We demonstrate a simple, efficient, yet versatile strategy for the synthesis of novel hierarchical heterostructures composed of TiO$_2$ nanofiber stem and various metal oxides (MOs) secondary nanostructures, including Co$_3$O$_4$, Fe$_2$O$_3$, Fe$_3$O$_4$, and CuO, by advantageously combining the versatility of the electrospinning technique and hydrothermal growth method, for which the controllable formation process and possible formation mechanism are also investigated. Moreover, as a proof-of-concept demonstration of the functional properties of these hierarchical heterostructures, the Co$_3$O$_4$/TiO$_2$ hierarchical heterostructures are investigated as the lithium-ion batteries (LIBs) anode materials for the first time, which not only delivers a high reversible capacity of 632.5 mAh g$^{-1}$ and 95.3% capacity retention over 480 cycles, but also shows excellent rate capability with respect to the pristine TiO$_2$ nanofibers. The synergetic effect between Co$_3$O$_4$ and TiO$_2$ as well as the unique feature of hierarchical heterostructures are probably responsible for the enhanced electrochemical performance.

Growth of functional semiconductor oxides with controllable hierarchical heterostructures has attracted tremendous attention because diverse properties can be integrated by tailoring the morphology, composition, and assembling organization of the primary nanobuilding blocks. Specifically, novel hierarchical heterostructures, in which the major 1D cores and branches consist of different materials, are more attractive in many nanoscale photonic and electron-optical device applications. Especially, to serve as materials for lithium-ion batteries (LIBs), the hierarchical heterostructures not only integrate the diverse properties from the different building blocks, but also exhibit intriguing properties by taking advantage of both the nanometer-size effects and the high stability of the secondary-structure assemblies. For instance, epitaxial growth of branched $\alpha$-Fe$_2$O$_3$/SnO$_2$ nano heterostructures could improve LIB performance due to the synergetic effect exerted by SnO$_2$ and $\alpha$-Fe$_2$O$_3$ as well as the unique branched structure. Furthermore, a novel high performance cathode material for LIBs has been developed by coating V$_2$O$_5$ on SnO$_2$ nanowires, utilizing the better conductivity of SnO$_2$ nanowires and the short diffusion distance of the thin V$_2$O$_5$ layer. Notwithstanding these advances, it is still of great challenge to develop a general approach with the characteristics of low cost, low growth temperature, environmental friendliness, process simplicity, and high yield to synthesize a control of size, dimension, and composition of the building blocks of hierarchical heterostructures in an expected way.

TiO$_2$, as an important functional material, has numerous applications as photocatalysis, electronic devices, conversion devices as well as promising electrode material due to its attractive advantages of high abundance, low cost, better safety, and environmental friendliness. Furthermore, the special structural characteristics and surface activity, together with the very low volume change during Li$^+$ insertion/desertion (3–4%), intrinsically endows TiO$_2$ good structural stability and long cycle life. Nevertheless, the main weaknesses of TiO$_2$ as anode materials for LIBs lie in the low theoretical capacity (168 mAh g$^{-1}$), even lower than that of commercial graphite.
~372 mAh g\(^{-1}\)) and the poor rate capability of TiO\(_2\) electrodes. Recently, different strategies, such as constructing one dimensional (1D) TiO\(_2\) nanostructures (nanorod, nanofiber, nanotube, and core-shell nanowire),\(^{20-21}\) and coating or mixing with more conductive materials, such as carbonaceous materials\(^{22-24}\), noble metals (Au, Ag etc)\(^{25-28}\), and RuO\(_2\),\(^{29}\) and/or doping with foreign atoms\(^{29,28}\) have been developed to overcome the ionic and electronic transport limitations and improve the rate capability of TiO\(_2\)-based anodes. However the strategies mentioned above still suffer from disadvantages such as high cost, complicated production procedure, and to add insult to injury decrease the capacity of TiO\(_2\), because these coating materials are not very active materials for reversible lithium storage. Therefore, it is urgently important to develop new strategies that can coat the active materials with high capacity and conductivity on the surface of TiO\(_2\) nanostructures. On the other hand, as a new class of promising anode materials for LIBs, transition-metal oxides (MOs) have shown desirable property of higher theoretical capacities (700–1000 mAh g\(^{-1}\)), which is much higher than that of commercial graphite and TiO\(_2\)\(^{29-34}\). However, an intrinsically drastic volume change during lithiation/delithiation process gives rise to pulverization that may break the electrical contact pathways in the MOs electrodes, thus leading to a rapid decay in capacity and limiting the practical use. Therefore, developing new synthetic strategies to fabricate high-performance MOs electrode materials with both large reversible capacity and long cycle life are highly desirable but still very challenging.

