Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

"Sea cucumber"-like Ti@MoO_3 nanorod arrays as self-supported lithium ion battery anodes with enhanced rate capability and durability

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Experimental

Sample Preparation: All chemical reagents were of analytical grade and were obtained commercially. Ti nanorod arrays were fabricated on circular Ti (Ti-Mo alloy, Mo=0.3 wt%) alloy foam plates purchased from Baiji Jinkai Corporation of China using a electroless wet chemical etching method. The etching was carried out in 0.25 wt% HF solution for 10 minutes. The obtained Ti nanorod arrays were rinsed with deionized water fully and dried overnight. A CHI 660D electrochemical workstation was used for electrodeposition. The acid peroxo-polymolybdate electrolyte was prepared by dissolving 3.0 g Mo powder (2 μm, Aladdin Chemistry) in 100 mL H_2O_2 at 60 °C following the reactions:

$$2Mo+10H_2O_2 \rightarrow Mo_2O_{11}^{2-}+2H^+ +9H_2O \quad (1)$$

When the metal powder was completely dissolved and the exothermic reaction had ended, a Pt foil was added to reduce the excess peroxide. Then the solution was

neutralized to be neutral with ammonia. The MoO_3 nanoparticles were electrodeposited at room temperature with a constant reduction current of 1 mA using 154 mm^2 Ti nanorod array slices, a Pt foil and a saturation mercury electrode (SCE) as the working, counter and reference electrodes, respectively. The electrochemical reaction followed equation 2. The as-deposited samples were heat-treated at 400 °C in Ar atmosphere for 3 h. The weight of MoO_3 on one slice was about 2 mg cm^{-2}.

$$Mo_2O_{11}^{2-}+(2+x)H^{+}+xe \rightarrow 2MoO_3+\frac{8-x}{4}O_2+\frac{2+x}{2}H_2O \quad . \qquad (2)$$

Structural and electrochemical characterization: Scanning electron microscope (SEM) images and Energy dispersive X-ray spectroscopy (EDS) were obtained on a Hitachi Su-8100. The X-ray diffraction (XRD) patterns were obtained on a PANalytical X´pert PRO X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). X-ray photoelectron spectra (XPS) were obtained with a K-Alpha electron spectrometer (Thermofish Scientific Company) using Al Kα (1486.6 eV) radiation. The base pressure was about 1×10^{-8} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. Transmission electron microscope (TEM) images was obtained on a FEI Tecnai G^2. The cyclic voltammetry (CV) tests of the batteries were carried out on the CHI 660 electrochemical workstation. The battery tests were carried out in the CR2025 button testing batteries consisting of Ti@MoO_3 nanorod arrays, microporous membrane (Celgard 2400) and lithium foil as the counter electrode. The electrolyte was $LiPF_6$ (1M) in a 50: 50 (V/ V) mixture of ethylene carbonate (EC) and diethyl carbonate (DMC) provided by Tinci Company (Guangzhou China). A BTS-2000 Neware Battery Testing System was employed for

charge/discharge testing in the voltage range of 3.0–0.02 V vs. Li^+/Li.

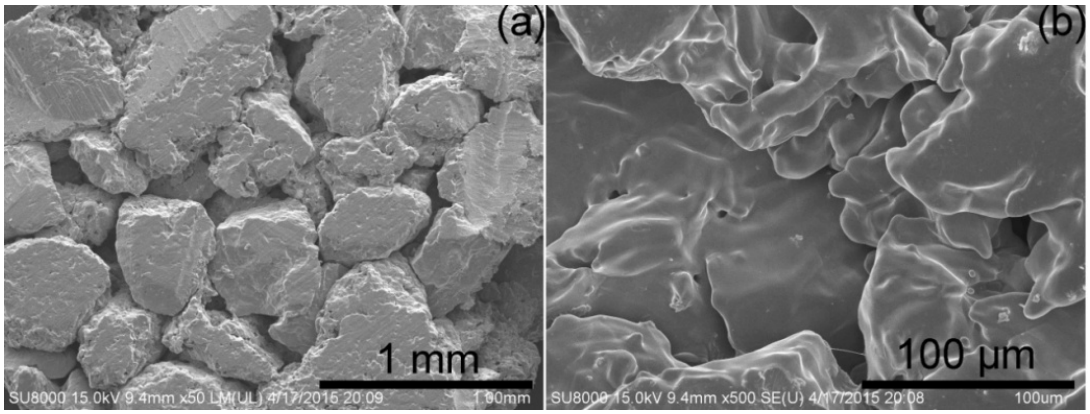


Fig. S1. SEM images of raw Ti foam.

