

Figure S1. The pristine $Co_2(OH)_2CO_3$ nanowire arrays. (a) Low-magnification SEM image of the $Co_2(OH)_2CO_3$ nanowire arrays on nickel foam and (b) corresponding XRD pattern. (c-e) TEM and HRTEM images of the nanowire (SAED pattern in inset).



Figure S2. ALD-TiO₂ nanotubes based on $Co_2(OH)_2CO_3$ nanowire template. (a) Lowmagnification SEM image of ALD-TiO₂ nanotube arrays on nickel foam. (b, c) TEM images of the as-deposited ALD-TiO₂ nanotube. The SAED pattern in inset shows that the nanotube wall is amorphous. (d) XRD pattern of ALD-TiO₂ nanotube arrays on nickel foam, showing the absence of $Co_2(OH)_2CO_3$ peak. XRD peak from TiO₂ is also not present due to the amorphous structure.



Figure S3. TiO₂/NiO core-branch hollow nanowire arrays. (a) Low-magnification SEM image on nickel foam. (b, c) SEM images on carbon cloth.



Figure S4. XPS spectra of TiO_2/NiO core-branch hollow nanowires: (a) Ni 2p, (b) Ti 2p, and (c) O1s. The O 1s spectrum is deconvoluted into two components. The main peak (529. 9 eV) is due to the typical metal-O bonds (Ti–O and Ni–O). The weak shoulder peak (531.5 eV) is ascribed to OH– due to the atmospheric contact.



Figure S5. (a, b) TEM-HRTEM images of ALD-TiO₂ nanotubes after annealing process (SAED pattern in inset). (c) BET measurement of TiO₂/NiO core-branch hollow nanowires. The calculated specific surface area is ~167 m²/g.



Figure S6. (a) Photograph of the assembled battery based on TiO₂/NiO core-branch hollow nanowire arrays as cathode. (b) Galvanostatic charge/discharge curves of tandem battery devices (three batteries in series).



Figure S7. Electrochemical characterization of TiO_2/Co_3O_4 core-branch hollow nanowire electrode. (a) CV curve of TiO_2/Co_3O_4 core-branch hollow nanowire at the scanning rate of 10 mV s⁻¹ in 2 M KOH. (b) Discharge curves at different current densities and (c) Specific capacities at different current densities.

The reaction in the CV curve can be simply illustrated as follows:

$$Co_3O_4 + OH^- + H_2O \leftrightarrow 3CoOOH + e^-$$

The TiO_2/Co_3O_4 core-branch nanowires electrode exhibits a capacity of 135 mAh/g at 2 A/g and 121mAh/g at 10 A/g, with a retention of 89.6 %.



Figure S8. Morphology of the TiO₂/NiO core-branch hollow nanowire arrays after 12,000 cycles at 2 A/g.

Preparation of TiO₂/Fe₂O₃ core-branch hollow nanowire arrays.

The self-supported TiO₂ nanotube arrays were used as the scaffold for Fe₂O₃ branch spikes growth through a simple hydrolysis deposition method. First, the TiO₂ nanotube arrays were coated with ZnO layer by a chemical bath deposition (CBD) at 50 °C for 12 h. The CBD solution was prepared by dissolving 0.6 g Zn(NO₃)₂, 0.15 g NH₄F, and 0.6 g CO(NH₂)₂ in 75 mL of distilled water. Afterwards, the sample was annealed at 350 °C in Argon for 2 h. Then, the sample was placed into a 50 mL solution containing 0.27 g of Fe(NO₃)₃ and kept still at room temperature for 10 h. After the immersion, it was taken out, dried in air, and treated at 350°C in air for 2 h to form TiO₂/Fe₂O₃ core-branch hollow nanowire arrays.