Stimulated by the above concerns, we envision building up an integrated smart architecture, in which structural features and electroactivities of each component are fully manifested, the interface/chemical distributions are homogeneous at a nanoscale and a fast ion and electron transfer is guaranteed. Herein, we propose and realize a facile, effective, and general strategy for preparing MOs/TiO\(_2\) hierarchical heterostructures by advantageously combining the electrospinning technique with the hydrothermal method, which holds many favorable merits including: (1) both the electrospinning and hydrothermal method have been proven to be a comparatively versatile, low cost, applicable and environmentally friendly technique. (2) This strategy can be extended to the fabrication of various hierarchical MOs, such as Co\(_3\)O\(_4\), Fe\(_3\)O\(_4\), Fe\(_2\)O\(_3\), CuO, on TiO\(_2\) nanofibers to form MOs/TiO\(_2\) hierarchical heterostructures. (3) The synergistic effects of nanobuilding blocks as well as the unique hierarchical heterostructures may contribute to the improved LIBs performance. With this design, not only all the desired functions of each constituent are effectively utilized, but also a strong synergistic effect can be realized. As MOs feature both high capacity and higher electronic conductivity (compared to TiO\(_2\)), hierarchical heterostructures composed of TiO\(_2\) nanofiber and various metal oxides (MOs) could simultaneously increase the rate capability and specific capacity of TiO\(_2\) and improve the cycling performance of MOs by the synergistic effect. As a proof-of-concept demonstration of the application of such hierarchical heterostructures, the Co\(_3\)O\(_4\)/TiO\(_2\) hierarchical heterostructures are tested as LIBs anode for the first time, which show high reversible capacity, improved cycling stability, and excellent rate capability with respect to the pristine TiO\(_2\).

**Results**

**Fabrication of MOs/TiO\(_2\) hierarchical heterostructures.** Four typical MOs, namely, Co\(_3\)O\(_4\), Fe\(_3\)O\(_4\), Fe\(_2\)O\(_3\), and CuO, are adopted as secondary nanostructures grown on primary TiO\(_2\) nanofiber to verify the feasibility and versatility of our protocol in achieving MO/ TiO\(_2\) hierarchical heterostructures. We firstly test this concept with Co\(_3\)O\(_4\) nanosheets grown on primary TiO\(_2\) nanofiber to form the Co\(_3\)O\(_4)/TiO\(_2\) hierarchical heterostructures. The morphology of the Co\(_3\)O\(_4)/TiO\(_2\) hierarchical heterostructures is investigated by scanning electron microscopy (SEM). As shown in Figure 1a, the obtained pristine TiO\(_2\) non-woven nanofibers with diameters ranging from 200 to 500 nm have a relatively smooth surface without secondary nanostructures. After applying the controllable solution growth of Co\(_3\)O\(_4\) nanosheets, the hierarchical heterostructures are formed (Figure 1b). Close observation on the nanofiber (Figure 1c) reveals that the high densities of secondary Co\(_3\)O\(_4\) nanosheets grow on the primary TiO\(_2\) nanofibers. Interestingly, compared with the hierarchical heterostructures before annealing treatment (Fig. S1a and b), it is obvious that many pores caused by the annealing treatment are found on the surface of the secondary Co\(_3\)O\(_4\) nanosheets. These pores may exhibit large surface area, which is very

