Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Contents

1. **Experimental Section**
2. **Figure S1. SEM images of (a) commercial Cu foil, and after treated in absolute alcohol for (b) 1 h (c) 2 h (d) 3 h (e) 4 h, and (f) 5 h, respectively.**
3. **Figure S2. Evolution scheme for the morphologies of Cu sheets for different time.**
4. **Figure S3. Cu 2p XPS spectrum of 3D Cu nanowire.**
5. **Figure S4. SEM images of the 3D Cu nanowires after plating (a) 0.5 mAh cm^{-2}, (b) 1.0 mAh cm^{-2}, (c) 2.0 mAh cm^{-2} and (d) 4.0 mAh cm^{-2} of Na at high resolution.**
6. **Figure S5. SEM images of the 3D Cu nanowires after stripping (a) 0.5 mAh cm^{-2}, (b) 1.0 mAh cm^{-2}, (c) 2.0 mAh cm^{-2} and (d) 4.0 mAh cm^{-2} of Na at high resolution.**
7. **Figure S6.The AFM height profiles after plating (a) 0.5 mAh cm^{-2}, (b) 1.0 mAh cm^{-2}, (c) 2.0 mAh cm^{-2}, and (d) 4.0 mAh cm^{-2} of Na into 3D Cu nanowires at the current density of 1.0 mA cm^{-2}.**
8. **Figure S7. Morphological evolution of Na plating on planar Cu foil, after plating (a) 0.5 mAh cm^{-2}, (b) 1.0 mAh cm^{-2}, (c) 2.0 mAh cm^{-2}, and (d) 4.0 mAh cm^{-2} of Na into planar Cu foil.**
9. **Figure S8. SEM image of Cu foil after stripping 4.0 mAh cm^{-2} of Na from planar Cu foil at the current density of 1.0 mA cm^{-2}.**
10. **Figure S9. Series of optical microscope images depicting the Na metal deposition processes on (a-d) planar Cu foil and (e-h) 3D Cu nanowires. Scale bar: 100 μm.**
11. **Figure S10. SEM images of Cu nanowires with thick diameter of ~ 300 nm at different resolution.**
12. **Figure S11. (a) Cycling performance at 0.5 mA cm^{-2} with (b) enlarged voltage profiles of the Cu nanowires with thick diameter of ~ 300 nm.**
13. **Figure S12. Cycling performance of planar Cu foil with different areal capacities from 1.0 to 3.0 mAh cm^{-2} at 1.0 mA cm^{-2}.**

14. **Figure S13. Galvanostatic plating/stripping curves of Na at different areal capacity on 2D Cu foil at the 60th cycle.**
15. **Figure S14. (a) Rate capability and (b) charge/discharge profiles of the full cells at current densities of 0.5, 1.0, 2.0, 5.0, and 10.0 C (1C = 118 mAh g^{-1}).**

Experimental Section

Material Synthesis. For fabricating 3D Cu nanowires, a piece of commercial Cu sheet (2 cm × 5 cm) was firstly washed with HCl solution (0.1 M) and deionized water for three times to remove the surface impurities. Then transforming the Cu sheet into an autoclave filled with 40 mL absolute alcohol. The mixture was then put into a Telfon vessel (50 mL) and heated to 160 °C for 3 h to obtain the final 3D Cu nanowires. By varying the reaction time from 1 h to 5 h, other Cu nanostructures including nanorod, nanobelt, nanoear, and nanoparticle were obtained. The hydrothermal atmosphere can afford certain temperature and pressure to provide energy for Cu foil. Thus, the treated Cu would be rearrangement in order to achieve high surface energy, leading to the transition from large size to small ones. This assumption is further confirmed by SEM images at different treating time as displayed in Figure S1. The rodlike structure was first formed on Cu surface after treating 1 h. Then it turned into ununiform nanobelt morphology as increasing the reaction time to 2 h. The nanobelt then progressively grows into uniform nanowire, nanoear, and nanoparticle as the reaction time increased from 3 h to 5 h. The structure evolution is presented in Figure S2.

