-assembling property to easy form 3D nanowire/nanorod superstructures, and enhanced structure-related performance for environmental and energy applications.²⁴⁻²⁷ More importantly, our recent study has revealed that the orthorhombic $\text{Nb}_3\text{O}_7(\text{OH})$ structure can be readily transformed into monoclinic phase Nb_2O_5 while preserving almost unchanged morphology and high surface area, which is unavailable by traditional preparation methods (*e.g.*, *sol-gel and electrospinning methods*).^{17, 18, 23, 24} This may inspire us to fully utilize 3D orthorhombic $\text{Nb}_3\text{O}_7(\text{OH})$ nanowire/nanorod superstructures' advantages such as high surface area, high crystallinity and easy low-temperature thermal transformation into Nb_2O_5 superstructures for energy storage and conversion applications. To the best of our knowledge, there have not been reported yet using 3D $\text{Nb}_3\text{O}_7(\text{OH})$ nanowire *array* superstructures and its thermally converted product of Nb_2O_5 with well-preserved 3D nanowire superstructures for meaningful comparison in energy storage and conversion applications.

Herein, we present template-free synthesis of three-dimensional (3D) orthorhombic $\text{Nb}_3\text{O}_7(\text{OH})$ superstructures assembled with highly-ordered single crystalline nanowire *arrays*. The resultant $\text{Nb}_3\text{O}_7(\text{OH})$ nanowire superstructures show a bimodal-pore structure (microporous and mesoporous) with a high surface area ($121.5 \text{ m}^2 \text{ g}^{-1}$). The 3D orthorhombic $\text{Nb}_3\text{O}_7(\text{OH})$ nanowire superstructures can be readily transformed into monoclinic Nb_2O_5 with well-preserved 3D nanowire superstructures possessing a surface area of $81.8 \text{ m}^2 \text{ g}^{-1}$ by low-temperature calcination at 450°C . Compared to the 3D $\text{Nb}_3\text{O}_7(\text{OH})$ nanowire superstructures, the thermally converted 3D Nb_2O_5 nanowire superstructures manifest higher capacity and good cycling stability when evaluated as anode material for LiBs, while as photoanode material the 3D $\text{Nb}_3\text{O}_7(\text{OH})$ nanowire superstructure film directly grown onto FTO conductive substrate without need for further calcination for DSSCs exhibits an overall light conversion efficiency of 6.38%,

higher than that of DSSCs made from 3D Nb₂O₅ nanowire superstructure film. The formation process of 3D nanowire superstructures with different compositions before and after calcination was investigated and discussed on the basis of our theoretical and experimental results, different from the proposed mechanisms in **reported results**.^{25, 27}

Results and Discussion

Figure 1A shows the XRD patterns of the as-synthesized and calcined samples. The XRD data reveal that the as-synthesized sample is an orthorhombic Nb₃O₇(OH) structure (JCPDS, Card No. 31-0928), similar to previous reports.^{24, 28} After calcination, the orthorhombic Nb₃O₇(OH) structure readily transforms into monoclinic Nb₂O₅ structure (JCPDS, Card No. 71-0005).²⁴ The SEM image shown in Figure 1B indicates that the as-synthesized Nb₃O₇(OH) structures possess an average size of $2.6 \pm 0.9 \mu\text{m}$. Interestingly, the obtained Nb₃O₇(OH) structures are composed of highly-ordered nanowire arrays with an average nanowire diameter of *ca.* 17.6 nm and a preferential growth orientation along each other perpendicular six directions (Figure 1C). The nanowire array constructed superstructure with preferential growth orientation was further confirmed by transmission electron microscopy (TEM) (Figure 1D). As shown in Figure 1C and D, the nanowires firstly grow along one direction to form highly-ordered nanowire array, and then the nanowire arrays along each other perpendicular six directions to form 3D superstructure. This can be further verified by strongly ultrasonic dispersed TEM sample (Figure S1, Supporting Information). TEM image of an individual Nb₃O₇(OH) nanowire is given in Figure 1E, confirming the Nb₃O₇(OH) single crystalline nanowire with a preferred growth along [010] direction. Figure 1F is the fast Fourier transformation image corresponding to the marked area in Figure 1E, indicating a good crystalline nature of the nanowire. After indexing the diffraction pattern in Figure 1E, the crystal structure exhibits (200) and (110) crystal

planes of the orthorhombic $\text{Nb}_3\text{O}_7(\text{OH})$ (Figure 1G).²⁴ The inverse FFT image further confirms that the fringe spacing of 1.04 nm, which is corresponding to the d value of (200) plane of the orthorhombic $\text{Nb}_3\text{O}_7(\text{OH})$ (Figure 1H).²⁴ After calcination, the superstructures assembled with highly-ordered nanowire arrays can be preserved very well (Figure S2A and B, Supporting Information). Compared to the $\text{Nb}_3\text{O}_7(\text{OH})$ nanowire superstructures, the calcined sample displays more compact nanowire assembly, which can be confirmed by TEM images (Figure S2C and D, Supporting Information). Further, SAED pattern and HRTEM image of an individual nanowire after calcination reveals good crystal nature, and the fringe spacings of 0.375 nm and 1.02 nm are corresponding to the d values of (110) and (101) crystal planes of monoclinic Nb_2O_5 , respectively.²⁴ In our previous work, the theoretical and experimental data have indicated that the OH groups in the (002) plane of orthorhombic $\text{Nb}_3\text{O}_7(\text{OH})$ can be readily removed by a dehydration process during low-temperature calcination, which results in a serious deformation of the $\text{Nb}_3\text{O}_7(\text{OH})$ crystal structure along z axis direction to form the monoclinic Nb_2O_5 .²⁴ Such structural property makes the orthorhombic $\text{Nb}_3\text{O}_7(\text{OH})$ easy transformation into the monoclinic Nb_2O_5 by low-temperature calcination while maintaining almost changed nanowire superstructures. An important advantage of such low-temperature calcination approach is that the obtained monoclinic Nb_2O_5 maintains 3D nanowire superstructures with a relatively high surface area, favorable for energy storage and conversion applications.