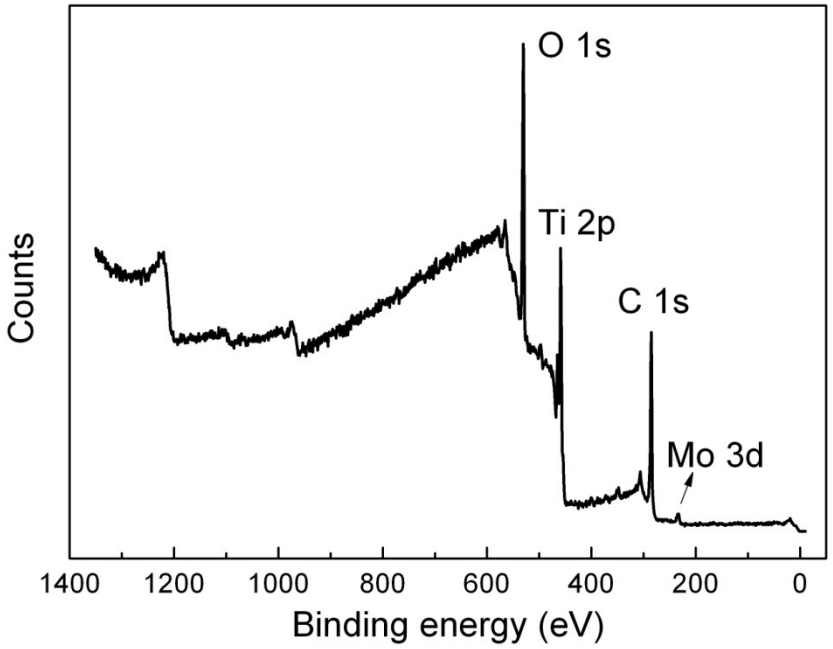
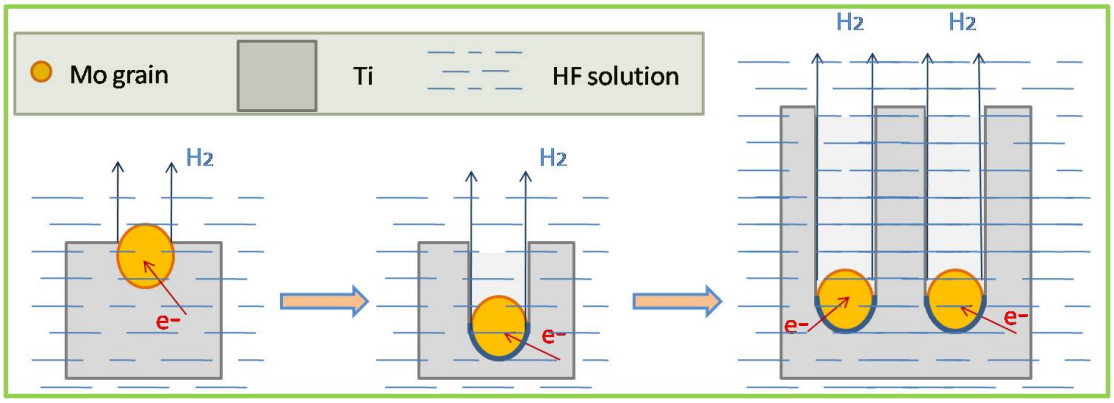


Fig. S2. XPS survey of the raw Ti-Mo alloy foam.



Scheme S1. Schematic diagram of preparing Ti nanorod arrays.