The $Na_3V_2(PO_4)_3$@C composite was prepared according to our previous work. In a typical synthesis, V_2O_5, $NH_4H_2PO_4$, and Na_2CO_3 were added to distilled water and magnetically stirred at room temperature. Then, ascorbic acid and polyethylene glycol were added to form a blue suspension, which then transferred to a Teflon-lined autoclave. The sealed autoclave was kept at 180 °C for 40 h, and then naturally cooled to room temperature. The resulting brown mixture was ultrasonically and then heated on a hot plate with stirring to evaporate water. The obtained brown sol was dried at 120 °C overnight. This precursor was thoroughly ground and preheated at 350 °C for 4 h. The preheated sample was ground to powders and finally calcined at 750 °C for 6 h in flowing Ar atmosphere. The carbon content of the $Na_3V_2(PO_4)_3$@C composite is ~ 12 %.

Materials characterization. XRD patterns were collected using a Rigaku MiniFlex600 with Cu Kα radiation between 10° and 70° at a scan rate of 4° s^{-1}. The morphology and structure of the as-prepared materials were characterized by SEM (JEOL, JSM-7500F) and TEM (JEOL, 2100F). XPS was performed on a Perkin Elmer PHI spectrometer at room temperature with Al Kα radiation. AFM experiments were conducted on Bruker Multimode 8. The optical microscope images were taken on the optical microscope from Olympus (MM6-AF).

Electrochemical Tests. The cells (CR2032 coin cells) were assembled in an argon - filled glove box ($O_2 \leq 0.1$ ppm, $H_2O \leq 0.5$ ppm, Mikrouna). Na metal act as the reference and counter electrodes. The separator was Celgard. The electrolyte was 1 M $NaPF_6$ in dimethyl ether (DME). Galvanostatic charge/discharge tests were tested on Land CT2001A battery. Cyclic voltammetry was carried out on Parstat 263A electrochemical workstation (AMTECT Company). The electrochemical impedance spectroscopy was measured using a Parstat 2273A workstation in the frequency from 100 KHz to 100 mHz. All the tested electrodes were taken out from the cycled cell and washed with DME in an argon-filled glove box.

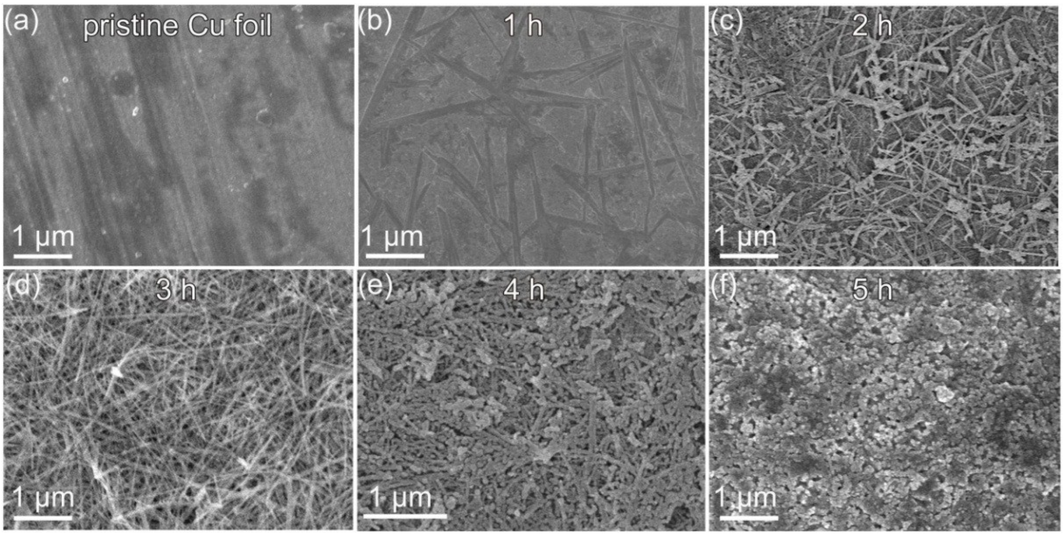

Figure S1. SEM images of (a) commercial Cu foil, and after treated in absolute alcohol for (b) 1 h (c) 2 h (d) 3 h (e) 4 h, and (f) 5 h, respectively.