The as-synthesized $\text{Nb}_3\text{O}_7(\text{OH})$ and calcined samples were further characterized by XPS technique. The XPS survey spectra show that no significant difference can be observed for these two samples (Figure S3A, Supporting Information). High resolution Nb 3d XPS spectra indicate that the peaks centred at 207.1 eV and 209.7 eV are attributed to the binding energy of Nb 3d_{5/2} and Nb 3d 3/2 electrons, respectively (Figure S3B, Supporting Information).^{18, 24} High resolution

O 1s XPS spectra (Figure S3C, Supporting Information) show that a main peak centered at 530.3 eV is ascribed to the oxygen anions (O^{2-}) bound to the niobium in the lattice for both $Nb_3O_7(OH)$ and Nb_2O_5 .^{18, 24} However, an additional peak at 532.9 eV can be clearly observed for the $Nb_3O_7(OH)$ sample, indicating the presence of OH groups.^{18, 24, 29} Also, similar Raman spectra of these two samples imply no important change in structure (Figure S4, Supporting Information), indicating their structure similarity. This can explain why the $Nb_3O_7(OH)$ nanowire superstructures can be readily transformed into monoclinic Nb_2O_5 nanowire superstructures by low-temperature treatment while maintaining almost changed structure property in this work. N_2 adsorption-desorption isotherm displays typical type IV curves (type H3 hysteresis loop) for both $Nb_3O_7(OH)$ and Nb_2O_5 samples.³⁰ The formation of the slit-like pores between nanowires should contribute the type H3 hysteresis loops which do not level off at relative pressures close to the saturation vapor pressure.³⁰ The results indicate that the 3D $Nb_3O_7(OH)$ superstructures assembled with single crystal nanowires possess a large surface area of $121.5 \text{ m}^2 \text{ g}^{-1}$ (Figure S5A, Supporting Information). After calcination, the monoclinic Nb_2O_5 nanowire superstructures show a surface area of $81.8 \text{ m}^2 \text{ g}^{-1}$ (Figure S5A, Supporting Information). Although the surface area of the calcined sample decreases, it is significantly higher than those of the monoclinic Nb_2O_5 nanostructures obtained by sol-gel and electrospinning methods owing to relatively low calcination temperature and unique 3D superstructure.^{18, 23} The pore size analysis demonstrates that these two $Nb_3O_7(OH)$ and Nb_2O_5 samples both display bimodal-pore structure characteristics, namely, micropores and mesopores. As shown, a narrow pore size distribution in microporous scope mainly centred at 1.3 nm and 1.1 nm can be achieved from the $Nb_3O_7(OH)$ and Nb_2O_5 samples, respectively (Figure S5B, Supporting Information), which significantly contribute the high specific surface areas of the $Nb_3O_7(OH)$ and Nb_2O_5 samples. Also, a wide

pore size distribution in mesoporous range centred at 19.8 nm and 25.3 nm can be obtained for the $\text{Nb}_3\text{O}_7(\text{OH})$ and Nb_2O_5 samples, respectively, which will also contribute the high surface area of the sample. More importantly, the mesoporous structures of the $\text{Nb}_3\text{O}_7(\text{OH})$ and Nb_2O_5 samples may be more favorable for mass transfer (*e.g.*, electrolyte transfer) when measured as energy materials for LiBs and DSSCs. Therefore, the unique bimodal-pore structure characteristics of such nanowire-constructed 3D superstructures may be beneficial for improving the performance of energy applications.

To investigate the formation progress of the 3D $\text{Nb}_3\text{O}_7(\text{OH})$ superstructures assembled with highly-ordered single crystal nanowire array, the effect of hydrothermal reaction time on the crystal structure and morphology of the resulting product was investigated experimentally. Figure 2A shows the XRD patterns of the products with different reaction times and their corresponding SEM images. Obviously, the XRD results indicate that the obtained products with short reaction time (*e.g.*, less than 9 h) possess different crystal structures from the products obtained by long hydrothermal reaction (*e.g.*, greater than 9 h). When the hydrothermal time is less than 9 h, the as-synthesized samples possess an cubic HNbO_3 structure with lattice parameters of $a = b = c = 7.645 \text{ \AA}$ (JCPDS, Card No. 36-0794) (Figure 2B). Moreover, the diffraction peak intensity of (100) plane of cubic HNbO_3 structure obviously decreases with reaction time. After 6 h of hydrothermal reaction, some new diffraction peaks appear, indicating the change in crystal structure. The samples after 9 h of reaction exhibit typical $\text{Nb}_3\text{O}_7(\text{OH})$ crystal structure (JCPDS, Card No. 31-0928). The above XRD data indicate that the $\text{Nb}_3\text{O}_7(\text{OH})$ structures could be formed through the structural rearrangement of the cubic HNbO_3 intermediates. The SEM images of the fabricated samples with different reaction times confirm this speculation. As shown, the as-synthesized samples with reaction times of 1 h, 3 h and 6 h