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**Figure 1 | Morphology characterization.** (a) SEM image of pristine TiO\(_2\) nanofibers. (b) Low- and (c) high-magnification SEM images of Co\(_3\)O\(_4)/TiO\(_2\) hierarchical heterostructures. (d) Typical TEM image of the single Co\(_3\)O\(_4)/TiO\(_2\) hierarchical nanofiber. (e) HRTEM image of the heterojunction region. (f) HRTEM image of the Co\(_3\)O\(_4\) nanosheet surface.
precious for LIBs materials. Further information about the Co3O4/TiO2 hierarchical heterostructures is obtained from transmission electron microscopy (TEM). The TEM image in Figure 1d shows an individual Co3O4/TiO2 hierarchical nanofiber. It can be clearly seen that the secondary Co3O4 nanosheets with many pores grow on the surface of TiO2 nanofibers, coinciding with the results from the SEM observations. The HRTEM image (Figure 1e) taken from the heterojunction region displays two set of lattice fringe spacings of 0.35 and 0.47 nm, corresponding to the (101) plane of the anatase crystal structure of TiO2 and the (111) plane of the cubic Co3O4, respectively, which clearly shows the simultaneous presence of TiO2 and Co3O4 crystal lattices in the region of the junction. Figure 1f further confirms the single-crystalline structure of the (311) plane of the cubic Co3O4.

To investigate the crystal phase of the samples, the X-ray diffraction (XRD) analysis is performed (Figure 2a). The XRD patterns reveal that all the diffraction peaks could be indexed to anatase TiO2 (JCPDS No. 21–1272) and face-centered cubic phase of Co3O4 (space group: Fd3m (227), JCPDS No. 43–1003). These results confirm that the synthesis strategy adopted successfully achieves Co3O4/TiO2 hierarchical heterostructures integrating the Co3O4 nanosheets and TiO2 nanofibers. Subsequently, the purity, composition and fine structure of the samples are further investigated. In XPS spectra, Fig. S2 shows the characteristic peaks of C 1s, N 1s, O 1s, and Co 2p, respectively, indicating the existence of carbon, nitrogen, oxygen, and cobalt elements in the Co3O4/TiO2 hierarchical heterostructures. The C 1s and N 1s peaks may be assigned to the pyrolysis products. As XPS is a highly surface-specific technique with a typical analysis depth of ~10 nm (lower than the thickness of the secondary Co3O4 shell), it is reasonable that TiO2 is not detected. This thus provides indirect experimental proof of the uniformity of the secondary Co3O4 nanosheets coating the TiO2 nanofibers. In Raman spectra (Figure 2b), four well-resolved peaks are observed around 143.6 (Eg), 399.1 (B1g), 519.3 (A1g), and 639.7 (Eg) cm⁻¹, corresponding to the characteristic Raman modes of anatase TiO2. After the growth of Co3O4 nanosheets, in addition to the peaks from anatase TiO2, the new peaks at 193.6 (B1g), 476.9 (Eg), 517.1 (F2g), 615.1 (F2g), 684.3 (A1g) cm⁻¹, corresponding to the characteristic Raman modes of Co3O4, are observed and demonstrate the successful introduction of Co3O4. These results demonstrate the existence of both anatase TiO2 and Co3O4 in the heterostructures.

The synthesis strategy can be readily extended to the growth of other MOs (e.g. Fe2O3, Fe3O4, and CuO) as secondary nanostructures on the primary TiO2 nanofibers, forming MOs/TiO2 hierarchical heterostructures. Similarly, the Fe2O3/TiO2 hierarchical heterostructure can also be easily synthesized through our general strategy. The low- and high-magnification SEM images (Figure 3a and b) show the secondary Fe2O3 nanorods grown on the primary TiO2 nanofibers to form Fe2O3/TiO2 hierarchical heterostructures with diameters of about 290 nm. The structure is further investigated by TEM in more detail. Figure 3c shows that Fe2O3 nanorods are uniformly attached on the primary TiO2 nanofibers surface, and the selected area is enlarged (Figure 3c, inset). The diameter and length of Fe2O3 nanorods are estimated to be about 22 and 45 nm, respectively. The HRTEM image (Figure 3d) further confirms the single-crystalline structure of the Fe2O3/TiO2 hierarchical heterostructures with a lattice fringe spacing of 0.37 nm from the (311) plane.