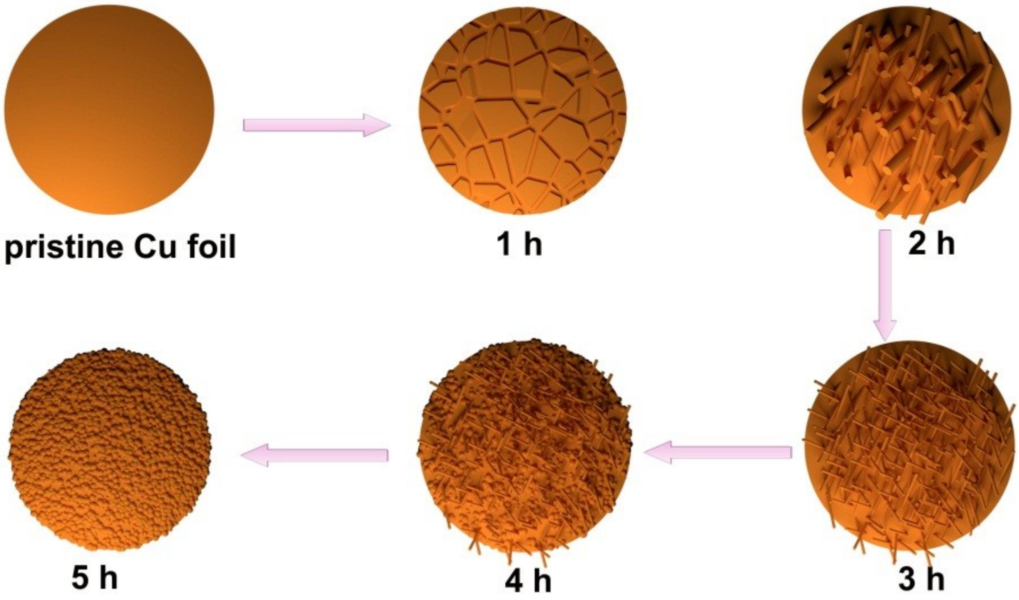

Figure S2. Evolution scheme for the morphologies of Cu foil at different treating time.

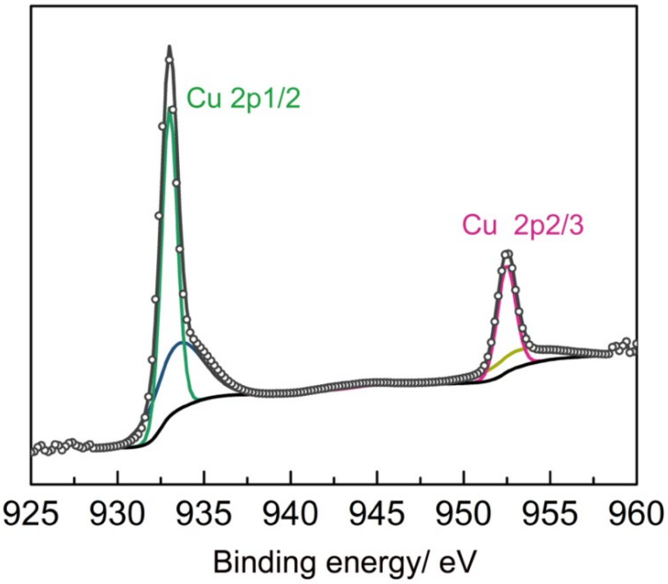

Figure S3. Cu 2p XPS spectrum of 3D Cu nanowires.