display approximately cube-shaped structures. Moreover, the sizes of the cube-shaped structures increase with increasing hydrothermal reaction time from *ca.* 750 nm for the sample with reaction time of 1 h to *ca.* 980 nm for the sample with reaction time of 6 h. When the reaction time was set at 9 h, the surface of the cube-shaped structure starts to appear sprout-like protuberances, meaning that the structural rearrangement occurs and the Nb₃O₇(OH) single crystal nanowires begin to grow with certainly preferential growth orientation (perpendicular to six exposed surfaces of the cube-shaped structure). Further increasing reaction time to 12 h and 18 h, nanowire structures can be obviously observed on the surface of cube-shaped structure. Moreover, the cube-shaped structure size increases from *ca.* 1.0 μm for the sample with reaction time of 9 h to *ca.* 2.3 μm for the sample with reaction time of 18 h. After 24 h of hydrothermal reaction, the 3D Nb₃O₇(OH) superstructures assembled with highly-ordered single crystal nanowire array can be perfectly formed (Figure 1B, C). Based on the above results, the formation process of the 3D Nb₃O₇(OH) nanowire superstructures can be proposed. In presence of the concentrated HCl, NbCl₅ as reaction precursor hydrolyzes slowly to form firstly HNbO₃ building blocks, as shown in equation (1):

Further, the HNbO₃ building blocks start to grow and form large size cube-shaped structures. With increasing reaction time, the size of cube-shaped structure obviously increases, indicating the growth of cubic HNbO₃ structure is predominant within short reaction time. After 6 h, the growth of cube-shaped structure reaches essentially equilibrium status. Further increasing reaction time (*e.g.*, 9 h), the surface of the cube-shaped structure begins to dissolve and rearrange, and the Nb₃O₇(OH) crystal structure starts to form and grow (see equation (2)). Finally, the 3D Nb₃O₇(OH) nanowire superstructures form after long reaction time (*e.g.*, 24 h). After calcination

at 450 °C, the orthorhombic Nb₃O₇(OH) can be readily transformed into monoclinic Nb₂O₅ (see equation (3)):

To further prove the validity of the above proposal, the theoretical calculations were performed in this work. Our results indicate that the reaction from cubic HNbO₃ to orthorhombic Nb₃O₇(OH) is thermodynamically favorable with an exothermic energy of -3.98 eV, as shown in Figure 2C, further confirming the speculation validity of the growth process of the 3D Nb₃O₇(OH) nanowire superstructure. Based on the foregoing results, the cubic HNbO₃ structure possesses six equivalent (100) planes (*d* value of 0.39 nm). With enough long reaction time (*e.g.*, 9 h), the six equivalent (100) planes occur to dissolve and rearrange to form Nb₃O₇(OH) crystal structure with a preferred growth along [010] orientation. Owing to the matching of HNbO₃ (100) plane and Nb₃O₇(OH) (010) plane, the 3D Nb₃O₇(OH) superstructures assembled with single crystalline nanowires along six directions can be obtained (Figure 2D). The above discussions on formation process of 3D Nb₃O₇(OH) nanowire superstructures are very different from the reported results possibly owing to different hydrothermal conditions.^{25, 27}

Monoclinic Nb₂O₅ has been widely investigated for lithium intercalation reaction ($x\text{Li} + xe^- + \text{Nb}_2\text{O}_5 \rightarrow \text{Li}_x\text{Nb}_2\text{O}_5$) owing to its great potential as electrode materials.^{18, 22, 31-33} In this work, the obtained orthorhombic Nb₃O₇(OH) and monoclinic Nb₂O₅ 3D nanowire superstructures were also investigated and compared as anode materials for lithium-ion batteries (LiBs). Figure 3A shows the discharge and charge curves of the Nb₃O₇(OH) and Nb₂O₅ electrodes in the voltage window of 1.2-3.0 V at the current density of 20 mA g⁻¹. As shown, although the Nb₂O₅