Apart from Co3O4 and Fe2O3, Fe3O4 and CuO nanoparticles grow on the primary TiO2 nanofibers are employed to further demonstrate the efficiency and generality of our strategy. The resulting composites exhibit the hierarchical nanostructure with secondary nanoparticles grown on the major nanofibers (Figure 4). In the case of Fe2O3/TiO2 hierarchical heterostructures, the secondary Fe2O3 nanoparticles with diameters of about 40 nm are grown on the TiO2 nanoparticle substrates. In the case of CuO/TiO2 hierarchical heterostructures, the secondary CuO nanoparticles with diameters of about 600 nm are grown on the TiO2 nanoparticle substrates. Furthermore, the crystal structure information and the chemical components of the heterostructure are characterized by XRD (Figure 5). Their XRD peaks can be well indexed as rhombohedral hematite Fe2O3 (JCPDS No. 33-0664), cubic magnetite Fe3O4 (JCPDS No. 19-0629) and tenorite CuO (JCPDS No. 48-1548), respectively. Strong and sharp diffraction peaks of the patterns suggest that the as-synthesized hierarchical heterostructures are highly crystallized.

**Formation mechanism of Co3O4/TiO2 hierarchical heterostructures.** Based on the above analysis, combining the versatility of the electrospinning technique and hydrothermal growth enables the fabrication of MO/TiO2 hierarchical heterostructures. Evidently, no surface pretreatments are needed to introduce new surface functional groups or additional covalent and/or noncovalent interconnectivity in our experiments. Subsequently, we take Co3O4/TiO2 hierarchical heterostructures as an example and investigate the formation mechanism of hierarchical heterostructures, as illustrated in Figure 6.

To get more insight into the actual evolution process of the Co3O4/TiO2 hierarchical heterostructures, a series of time-dependent experiments is conducted, and the intermediate solids at the different reaction stages (nucleation, growth, etc.) are examined. Figure 6a-f show representative SEM images for the samples collected stepwise.

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**Figure 2 | Phase analysis.** (a) XRD patterns of pristine TiO2 nanofibers and Co3O4/TiO2 hierarchical heterostructures. (b) Raman spectra of pristine TiO2 nanofibers, Co3O4 nanostuctures, and Co3O4/TiO2 hierarchical heterostructures.
after 1, 1.5, 2, 4, 6, and 9 h of reaction. These sequential images reveal a morphological and structural transformation from pristine TiO$_2$ nanofibers to Co$_3$O$_4$/TiO$_2$ hierarchical nanofibers. Evidently, in the initial stage (1 h) of the hydrothermal reaction, there is no visible change to the pristine TiO$_2$ nanofibers (Figure 6a). However, after 1.5 h growth, tiny nanowires nucleated on the surfaces of the TiO$_2$ nanofibers are observed (Figure 6b). When the reaction time is extended to 2 h, although a few nanosheets have already formed, most TiO$_2$ nanofibers appeared to be surrounded by tiny nanowires (Figure 6c). When the reaction time is further extended to 4 h, the continuous growth results in the disappearance of the tiny nanowires. As a result, the secondary nanosheets grow on the primary TiO$_2$ nanofibers (Figure 6d). However, by further increasing the reaction time, the overall morphology scarcely shows any change (Figure 6e and f).

Based on the time-dependent experiments, the possible mechanism is proposed to explain the formation of these hierarchical heterostructures (Figure 6g). Firstly, the electrospun TiO$_2$ nanofibers provide negative charges on the surface, which is demonstrated by its negative zeta potential (−29.4 mV). It is well known that when two components with opposite charges are carefully introduced together, the mutual electrostatic interactions drive Co$^{2+}$ to attach on the surfaces of the TiO$_2$ nanofibers. Then, the reaction of Co$^{2+}$ and urea takes place and the formed cobalt-hydroxide-carbonate nuclei attach...
to the surface of pristine TiO2 nanofibers. In the reaction, TiO2 nanofibers are used as the substrate, which can guide the secondary nanoparticles self-assembling growth in aqueous solution without surfactant and stabilizers. In this key step, the uniform small nuclei are very important because they could determine the growth kinetics of the nanosheets on the surface of the TiO2 nanofibers36. Then the oriented attachment can guide the nanoparticles growth37. With the continuously reaction proceeding, the precursors are consumed for the oriented growth to form large-scale nanosheets surrounding the TiO2 nanofibers. With our starting chemical precursors, the formation of the cobalt-hydroxide-carbonate phase can be demonstrated by the XRD patterns (Fig. S3), which agrees well with previous reports38,39. Finally, the cobalt-hydroxide-carbonate transforms into Co3O4 induced by the thermal annealing. Upon annealing for 4 h in air, cobalt-hydroxide-carbonate decomposes gradually and black Co3O4 nanosheets are obtained accordingly. Obviously, large quantities of pores are widely distributed on the surface of Co3O4 nanosheets, the yield of which would mainly rely on the pyrolysis of hydroxide-carbonate and the release of gases (CO2, H2O) during the calcination process40.