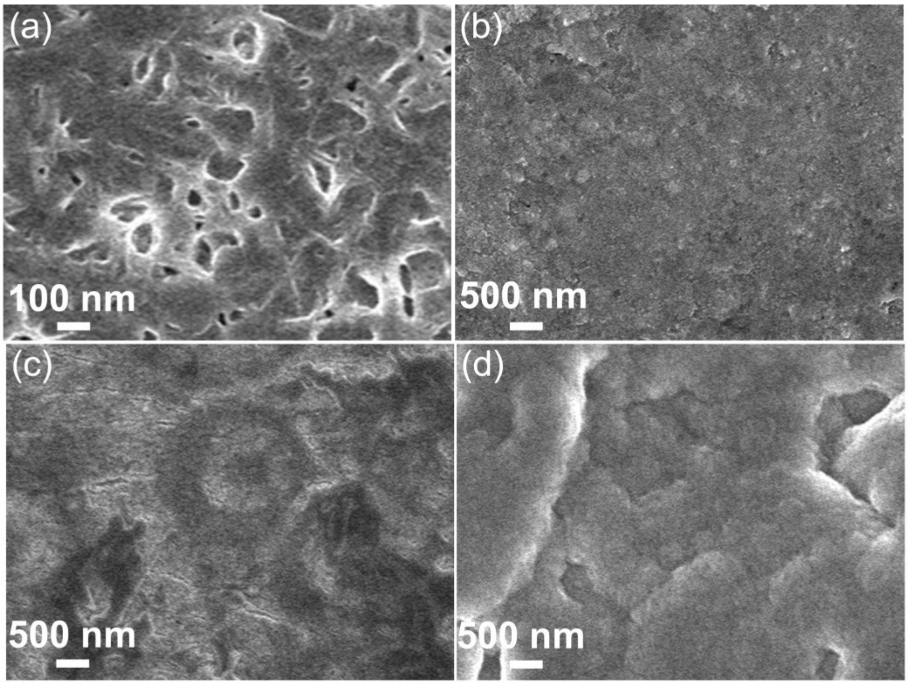

Figure S4. SEM images of the 3D Cu nanowires after plating (a) 0.5 mAh cm^{-2}, (b) 1.0 mAh cm^{-2}, (c) 2.0 mAh cm^{-2} and (d) 4.0 mAh cm^{-2} of Na at high resolution.

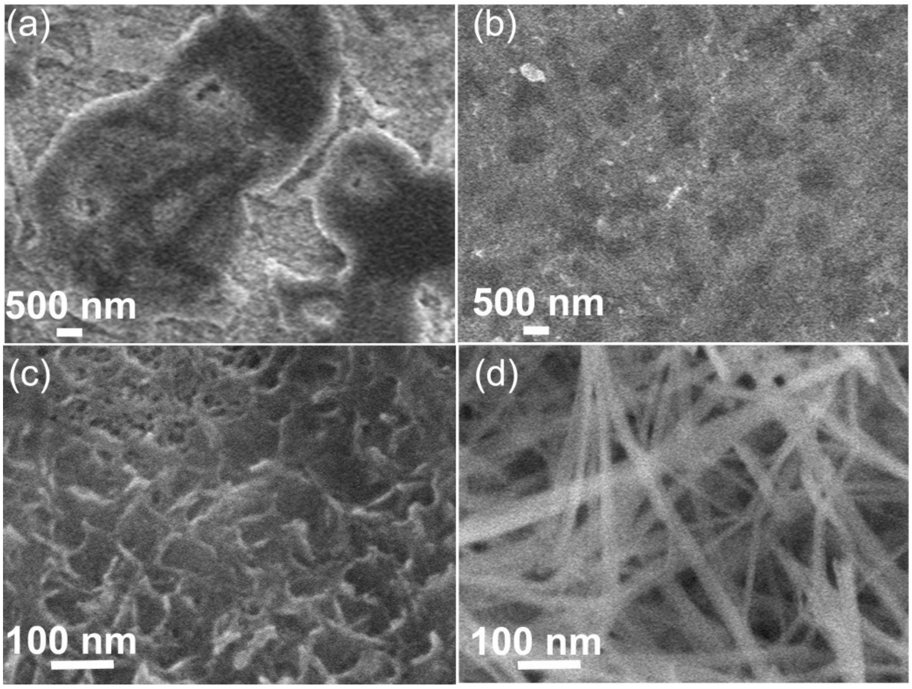

Figure S5. SEM images of the 3D Cu nanowires after stripping (a) 0.5 mAh cm^{-2}, (b) 1.0 mAh cm^{-2}, (c) 2.0 mAh cm^{-2} and (d) 4.0 mAh cm^{-2} of Na at high resolution.