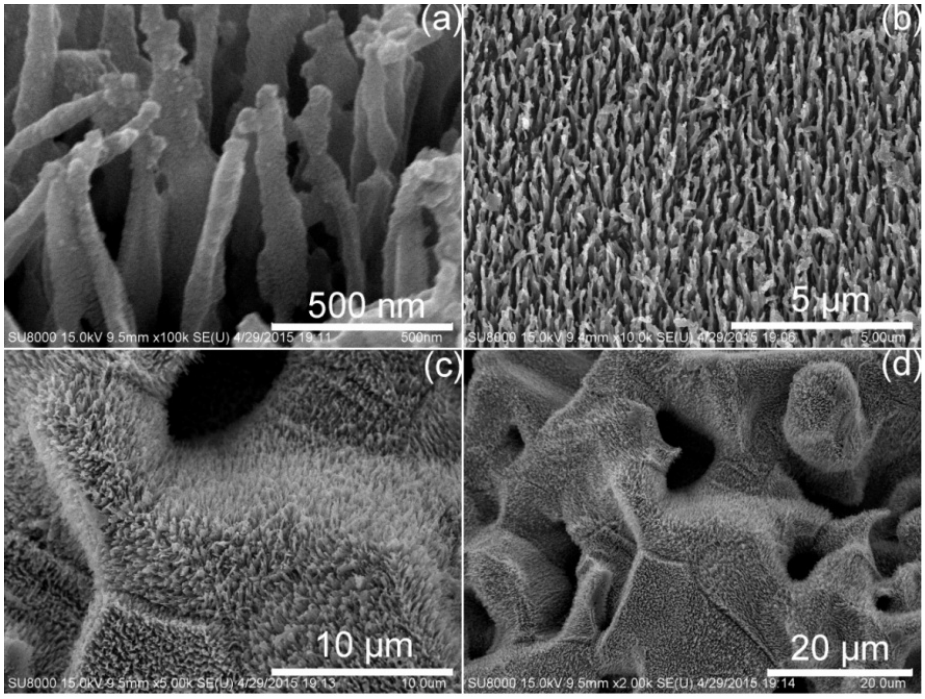


Fig. S3. SEM images of Ti nanorod arrays obtained from wet corrosion.

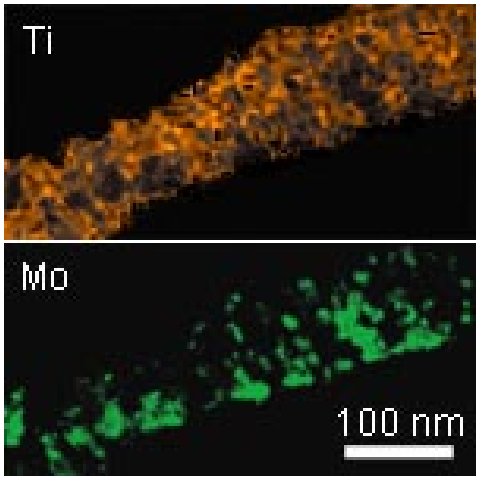


Fig. S4. EDS mapping images of a Ti@MoO3 nanorod.

Table S1. Capacity retention (%) of the samples from different current densities.

Sample preparation	Capacity retention (%) at various rate current densities (A g^{-1})						
condition (mA cm^{-2})	1	5	10	20	50	100	1
2	64.2	44.3	36.4	28.5	17.4	9.8	59.9
4	72.7	58.7	51.8	42.3	29.5	20.9	71.2
5	67.2	48.4	35.2	25.2	15.0	—	67.1

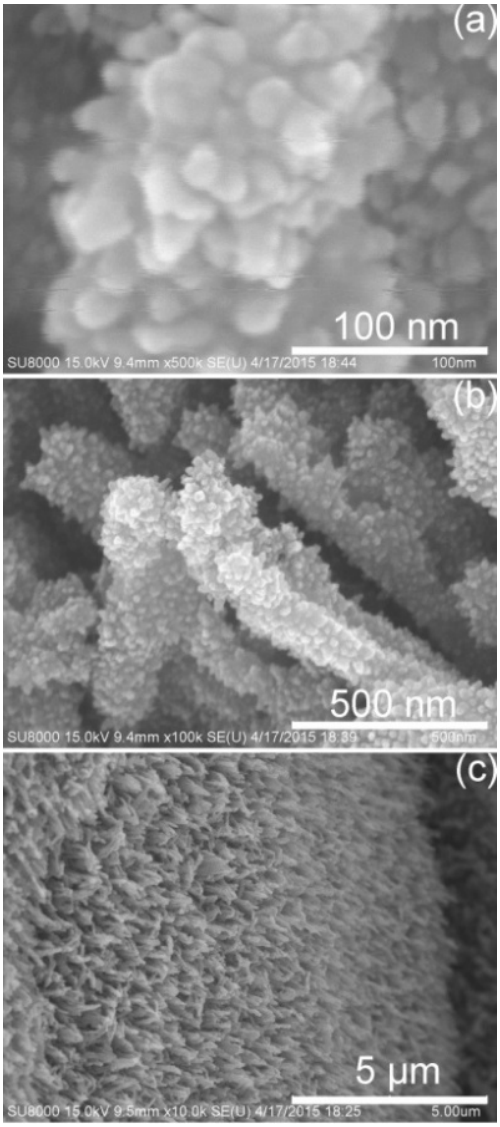


Fig. S5. SEM images with different magnifications of Ti@MoO_3 nanorod arrays.