structures have a decreased surface area compared to the $\text{Nb}_3\text{O}_7(\text{OH})$ structures, the Nb_2O_5 electrode exhibits significantly higher charge and discharge specific capacities than those of the $\text{Nb}_3\text{O}_7(\text{OH})$ electrode. The initial discharge capacities for the $\text{Nb}_3\text{O}_7(\text{OH})$ and Nb_2O_5 electrodes are 152 and 225 mA hg^{-1} , which are corresponding to $x = 2.3$ for $\text{Li}_x\text{Nb}_3\text{O}_7(\text{OH})$ and $x = 2.2$ for $\text{Li}_x\text{Nb}_2\text{O}_5$, respectively.^{22, 31-33} After two cycles, the discharge capacity of the Nb_2O_5 electrode still keeps relatively stable and reaches as large as 203 mA hg^{-1} , while the $\text{Nb}_3\text{O}_7(\text{OH})$ electrode displays an importantly decreased discharge capacity (55 mA hg^{-1}), indicating higher stability of the Nb_2O_5 electrode. Further, the rate performance of the $\text{Nb}_3\text{O}_7(\text{OH})$ and Nb_2O_5 electrodes at different current densities demonstrates that the Nb_2O_5 electrode possesses higher specific capacity for LiBs and better reversible charge-discharge cycle capability (Figure 3B). Moreover, the cycle performance of the Nb_2O_5 electrode with a constant charge/discharge current density (100 mA g^{-1}) further indicates that the Nb_2O_5 electrode has high capacity and excellent cycling stability (177 mA hg^{-1} after 150 cycles, Figure S6 in Supporting Information). Based on the above results, the $\text{Nb}_3\text{O}_7(\text{OH})$ and Nb_2O_5 electrodes have very similar lithium intercalation number (2.3 for $\text{Li}_x\text{Nb}_3\text{O}_7(\text{OH})$ and $x = 2.2$ for $\text{Li}_x\text{Nb}_2\text{O}_5$), which can be attributed to the similar structures of the $\text{Nb}_3\text{O}_7(\text{OH})$ and Nb_2O_5 . The atomic structures of the $\text{Nb}_3\text{O}_7(\text{OH})$ and Nb_2O_5 (Figure S7, Supporting Information) show that they possess very similar channel structure, which is beneficial to lithium intercalation.³⁴⁻³⁶ However, an important difference is that there are hydroxyl groups in $\text{Nb}_3\text{O}_7(\text{OH})$. Our previous theoretical calculations have indicated that the most stable $\text{Nb}_3\text{O}_7(\text{OH})$ crystal structure is to be configured by the H atom bonding to one O atom at the (002) plane and interacting with another nearest O atom at the same plane through a hydrogen bond to form $\text{O}-\text{H}\cdots\text{O}$.²⁴ The presence of the hydroxyl groups in the $\text{Nb}_3\text{O}_7(\text{OH})$ could be disadvantageous for the resulting performance of LiBs, due to high stability of $-\text{OH}$ groups in

$\text{Nb}_3\text{O}_7(\text{OH})$ structure during charge and discharge processes, possibly occupying a mass of active sites for Li^+ intercalation.³⁷⁻³⁹ In addition, the large molecular weight of the $\text{Nb}_3\text{O}_7(\text{OH})$ is also unfavorable to high capacity in comparison with the Nb_2O_5 with relatively small molecular weight. In a word, although the 3D $\text{Nb}_3\text{O}_7(\text{OH})$ nanowire superstructures possess higher surface area than that of Nb_2O_5 nanowire superstructures, as electrode material for LiBs, the 3D Nb_2O_5 nanowire superstructures exhibit higher capacity and cycling stability.

In our previous report, single crystal $\text{Nb}_3\text{O}_7(\text{OH})$ nanorod film onto FTO substrate without need for calcination has been directly used as photoanode for dye-sensitized solar cells (DSSCs), exhibiting an impressive overall efficiency of 6.77%.²⁴ In this work, the 3D $\text{Nb}_3\text{O}_7(\text{OH})$ nanowire superstructure film can be also directly grown onto FTO substrate by simple hydrothermal method (see experimental section for details). XRD data demonstrate that the fabricated film sample possesses similarly orthorhombic $\text{Nb}_3\text{O}_7(\text{OH})$ crystal structure (Figure S8, Supporting Information). Surface SEM image shows that the formed $\text{Nb}_3\text{O}_7(\text{OH})$ nanostructured film is composed of nanowire superstructures (Figure 4A). Figure 4B shows the cross-sectional SEM image of the obtained $\text{Nb}_3\text{O}_7(\text{OH})$ nanostructured film. As shown, the formed film possesses a thickness of *ca.* 17.5 μm . Interestingly, a highly-ordered nanowire layer directly grown onto FTO substrate can be obviously observed between nanowire superstructure layer and FTO substrate (Figure 4C and D). The formed highly-ordered $\text{Nb}_3\text{O}_7(\text{OH})$ nanowire layer has a thickness of *ca.* 580 nm and the nanowires possess a diameter of *ca.* 23 nm. The nanowire layer could play an important role in connecting $\text{Nb}_3\text{O}_7(\text{OH})$ nanowire superstructures and FTO substrate to therefore form high stable film structure. As photoanode material for DSSCs, the nanowire layer can act as an effective blocking layer to prevent photoelectron leakage at the interface between the nanowire superstructure layer and FTO substrate, thus improving DSSCs

efficiency.^{40, 41} Additionally, the highly ordered single crystalline nanowires are also beneficial to enhancing the photoelectron transport of the photoanode film, thus the DSSCs performance.^{42,}