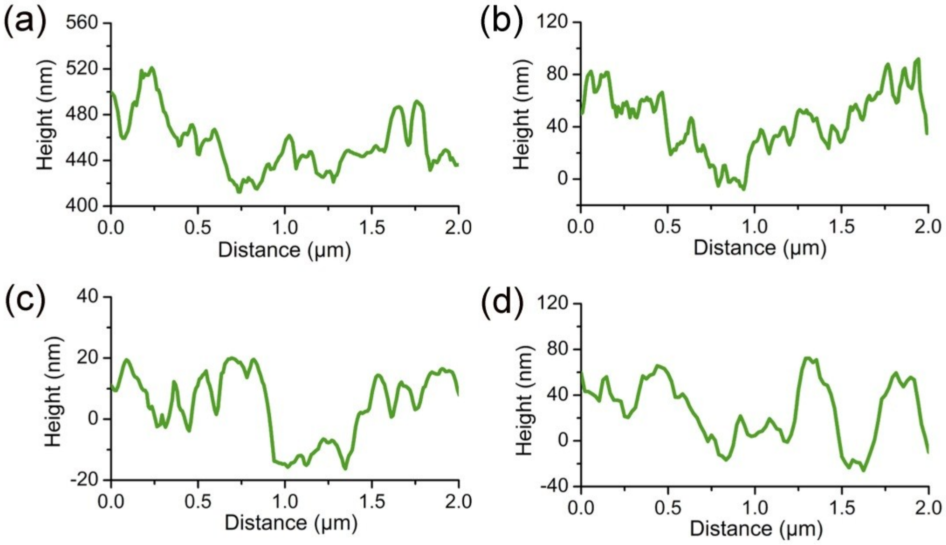

Figure S6. The AFM height profiles after plating (a) 0.5 mAh cm^{-2}, (b) 1.0 mAh cm^{-2}, (c) 2.0 mAh cm^{-2}, and (d) 4.0 mAh cm^{-2} of Na into 3D Cu nanowires at the current density of 1.0 mA cm^{-2}.

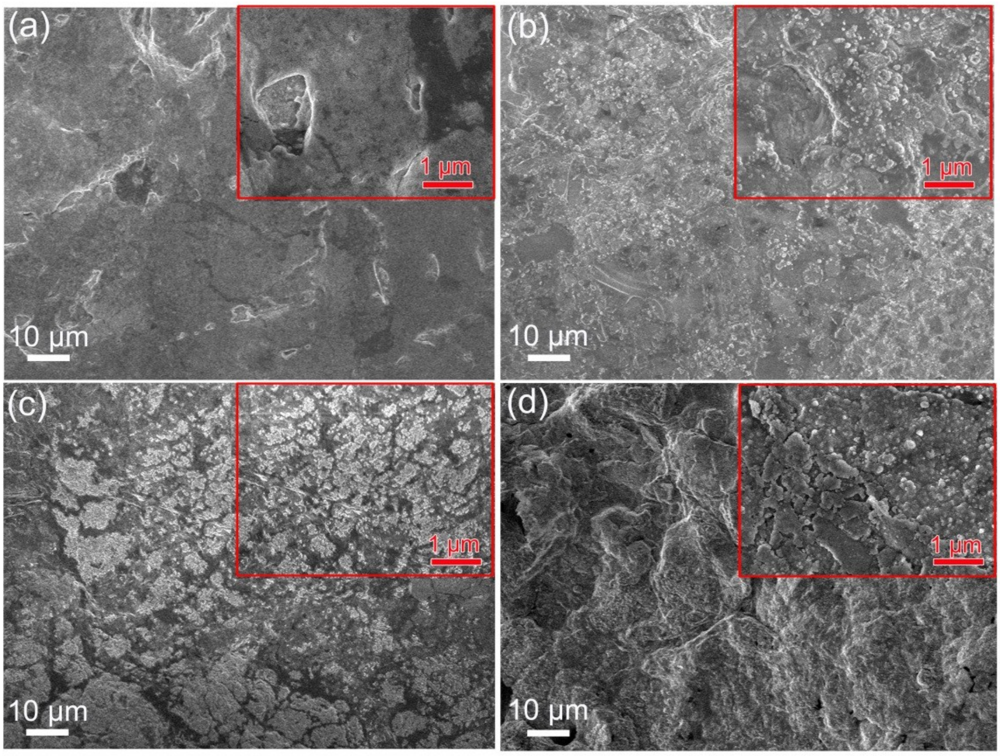

Figure S7. Morphological evolution of Na plating on planar Cu foil, after plating (a) 0.5 mAh cm^{-2}, (b) 1.0 mAh cm^{-2}, (c) 2.0 mAh cm^{-2}, and (d) 4.0 mAh cm^{-2} of Na into planar Cu foil. The inset is the corresponding SEM images at high magnification.

