## Supplementary Information

## *In situ* investigation of Li and Na ion transport with single nanowire electrochemical devices

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**Figure S1.** X-ray diffraction (XRD) pattern (a), TEM image (b), HRTEM image (c) and the fourier transform of the image (d) of  $H_2V_3O_8$  nanowires.



**Figure S2.** I-V curves of section 1-2, 2-3, 3-4 (a-c) of the nanowire before and after the immersion of electrolyte, respectively; (d) I-V curve of the Au electrodes.



Figure S3. CV curves with (red line) and without (black line) nanowire at the scan rate of 0.5 mV/s.



**Figure S4.** SEM (a) and element mapping (b) of HOPG flake after reaction. (c) Energy-dispersive X-ray spectroscopic (EDS) result of HOPG flake immersed in electrolyte without reaction.



**Figure S5.** I-V curves of section 1-2, 2-3, and C before (red line) and after (black line) the electrochemical process when Na ions were the charge carriers, respectively. The nanowire conductance decreased 97.8%, 3.4% for section A and B, and there was no decrease for section 3-4.



**Figure S6.** Typical optical image of the nanowire electrode with the second configuration. The nanowire was covered by passivation layer with only one end immersing in the electrolyte. The red box shows the exposing end of the nanowire.



Figure S7. The crystal structure of  $H_2V_3O_8$ . The V atoms are blue, and O atoms are red.



**Figure S8.** Battery performance of vanadium oxide nanowire cathodes for lithium batteries (a) and sodium batteries (b) at the current density of 200 mA/g. Insets are the corresponding charge–discharge curves.