**Electrochemical performance of Co3O4/TiO2 hierarchical heterostructures.** To demonstrate the effectiveness of the TiO2-based hierarchical nanofibers in improving the lithium storage performance, we take Co3O4/TiO2 hierarchical heterostructures as a representative example and investigate the electrochemical properties of them as anode materials for LIBs, since Co3O4 has high theoretical capacity (~890 mA h g⁻¹), and is widely considered to be an attractive anode material for next-generation LIBs.

Figure 7a shows the representative cyclic voltammetry (CV) curves of the Co3O4/TiO2 hierarchical heterostructures in the voltage range of 0.01–3 V. Evidently, a pronounced reduction/oxidation peak appeared at 1.7/2.1 V is as the same as that reported for anatase TiO2, characteristic for the lithium storage mechanism between tetragonal anatase and orthorhombic LiₓTiO2 (TiO2 + xLi⁺ + xe⁻ ↔ LiₓTiO2)24,41,42. In addition, the reduction peak at ~0.98 V and ~0.66 V during the cathodic process in the first cycle can be ascribed to the initial reduction of Co3O4 to Co, the electrochemical formation of amorphous Li2O, and the formation of a partially irreversible solid electrolyte interphase (SEI) layer23–34. It is noted that reversible formation could be electrochemically driven by the metal

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**Figure 5 | Phase analysis.** XRD patterns of (a) Fe2O3/TiO2, (b) Fe3O4/TiO2, and (c) CuO/TiO2 hierarchical heterostructures.

**Figure 6 | Formation mechanism of Co3O4/TiO2 hierarchical heterostructures.** SEM images of Co3O4/TiO2 hierarchical heterostructures (before annealing) at various reaction stages by setting the reaction time 1 h (a), 1.5 h (b), 2 h (c), 4 h (d), 6 h (e), and 9 h (f). And schematic of the formation process of Co3O4/TiO2 hierarchical heterostructures (g).
nanoparticles formed in situ. Hence, the presence of Co nanoparticles at the interface between TiO$_2$ and Co$_3$O$_4$ may improve the reversibility reaction of the anatase TiO$_2$ and further result in a reversible capacity\textsuperscript{5}. In general, during the anodic process, the oxidation of metallic Co to Co$_3$O$_4$ and the decomposition of Li$_2$O could result in the appearance of the oxidation peak at $\sim$2.1 V\textsuperscript{32–34}. Interestingly, in present case, only one oxidation peak at about 2.1 V is observed, it is obvious that these two oxidation peaks coincide with each other. Note that, the second and onward CV curves remain steady, indicating the excellent cycle stability of the hierarchical heterostructures. Subsequently, the lithium storage performance of the Co$_3$O$_4$/TiO$_2$ hierarchical heterostructures is investigated. Figure 7b shows the discharge and charge curves at a current density of 200 mA g\textsuperscript{-1}. Consistent with the above CV analysis, the similar current peaks can be identified. These voltage profiles are characteristic of both Co$_3$O$_4$-based and TiO$_2$-based materials. It is observed that the initial discharge and charge capacities of the Co$_3$O$_4$/TiO$_2$ hierarchical heterostructures electrode are 632.5 and 499.7 mAh g\textsuperscript{-1}, respectively, corresponding to an irreversible capacity loss of 21.0%. The capacity of the Co$_3$O$_4$/TiO$_2$ hierarchical heterostructures electrode does not decay, and it can deliver a reversible capacity of 602.8 mAh g\textsuperscript{-1} even after 480 cycles (Figure 7b and c). Importantly, the Co$_3$O$_4$/TiO$_2$ hierarchical heterostructures electrode still exhibits an excellent cyclic performance at a higher current density of 500 mA g\textsuperscript{-1}, and the capacity still reaches 302.9 mAh g$^{-1}$ after 250 discharge and charge cycles (Fig. S4). In contrast, the pristine TiO$_2$ nanofibers electrode only exhibits a very lower capacity (initial discharge and charge capacities of 275.8 and 159.8 mAh g$^{-1}$), and the single Co$_3$O$_4$ nanostructures electrode loses the capacity severely (the discharge capacity of 381.4 mAh g$^{-1}$ after only 90 charge-discharge cycles) (Fig. S5). Evidently, the composite hierarchical heterostructures inherit the advantages of high capacity from Co$_3$O$_4$ component and the excellent stability of TiO$_2$ component. To better understand the advantage of the hierarchical heterostructures in lithium storage, the rate performance of the Co$_3$O$_4$/TiO$_2$ hierarchical heterostructures is investigated (Figure 7d). Obviously, compared with the pristine TiO$_2$ nanofibers, the specific capacity of the hierarchical heterostructures is substantially increased at all investigated charge-discharge rates from 100 to 2000 mA g$^{-1}$. For example, the Co$_3$O$_4$/TiO$_2$ hierarchical heterostructures exhibit much superior rate performance with 475.8 and 449.5 mAh g$^{-1}$, which is about three times larger than that of pristine TiO$_2$ electrode (143.2 and 115.3 mAh g$^{-1}$), at current densities of 400 and 1000 mA g$^{-1}$ respectively. At the high current rate (2000 mA g$^{-1}$), the hierarchical heterostructures exhibit a downward trend, which can be ascribed to the partial collapse of the electrode materials during the charge-discharge at a high current density. Further investigations are ongoing to improve the capacity retention at high discharge rates. However, the difference of rate performance between the two materials is quite more remarkable even at high current density. Importantly, the high capacity of the hierarchical composite electrode can be recovered to the initial values even after 70 discharge and charge cycles, implying their good reversibility.