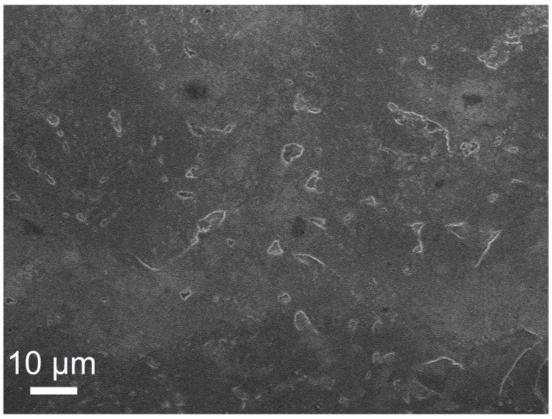

Figure S8. SEM image of Cu foil after stripping 4.0 mAh cm^{-2} of Na from planar Cu foil at the current density of 1.0 mA cm^{-2}.

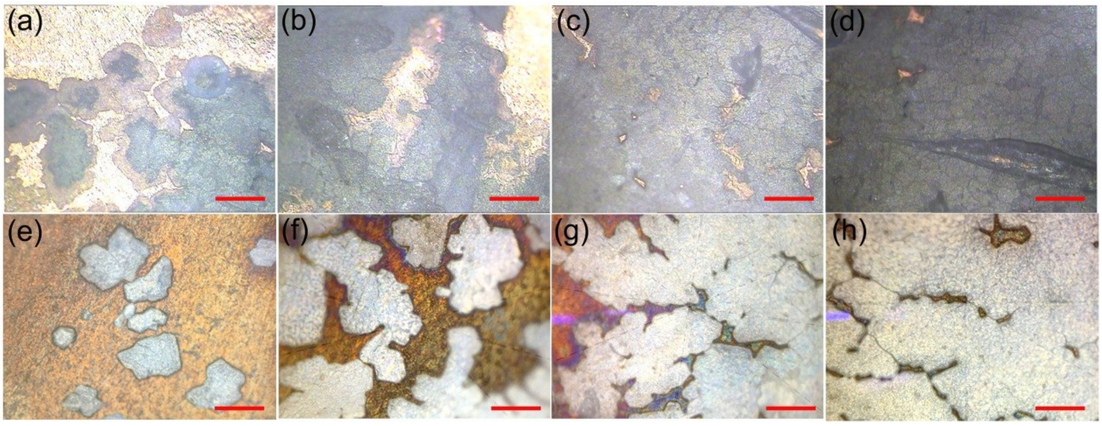

Figure S9. Series of optical microscope images depicting the Na metal deposition processes on (a-d) planar Cu foil and (e-h) 3D Cu nanowires. Scale bar: 100 μm.

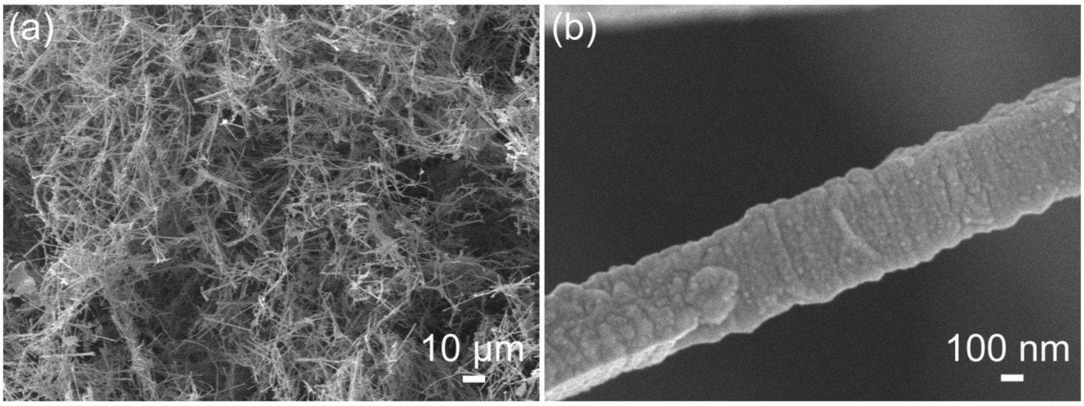

Figure S10. SEM images of Cu nanowires with thick diameter of ~ 300 nm at different resolution.