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Without need for further calcination, the obtained Nb₃O₇(OH) nanostructured film onto FTO substrate was directly used as photoanode for DSSCs measurement. For comparison, the Nb₂O₅ nanostructured film was also evaluated by thermal treatment of Nb₃O₇(OH) film at 450 °C. The resulting performance of DSSCs assembled with the dye N719 sensitized photoanodes was measured under the standard AM 1.5 simulated sunlight (100 mW cm⁻²). Figure 5 shows photocurrent-photovoltage curves (*J-V* curves) of the DSSCs assembled with Nb₃O₇(OH) and Nb₂O₅ film photoanodes. As shown, the Nb₃O₇(OH) photoanode exhibits an overall efficiency of 6.38% with a short-circuit current density (*J*_{sc}) of 12.76 mA cm⁻², an open-circuit voltage (*V*_{oc}) of 731 mV, and a fill factor (*FF*) of 68.4%. After calcination, the Nb₂O₅ photoanode possesses slightly good *V*_{oc} and *FF* values compared to the Nb₃O₇(OH) photoanode. However, the decreased DSSCs efficiency (5.87%) of the Nb₂O₅ photoanode can be due to the decreased surface area after calcination, which results in the decreased dye loading amount (1.71×10^{-7} mol cm⁻² for Nb₃O₇(OH) film and 1.53×10^{-7} mol cm⁻² for Nb₂O₅ film), thus decreasing *J*_{sc} and DSSCs efficiency (Figure 5). Many studies have demonstrated that improving light utilization efficiency of the photoanode film can importantly increase the *J*_{sc}, thus DSSCs performance.^{44, 45} Diffuse reflectance spectra of the Nb₃O₇(OH) and Nb₂O₅ films with similar thickness indicate that all investigated films possess high light reflectance ability over the entire visible and near-infrared ranges, demonstrating superior light scattering property of the investigated photoanode films (Figure S9A, Supporting Information).⁴⁴⁻⁴⁶ The superior light scattering ability of the photoanode films can be ascribed to the large sizes of the cube-shaped structures.⁴⁴⁻⁴⁶ Compared

to the $\text{Nb}_3\text{O}_7(\text{OH})$ film, the Nb_2O_5 film has a higher light scattering ability possibly owing to the formation of cube-shaped structure aggregates with larger sizes after calcination, which means the Nb_2O_5 film possesses higher light utilization efficiency. However, the low DSSCs efficiency of the Nb_2O_5 photoanode confirms that the decreased surface area after calcination is mainly responsible for the decreased J_{sc} , thus DSSCs performance, which has been further supported by the measured incident photon to current conversion efficiency (IPCE) spectra (Figure S9B, Supporting Information).

Conclusions

In summary, highly-ordered single crystalline nanowire array constructed $\text{Nb}_3\text{O}_7(\text{OH})$ superstructures with high surface area of $121.5 \text{ m}^2 \text{ g}^{-1}$ have been successfully fabricated by simple hydrothermal method. Owing to similar structure property, the orthorhombic $\text{Nb}_3\text{O}_7(\text{OH})$ nanowire superstructures can be readily transformed into monoclinic Nb_2O_5 nanowire superstructures with a surface area of $81.8 \text{ m}^2 \text{ g}^{-1}$ by low-temperature calcination at 450°C , which is unavailable using traditional sol-gel and electrospinning methods. The obtained Nb_2O_5 nanowire superstructures as anode material exhibits high capacity of 177 mA h g^{-1} at a constant charge/discharge current density of 100 mA g^{-1} and excellent cycling stability for lithium-ion batteries. Additionally, the $\text{Nb}_3\text{O}_7(\text{OH})$ nanowire superstructure film onto FTO substrate can be constructed by a facile hydrothermal method, and directly used as photoanode, displaying an overall efficiency of 6.38% for dye-sensitized solar cells. This work indicates a feasibility of using 3D niobium-based nanowire superstructures as promising energy materials for energy storage and conversion applications.

Experimental Section

Synthesis of 3D Nb₃O₇(OH) and Nb₂O₅ nanowire superstructures: 3D Nb₃O₇(OH) superstructures assembled with highly-ordered single crystalline nanowire arrays were synthesized with a similar method reported by our previous work.²⁴ In a typical synthesis, 0.5403 g of niobium (V) chloride (NbCl₅, Aldrich) was firstly dissolved in a 40 mL of 6.6 M hydrochloric acid (HCl, 32%, Sigma-Aldrich) solution. The concentration of NbCl₅ is 0.05 M in reaction solution. After stirring for 2 min, the resulting solution was transferred into a Teflon-lined stainless steel autoclave with a volume of 100 mL. The hydrothermal reaction was kept at 200 °C for 24 h. After hydrothermal reaction, the autoclave was cooled to room temperature, and the as-synthesized product was adequately washed with deionized water and collected by centrifugation. The fabricated product was allowed to dry in a nitrogen stream for further characterization and use. For the fabrication of Nb₃O₇(OH) film, a piece of pre-treated FTO conducting glass (15 Ω/square, Nippon Sheet Glass, Japan) with conductive facing up was firstly immersed into the precursor solution prior to hydrothermal reaction. After hydrothermal reaction, the FTO substrate was taken out, rinsed adequately with deionized water and dried in a nitrogen stream. The Nb₂O₅ nanostructures (films) were obtained by thermal conversion of the as-synthesized Nb₃O₇(OH) nanostructures (films) at 450 °C for 2 h. The resultant Nb₃O₇(OH) and Nb₂O₅ samples as electrode materials were subsequently evaluated in lithium-ion batteries and dye-sensitized solar cells.

Characterization. SEM (JSM-7001), TEM (Philips F20), and XRD (Shimadzu XRD-6000 diffractometer) were employed for characterizing the prepared samples. Chemical compositions of the samples were analysed by X-ray photoelectron spectroscopy (XPS, Kratos Axis ULTRA incorporating a 165 mm hemispherical electron energy analyzer). Nitrogen adsorption-desorption isotherms of the samples were obtained on a Quantachrome Autosorb-1 surface area and pore

size analyser. The pore size distributions of the samples were derived from the adsorption branches of the isotherms based on the Barrett–Joyner–Halenda (BJH) model. Diffuse reflectance spectra of the films were recorded on a Varian Cary 5E UV-vis-NIR spectrophotometer. Raman spectra were collected with a Renishaw 100 system Raman spectrometer using a 632.8 nm He-Ne laser. The scattered light was detected with a Peltier-cooled CCD detector with spectral resolution of 2.0 cm^{-1} . The grating was calibrated using the 520.0 cm^{-1} silicon band.