**Discussion**

The above obtained improved electrochemical properties of the Co$_3$O$_4$/TiO$_2$ hierarchical heterostructures are not simply a result of the mix of the two components. Instead, it more likely originates...
from the successful integration of the respective advantages from both TiO2 and Co3O4 individual components into the unique hierarchical heterostructures, which is elaborated as follows. On one hand, the improved capacity of hierarchical heterostructures compared with the pristine TiO2 nanofibers can be easily understood by the addition of a higher capacity Co3O4 component and the synergistic effect of Co3O4 nanosheets and TiO2 stems mentioned above. It is well-known that one advantage of transition-metal oxides in lithium storage is their high theoretical specific capacity. Hence, a large content of Co3O4 could give rise to a high specific capacity. On the other hand, the synergistic effect of the successful integration of the Co3O4 nanosheets and TiO2 nanofibers contributes more to the improved cycling stability and excellent rate capability of the Co3O4/TiO2 hierarchical heterostructures. Herein, the reason can be the following: the Co3O4 nanosheets with many spaces each other have an increased portion of exposed surfaces and ensure a high utilization of electrode materials, thus a high capacity. Besides, the ultra-long hierarchical heterostructures can suppress the self-aggregation, buffer the volume changes of Co3O4 nanosheets, and keep the effective contact areas of active materials and electrolyte large and sufficient during the cycling, thereby resulting in better cyclic stability and rate capability of the Co3O4/TiO2 hierarchical heterostructures. Herein, the reason can be the following: the Co3O4 nanosheets with many spaces each other have an increased portion of exposed surfaces and ensure a high utilization of electrode materials, thus a high capacity. Besides, the ultra-long hierarchical heterostructures can suppress the self-aggregation, buffer the volume changes of Co3O4 nanosheets, and keep the effective contact areas of active materials and electrolyte large and sufficient during the cycling, thereby resulting in better cyclic stability and rate capability of the Co3O4/TiO2 hierarchical heterostructures. However, the difference in the conductivity between them should be taken into account. To probe the kinetic properties of the hierarchical heterostructures, we take the electrochemical impedance spectroscopy (EIS) measurements. All three plots show partially overlapping semicircles at high-to-medium frequencies, and a line was observed at low frequencies in Figure 8. Apparently, the charge transfer resistances $R_t$ for the three samples is in the ascending order of TiO2 (730.0 $\Omega$) > Co3O4/TiO2 (170.9 $\Omega$) > Co3O4 (137.2 $\Omega$), whilst the contact resistances (see the intercept of the real axis in Figure 8) between electrolyte and electrode materials are similar, which indicates that the secondary Co3O4 nanosheets coating could enable much easier charge transfer at the electrode/electrolyte interface (compared with TiO2 nanofibers) and boost the electronic conductivity. Thus, the improved electronic conductivity is considered to be a key factor in improving the rate capability and cyclic life of the Co3O4/TiO2 hierarchical heterostructures.