Cu nanowires with thick diameter of ~ 300 nm are prepared according to the literature.[1] In details, NaOH, $Cu(NO_3)_2$, EDA, and N_2H_4 were mixed in sequence in a 50 mL round bottom flask. Then, the solution was heated to 80 ˚C under a stirring speed at 200 rpm. After the mixture turned into colorless, the solution was transferred into a 50 ml centrifuge tube immersed in an ice bath, and PVP (0.4 wt%) aqueous solution was added to the top of the reaction solution gently. CuNWs floated on the top of the reaction solution after 1 hour of growth. Then, they were re-dispersed in an aqueous washing solution containing N_2H_4 (3 wt%) and PVP (1 wt%). The combined solution was centrifuged at 2,000 rpm for 5 minutes. The purification process was repeated by three times to eliminate redundant reaction agents. Finally, after three times of purification by deionized water via centrifugation at 2,000 rpm for 5 minutes and freeze process, Cu nanowires were obtained.

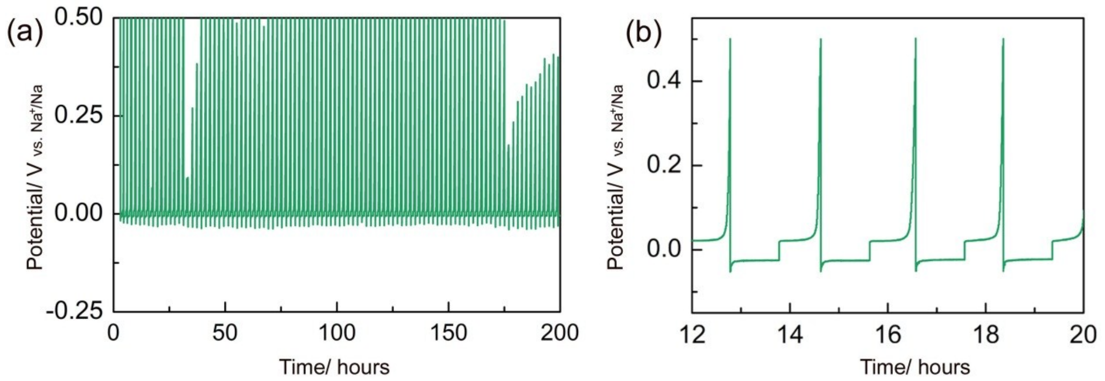

Figure S11. (a) Cycling performance at 0.5 mA cm^{-2} with (b) enlarged voltage profiles of the Cu nanowires with thick diameter of ~ 300 nm.

The plating/stripping cycles display the unstable performance and low Coulombic efficiency of thick Cu nanowires.

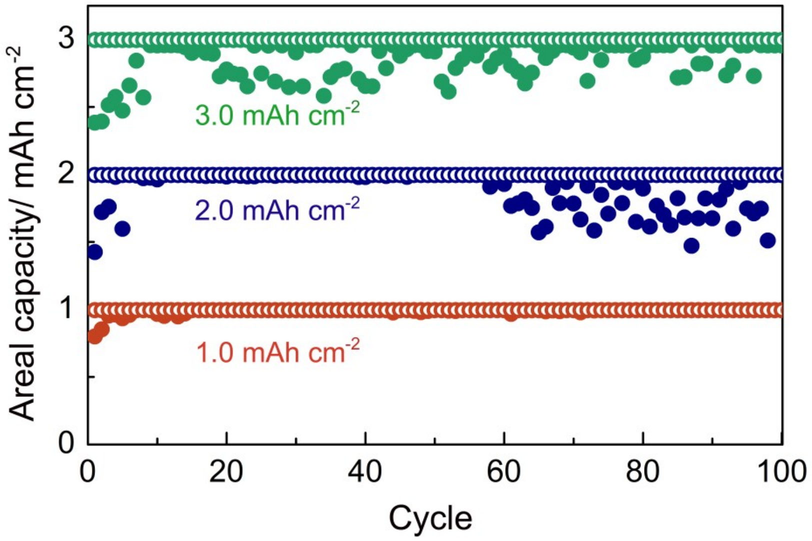

Figure S12. Cycling performance of planar Cu foil with different areal capacities from 1.0 to 3.0 mAh cm^{-2} at 1.0 mA cm^{-2}.