Theoretical Calculations. All computations are performed using the Vienna *ab initio* simulation package (VASP) based on the all-electron projected augmented wave (PAW) method.^{47,48} A plane-wave basis set is employed to expand the smooth part of wave functions with a kinetic energy cut-off of 520 eV. For the electron-electron exchange and correlation interactions, the functional of PBE,⁴⁹ a form of the general gradient approximation (GGA), is used throughout. The Brillouin-zone integrations were performed using Monkhorst-Pack grids of special points, with gamma-point centered ($2 \times 8 \times 8$) k -points meshes used for the bulk cells. When the geometry is optimized, all atoms are allowed to relax. A variable cell technique is employed to simultaneously optimize the lattice constant and the atomic structure to encounter the complexity and low-symmetry of the HNbO_3 and $\text{Nb}_3\text{O}_7(\text{OH})$ crystals. And the lattice constants and geometric structure are optimized until the residual forces were below $0.001\text{ eV/\AA}$.

Measurements.

(1) Lithium-ion batteries (LiBs)

To test the electrochemical performance, the as-prepared sample was mixed at a ratio of 80 wt% active materials ($\text{Nb}_3\text{O}_7(\text{OH})$ and Nb_2O_5) with 10 wt% carbon black and 10 wt% binder, poly(vinylidene fluoride) (PVDF). The slurry made by using *N*-methyl-2-pyrrolidone (NMP) as the solvent was uniformly pasted onto pieces of Al foil with an area of 1.0 cm^2 . Such prepared

electrode sheets were dried at 100 °C in a vacuum oven for 12 h. Then, the electrodes were compressed before making the cells. The electrochemical cells (CR 2032 coin-type cells) that were prepared for testing included the as-prepared sample on Al foil as the working electrode, Li foil as the counter and reference electrode, a porous polypropylene film as the separator, and 1.0 M LiPF₆ (battery grade 99.99%, Aldrich) in a 1 : 2 (v/v) mixture of ethylene carbonate (EC, anhydrous 99%, Sigma-Aldrich) and diethyl carbonate (DEC, anhydrous 99+%, Sigma-Aldrich) as the electrolyte. The cells were assembled in an Ar-filled glove box. The cells were cycled at a current density of 20 mA g⁻¹ for the first 5 cycles and then cycled at different current densities for the following cycles between 1.2 and 3 V using a computer-controlled charger system manufactured by Land Battery Testers. The typical electrode weight was approximately 3.0 mg cm⁻².

(2) Dye-sensitized solar cells (DSSCs)

Prior to DSSCs measurements, all niobium oxide-based photoanodes were sensitized with dye N719 (3×10^{-4} mol L⁻¹) for 24 h. A series of DSSCs were fabricated with traditional sandwich type configuration by using a dye-anchored niobium oxide-based film and a platinum counter electrode deposited on FTO conducting glass. A mask with a window area of 0.15 cm² was applied on the Nb₃O₇(OH) and Nb₂O₅ photoanode film side to define the active area of the cells. A 500 W Xe lamp (Trusttech Co., Beijing) with an AM 1.5G filter (Sciencetech, Canada) was used as the light source. The light intensity was measured by a radiant power meter (Newport, 70260) coupled with a broadband probe (Newport, 70268). The photovoltaic measurements of DSSCs were recorded by a scanning potentiostat (Model 362, Princeton Applied Research, US). The IPCE as a function of wavelength was measured with QE/IPCE measurement kit (NewSpec).

Conflict of Interest: The authors declare no competing financial interest.

Acknowledgement. This work was financially supported by the Natural Science Foundation of China (Grant No. 51472246 and 51072199), the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDA09030200), and the CAS/SAFEA International Partnership Program for Creative Research Teams of Chinese Academy of Sciences, China, and the CAS Pioneer Hundred Talents Program.

Supporting Information. Supported images, XPS, Raman, UV-vis Diffuse Reflection spectra of $\text{Nb}_3\text{O}_7(\text{OH})$ and Nb_2O_5 and some theoretical calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.”