**Methods**

**Sample synthesis.** The MO/TiO2 hierarchical nanostructures were prepared by the electrosprining and hydrothermal method[44]. Typically, 0.2429 g Co(NO$_3$)$_2$·6H$_2$O and 0.25 g urea were dissolved in 25 ml deionized water under magnetic stirring. Then the resulting solution was transferred into a 50 ml Teflon-lined autoclave with electrosprun TiO2 nanofibers (20 mg). The autoclave was sealed and heated at 120 $^\circ$C for 6 h, and cooled to room temperature. The film was collected out, washed with ethanol and deionized water, respectively, and then dried under vacuum at 50 $^\circ$C for 12 h. Then the as-collected films were calcined at 400 $^\circ$C for 4 h. For comparison, the single Co3O4 nanostructures were also prepared under the same conditions instead of the addition of TiO2 nanofibers. When Co3O4 precursor solution was replaced by Fe$_2$O3 precursor solution (0.243 g FeCl$_3$ and 30 ml deionized water), Fe$_2$O3 (252.5 g FeCl$_3$·6H$_2$O, 0.25 g polyethylene glycol, 0.9 g sodium acetate and 25 ml ethylene glycol), and CuO precursor solution (0.2557 g CuCl$_2$·2H$_2$O, 0.3 g urea and 30 ml deionized water), and the autoclave was sealed and heated at 90 $^\circ$C for 6 h (Fe$_2$O3), at 200 $^\circ$C for 16 h (Fe$_2$O3), or at 180 $^\circ$C for 12 h (CuO), then the as-collected films were calcined at 500 $^\circ$C for 2 h except Fe$_2$O3/TiO2 hierarchical nanostructures.

**Sample characterization.** The morphology and crystal structure of as-obtained samples were characterized with scanning electron microscopy (SEM Hitachi S-4800) and transmission electron microscope (TEM) recorded on a Tecnai G2 operating at 200 kV. X-ray diffraction (XRD) patterns were recorded on a Rigaku D-Max 2500 diffractometer with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) analysis was carried on an ESCALAB MK X-ray photoelectron spectrometer. Zeta potential was measured by dynamic light scattering (Malvern Nano-ZS). Raman measurements were performed at room temperature using an inVia Reflex Raman spectrometer with Raman shift from 100 to 1000 cm$^{-1}$.

**Electrochemical evaluation.** The electrodes were prepared by mixing active materials (70 wt%), acetylene black (20 wt%), and polyvinylidene fluoride (PVDF, 10 wt%) in N-methyl-2-pyrrolidone (NMP). After the above slurries were uniformly spread onto a copper foil, the electrodes were dried at 80 $^\circ$C in vacuum for 6 h. Then the electrodes were pressed and cut into disks before transferring into an Ar-filled glove box. Coin cells (CR2025) were laboratory-assembled using lithium metal as the counter electrode, Celgard 2400 membrane as the separator and LiPF$_6$ (1 M) in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 vol%) as the electrolyte. The galvanostatic charge-discharge tests were carried out on a Land Battery Measurement System (Land, China). Cyclic voltammetry (CV) and impedance were performed using a VMP3 Electrochemical Workstation (Bio-logic Inc.).

In summary, a simple, general yet effective strategy is developed based on the advantageous combination of the versatility of the electrosprining technique and hydrothermal growth to achieve various MOs, including Co$_3$O$_4$, Fe$_2$O$_3$, Fe$_3$O$_4$, and CuO, grown on pristine TiO$_2$ nanofibers to form MO/TiO$_2$ hierarchical heterostructures. As potential anode materials for LIBs, the as-formed Co$_3$O$_4$/TiO$_2$ hierarchical heterostructures exhibit high reversible capacity, improved cycling stability and rate capability with respect to the pristine TiO$_2$ nanofibers. The improved electrochemical performance is ascribed to the synergistic effect of the advantageous integration of Co$_3$O$_4$ and TiO$_2$ hierarchical nanostructure. The proposed synthesis strategy would open up new opportunities in the development of high performance next-generation LIBs used for alternative energy and electric transportation. Such hierarchical heterostructures might also be used in broad fields including photoelectrochemical water splitting and gas sensors.
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Additional information
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