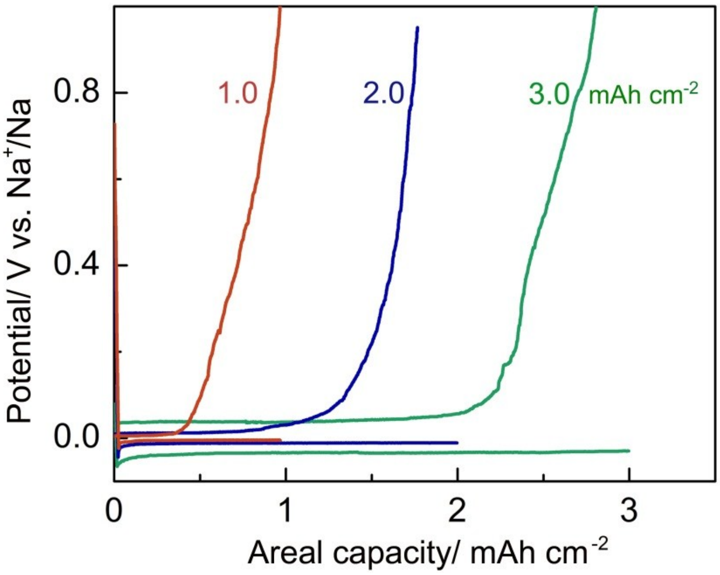

Figure S13. Galvanostatic plating/stripping curves of Na at different areal capacity on planar Cu foil at the 60th cycle.

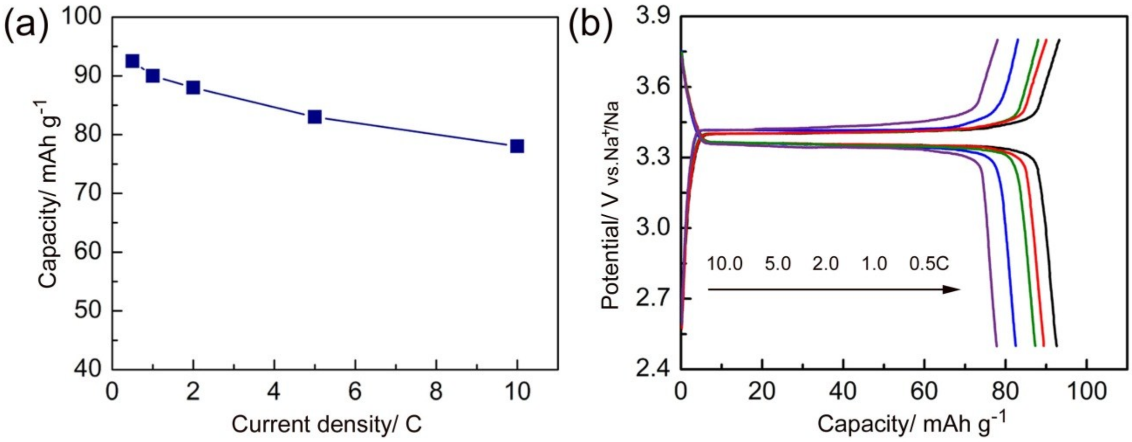

Figure S14. (a) Rate capability and (b) charge/discharge profiles of the full cells at current densities of 0.5, 1.0, 2.0, 5.0, and 10.0 C (1C = 118 mAh g^{-1}).

Reference:

1. Y. Tang, K. L. Yeo, Y. Chen, L. M. Yap, W. Xiong, W. L. Cheng, *J. Mater. Chem. A*, 2013, **1**, 6723-6726.