Experimental Section

Synthesis of FeVO₄ nanosheet arrays

In a typical synthesis, VCl₃ powders (Merck, 99%) were loaded in an alumina crucible and placed in the middle of the horizontal tube furnace (Lingberg Blue M). Cleaned-stainless steel (SS304) foils ($1 \times 1 \times 0.01$ cm) were placed downstream at 4-15 cm away from the center of crucible. Before the deposition, the quartz tube was evacuated to ~ 10^{-2} mbar and flowed with compressed air (21% O₂, 79% N₂) at a rate of 100 sccm using a mass flow meter controller. The furnace was then heated to 723 K at a rate of 20 K min⁻¹ and held at 723 K for 1 h. The ambient pressure was ~0.82mbar during the growth process. Subsequently, the furnace was cooled to room temperature. The loading density of the FeVO₄ nanosheets was about 0.5 mg cm⁻².

Materials Characterization

X-ray powder diffraction (XRD) patterns were recorded on a Bruker AXS D8 advance X-ray diffractometer for 20 range of 10 to 70° using Cu K_a radiation. The morphology was investigated by using a field-emission scanning electron microscopy (FESEM) system (JEOL, Model JSM-7600F), and the nanostructures were characterized by using a transmission electron microscopy (TEM) instrument (JEOL, Model JEM-2010 and 2100F) operating at 200 kV. Elemental mapping was conducted using an energy dispersive spectroscopy attachment to the TEM (JEOL 2100F). For TEM observation, the as-prepared sample on the surface of SS foil was ultrasonicated in an ethanol solution for 30 min, and the suspension was then dropped onto carbon copper grids. Inductively coupled plasma (ICP, Dual-view Optima 5300 DV ICP-OES system) was employed to measure the elemental contents of iron and vanadium. For ICP measurement, the as-prepared sample on the surface of SS foil was peeled off by adhesive tape, and then dissolved in 40% of hydrofluoric acid. X-Ray photoelectron spectroscopy (XPS) measurement was performed on VG Escalab 250 spectrometer using an Al K α 1846.6 eV anode.

Electrochemical Measurements

The coin-type cells were assembled in an argon-filled glove-box, where both moisture and oxygen levels were less than 1 ppm. The as-grown samples were directly used as working electrodes without any further treatments. Lithium foils were used as the counter/reference electrode, and the electrolyte solution was made of 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1, w/w). The cells were tested on a NEWARE multi-channel battery test system with galvanostatic charge and discharge in the voltage window of 0.005-3.5 V (vs. Li/Li⁺).



Figure S1. Schematic of 2D nanosheet arrays directly growing on a current-collecting substrate as anodes for LIBs, showing efficient electron transport and fast lithium diffusion.



Figure S2. Temperature profile of the tube furnace at 723 K.



Figure S3. (a) EDX spectrum of a single nanosheet (inset), and corresponding elemental mappings of Fe (b), V(c) and O (d), showing that Fe, V and O are homogeneously dispersed in the nanosheet. XPS spectra of Fe 2p (e) and V 2p (f) obtained from the as-grown nanosheet arrays.



Figure S4. XRD patterns of CVD-grown FeVO₄ nanosheet arrays on SS foil and SS foil, and standard Fe₂O₃, Fe₃O₄, FeVO₄ and Fe₂V₄O₁₃ for comparison.



Figure S5. FESEM images of untreated (a-b) and annealed (c) SS foils. The nanosheets in (c) are indicated by the red arrows. (d) TEM image of a single nanosheet from the annealed SS foil and corresponding SAED pattern (inset).



Figure S6. FESEM images of as-grown films on a SS substrate collected at (a) $d_{sub} = 4$ cm, (b-d) $d_{sub} = 7$ cm and (e) $d_{sub} = 15$ cm.



Figure S7. CV curves of amorphous FeVO4 nanosheet arrays for the first three cycles at a scan rate of 0.2 mV s⁻¹.



Figure S8. Ex situ XPS of Fe and V 2p spectra obtained from the FeVO₄ electrode on the fully charge and discharge states during the first cycle. (a) Fe 2p, 1st-discharge; (b) V 2p, 1st-discharge; (c) Fe 2p, 1st-charge; and (d) V 2p, 1st-charge.