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REFERENCES

1. Whitesides, G. M.; Grzybowski, B. *Science* **2002**, 295, (5564), 2418-2421.
2. Gao, Y.; Tang, Z. Y. *Small* **2011**, 7, (15), 2133-2146.
3. Jiang, J.; Li, Y.; Liu, J.; Huang, X.; Yuan, C.; Lou, X. W. *Adv. Mater.* **2012**, 24, (38), 5166-5180.
4. Dong, Z.; Lai, X.; Halpert, J. E.; Yang, N.; Yi, L.; Zhai, J.; Wang, D.; Tang, Z.; Jiang, L. *Adv. Mater.* **2012**, 24, (8), 1046-1049.
5. Wang, J.; Yang, N.; Tang, H.; Dong, Z.; Jin, Q.; Yang, M.; Kisailus, D.; Zhao, H.; Tang, Z.; Wang, D. *Angew. Chem., Int. Ed.* **2013**, 52, (25), 6417-6420.
6. Pan, A.; Wu, H. B.; Yu, L.; Lou, X. W. *Angew. Chem., Int. Ed.* **2013**, 52, (8), 2226-2230.
7. Ji, L.; Lin, Z.; Alcoutlabi, M.; Zhang, X. *Energy Environ. Sci.* **2011**, 4, (8), 2682-2699.
8. Dong, Z. H.; Ren, H.; Hessel, C. M.; Wang, J. Y.; Yu, R. B.; Jin, Q.; Yang, M.; Hu, Z. D.; Chen, Y. F.; Tang, Z. Y.; Zhao, H. J.; Wang, D. *Adv. Mater.* **2014**, 26, (6), 905-909.
9. Xu, S. M.; Hessel, C. M.; Ren, H.; Yu, R. B.; Jin, Q.; Yang, M.; Zhao, H. J.; Wang, D. *Energy Environ. Sci.* **2013**, 7, (2), 632-637.
10. Li, G. L.; Liu, J. Y.; Lan, J.; Li, G.; Chen, Q. W.; Jiang, G. B. *Crystengcomm* **2014**, 16, (46), 10547-10552.
11. Heiniger, L. P.; Giordano, F.; Moehl, T.; Gratzel, M. *Adv. Energy Mater.* **2014**, 4, (12), 1400168.

12. Ren, H.; Yu, R. B.; Wang, J. Y.; Jin, Q.; Yang, M.; Mao, D.; Kisailus, D.; Zhao, H. J.; Wang, D. *Nano Lett.* **2014**, 14, (11), 6679-6684.
13. Lai, X. Y.; Halpert, J. E.; Wang, D. *Energy Environ. Sci.* **2012**, 5, (2), 5604-5618.
14. Zhao, Y.; Zhou, X.; Ye, L.; Tsang, S. C. E. *Nano Rev.* **2012**, 3, 17631.
15. Chambon, L.; Maleysson, C.; Pauly, A.; Germain, J. P.; Demarne, V.; Grisel, A. *Sensors and Actuators, B* **1997**, B45, (2), 107-114.
16. Aegerter, M. A. *Solar Energy Mater. Solar Cells* **2001**, 68, (3-4), 401-422.
17. Le Viet, A.; Jose, R.; Reddy, M. V.; Chowdari, B. V. R.; Ramakrishna, S. *J. Phys. Chem. C* **2010**, 114, (49), 21795-21800.
18. Le Viet, A.; Reddy, M. V.; Jose, R.; Chowdari, B. V. R.; Ramakrishna, S. *J. Phys. Chem. C* **2010**, 114, (1), 664-671.
19. Wang, Z.; Hou, J.; Yang, C.; Jiao, S.; Huang, K.; Zhu, H. *Phys. Chem. Chem. Phys.* **2013**, 15, (9), 3249-3255.
20. Betzler, S. B.; Wisnet, A.; Breitbach, B.; Mitterbauer, C.; Weickert, J.; Schmidt-Mende, L.; Scheu, C. *J. Mater. Chem. A* **2014**, 2, (30), 12005-12013.
21. Zhang, H.; Li, Y.; Wang, Y.; Liu, P.; Yang, H.; Yao, X.; An, T.; Wood, B. J.; Zhao, H. *J. Mater. Chem. A* **2013**, 1, (22), 6563-6571.
22. Wei, M.; Wei, K.; Ichihara, M.; Zhou, H. *Electrochem. Commun.* **2008**, 10, (7), 980-983.
23. Guo, P.; Aegerter, M. A. *Thin Solid Films* **1999**, 351, (1,2), 290-294.
24. Zhang, H.; Wang, Y.; Yang, D.; Li, Y.; Liu, H.; Liu, P.; Wood, B. J.; Zhao, H. *Adv. Mater.* **2012**, 24, (12), 1598-1603.
25. Betzler, S. B.; Wisnet, A.; Breitbach, B.; Mitterbauer, C.; Weickert, J.; Schmidt-Mende, L.; Scheu, C. *J. Mater. Chem. A* **2014**, 2, (30), 12005-12013.
26. Hmadeh, M.; Hoepfner, V.; Larios, E.; Liao, K.; Jia, J.; Jose-Yacaman, M.; Ozin, G. A. *Chemsuschem* **2014**, 7, (8), 2104-2109.
27. Hu, P.; Hou, D. F.; Wen, Y. W.; Shan, B.; Chen, C. J.; Huang, Y. H.; Hu, X. L. *Nanoscale* **2015**, 7, (5), 1963-1969.
28. Izumi, F.; Kodama, H. Z. *Anorg. All. Chem.* **1978**, 441, 196-204.
29. Oliveira, L. C. A.; Ramalho, T. C.; Goncalves, M.; Cereda, F.; Carvalho, K. T.; Nazzarro, M. S.; Sapag, K. *Chem. Phys. Lett.* **2007**, 446, (1-3), 133-137.
30. Kruk, M.; Jaroniec, M. *Chem. Mater.* **2001**, 13, (10), 3169-3183.
31. Sasidharan, M.; Gunawardhana, N.; Yoshio, M.; Nakashima, K. *Mater. Res. Bull.* **2012**, 47, (9), 2161-2164.
32. Kodama, R.; Terada, Y.; Nakai, I.; Komaba, S.; Kumagai, N. *J. Electrochem. Soc.* **2006**, 153, (3), A583-A588.
33. Kumagai, N.; Tanno, K.; Nakajima, T.; Watanabe, N. *Electrochimica Acta* **1983**, 28, (1), 17-22.
34. Xiao, J.; Mei, D.; Li, X.; Xu, W.; Wang, D.; Graff, G. L.; Bennett, W. D.; Nie, Z.; Saraf, L. V.; Aksay, I. A.; Liu, J.; Zhang, J.-G. *Nano Lett.* **2011**, 11, (11), 5071-5078.
35. Liu, H.; Bi, Z.; Sun, X.-G.; Unocic, R. R.; Paranthaman, M. P.; Dai, S.; Brown, G. M. *Adv. Mater.* **2011**, 23, (30), 3450-3454.
36. Li, J.; Wan, W.; Zhou, H.; Li, J.; Xu, D. *Chem. Commun.* **2011**, 47, (12), 3439-3441.
37. Xun, S.; Song, X.; Wang, L.; Grass, M. E.; Liu, Z.; Battaglia, V. S.; Liu, G. J. *Electrochem. Soc.* **2011**, 158, (12), A1260-A1266.
38. Choi, N.-S.; Yew, K. H.; Lee, K. Y.; Sung, M.; Kim, H.; Kim, S.-S. *J. Power Sources* **2006**, 161, (2), 1254-1259.

39. Shao, Y. Y.; Xiao, J.; Wang, W.; Engelhard, M.; Chen, X. L.; Nie, Z. M.; Gu, M.; Saraf, L. V.; Exarhos, G.; Zhang, J. G.; Liu, J. *Nano Lett.* **2013**, 13, (8), 3909-3914.
40. Xia, J.; Masaki, N.; Jiang, K.; Yanagida, S. *Chem. Commun.* **2007**, (2), 138-140.
41. Kim, J.; Kim, J. *J. Nanosci. Nanotechnol.* **2011**, 11, (8), 7335-7338.
42. Kang, S. H.; Choi, S.-H.; Kang, M.-S.; Kim, J.-Y.; Kim, H.-S.; Hyeon, T.; Sung, Y.-E. *Adv. Mater.* **2008**, 20, (1), 54-58.
43. Zhang, H.; Liu, X.; Li, Y.; Sun, Q.; Wang, Y.; Wood, B. J.; Liu, P.; Yang, D.; Zhao, H. *J. Mater. Chem.* **2012**, 22, (6), 2465-2472.
44. Chen, D.; Huang, F.; Cheng, Y.-B.; Caruso, R. A. *Adv. Mater.* **2009**, 21, (21), 2206-2210.
45. Zhang, H.; Han, Y.; Liu, X.; Liu, P.; Yu, H.; Zhang, S.; Yao, X.; Zhao, H. *Chem. Commun.* **2010**, 46, (44), 8395-8397.
46. Bai, Y.; Yu, H.; Li, Z.; Amal, R.; Lu, G. Q.; Wang, L. Z. *Adv. Mater.* **2012**, 24, (43), 5850-5856.
47. G. Kresse, J. Furthmüller, *Comput. Mat. Sci.* **1996**, 6, 15-50.
48. G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, 59, 1758-1775.
49. J.P. Perdew, W. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, 77, 3865-3868.

Figure Captions:

Figure 1. (A) XRD patterns of as-synthesized sample obtained at 200 °C for 24 h and calcined sample at 450 °C for 2 h. (B) Surface SEM image of as-synthesized Nb₃O₇(OH) structures. (C) SEM image of an individual Nb₃O₇(OH) structure. (D) TEM image of an individual Nb₃O₇(OH) structure; the arrows in (C) and (D) denote the preferential growth orientation of single crystalline nanowires. (E) TEM image of an individual Nb₃O₇(OH) nanowire. (F) FFT image. (G) Index of the FFT image (F). (H) Inverse FFT image from the marked area in (E).

Figure 2. (A) XRD patterns of as-synthesized samples obtained at 200 °C with different hydrothermal reaction times and their corresponding SEM images. (B) Atomic structure model of cubic HNbO₃. (C) Atomic structure models of HNbO₃ and Nb₃O₇(OH), and the calculated thermodynamic reaction energy. (D) Atomic structure models of HNbO₃ (100) plane and Nb₃O₇(OH) (010) plane. Atom colour code: green-Nb, red-O, pink-H, green octahedron: [NbO₆].

Figure 3. (A) The discharge-charge curves of $\text{Nb}_3\text{O}_7(\text{OH})$ and Nb_2O_5 electrodes in the voltage window of 1.2-3.0 V at the current density of 20 mA g^{-1} . (B) Rate performance and columbic efficiency of $\text{Nb}_3\text{O}_7(\text{OH})$ and Nb_2O_5 electrodes at different current rates.

Figure 4. (A) Surface SEM image of as-synthesized $\text{Nb}_3\text{O}_7(\text{OH})$ film onto FTO substrate. (B) Low magnification and (C) High magnification cross-sectional SEM images of as-synthesized $\text{Nb}_3\text{O}_7(\text{OH})$ film onto FTO substrate. (D) Cross-sectional SEM image of $\text{Nb}_3\text{O}_7(\text{OH})$ single crystalline nanowire layer.

Figure 5. Photocurrent as a function of photovoltage for DSSCs assembled with $\text{Nb}_3\text{O}_7(\text{OH})$ and Nb_2O_5 film photoanodes.