Supporting Information

Vertical and Cross-linked $Ni(OH)_2$ Network on Cellulose-fiber Covered with Graphene as Binder-free Electrodes for Advanced Asymmetric Supercapacitor

Lin-Lin Zhang, Huan-Huan Li, Chao-Ying Fan, Kang Wang, Xing-Long Wu, Hai-Zhu Sun, Jing-Ping Zhang**

Faculty of Chemistry, National & Local United Engineering Laboratory for Power Batteries, Northeast Normal University, Changchun 130024, China.
Email: *jpzhang@nenu.edu.cn; sunhz335@nenu.edu.cn.*

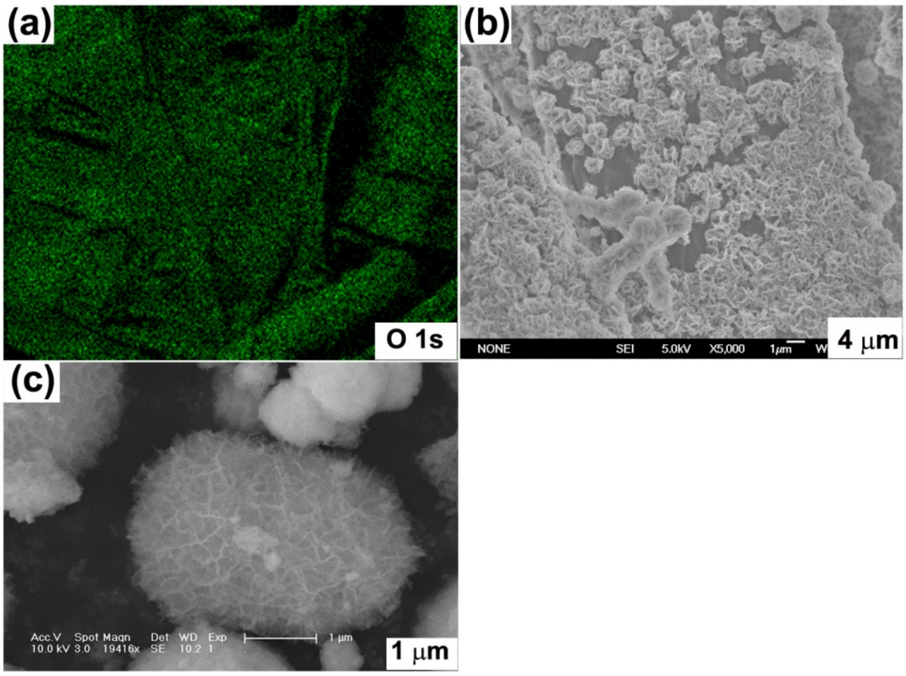

Fig. S1 (a) O 1s elemental mapping image of carbon fiber covered by graphene (CFG). (b) and (c) are SEM images of the $Ni(OH)_2$-CF composite and $Ni(OH)_2$, respectively.

As shown in Fig. S1a, oxygen element uniformly distributes on the carbon fiber covered with graphene. Moreover, the oxygen functional groups can enhance the wettability of the hybrid, which is favor to the grown of the $Ni(OH)_2$ to form the vertically nanosheet-like structure via electrostatic interaction with nickel ion on the CFG surface. However, the morphology of the $Ni(OH)_2$-CF composite without the graphene layer shows microsphere structure and heterogeneously disperses on the pure carbon fiber shown in Fig. S1b. The interconnected nanosheet-like pure $Ni(OH)_2$ crystal also assembles into irregular microsphere with several micron (Fig. S1c).

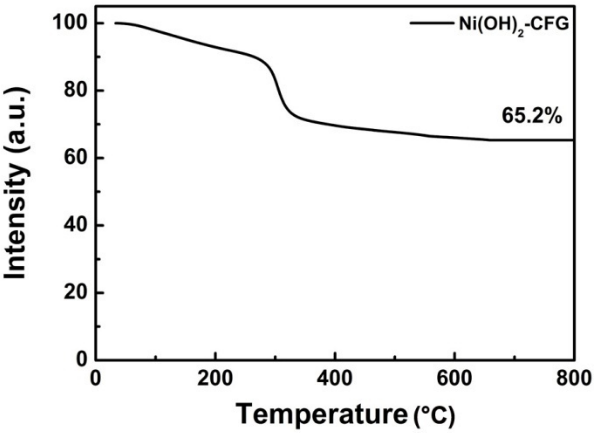

Fig. S2 The TGA curve of the $Ni(OH)_2$-CFG composite in an air atmosphere.

The weight percentage of $Ni(OH)_2$ in the $Ni(OH)_2$-CFG composites was determined by TGA via oxidative decomposition under air atmosphere. As shown in Fig. S2, the $Ni(OH)_2$-CFG composite shows a slight weight loss below 200°C, which attributes to the evaporation of physical adsorbed water molecules. The sharp weight change between 300°C and 400°C in TGA curves is due to both the decomposition of $Ni(OH)_2$ to NiO ($Ni(OH)_2 \rightarrow NiO + H_2O$) and the combustion of CFG. According to Fig. S2, the 65.2 wt% residual weight is NiO, indicating the weight percentage of $Ni(OH)_2$ in the $Ni(OH)_2$-CFG composite is 80.9 wt%. It was also calculated (79.8 wt%) by the mass difference before and after the reaction, which was in accordance with the result of TGA.

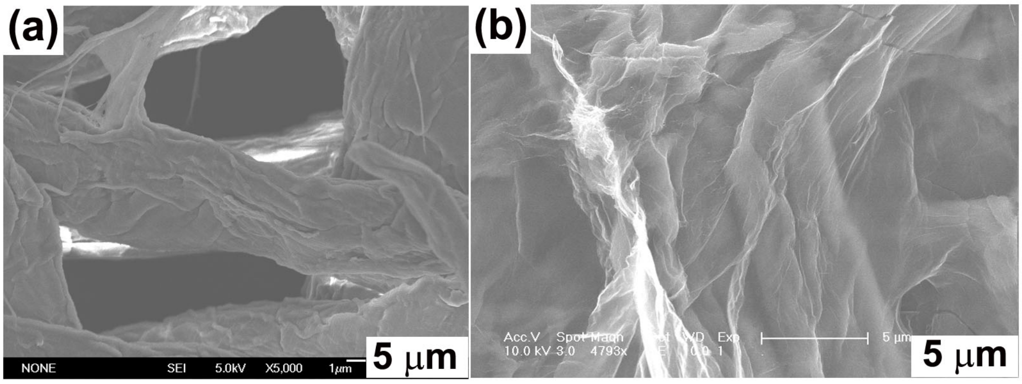

Fig. S3 SEM images of carbon fiber (CF) without graphene (a) and the carbon fiber covered by graphene (CFG) (b).

SEM images of CF and CFG are shown in Fig. S3a and b. It is observed that the pure CNFs present a micro-bundle-like shape while there are many wrinkles on the surface of CNFs covered with graphene. The introduction of this graphene layer is beneficial for the vertical growth of nickel hydroxide and good conductivity in the binder-free electrode materials.

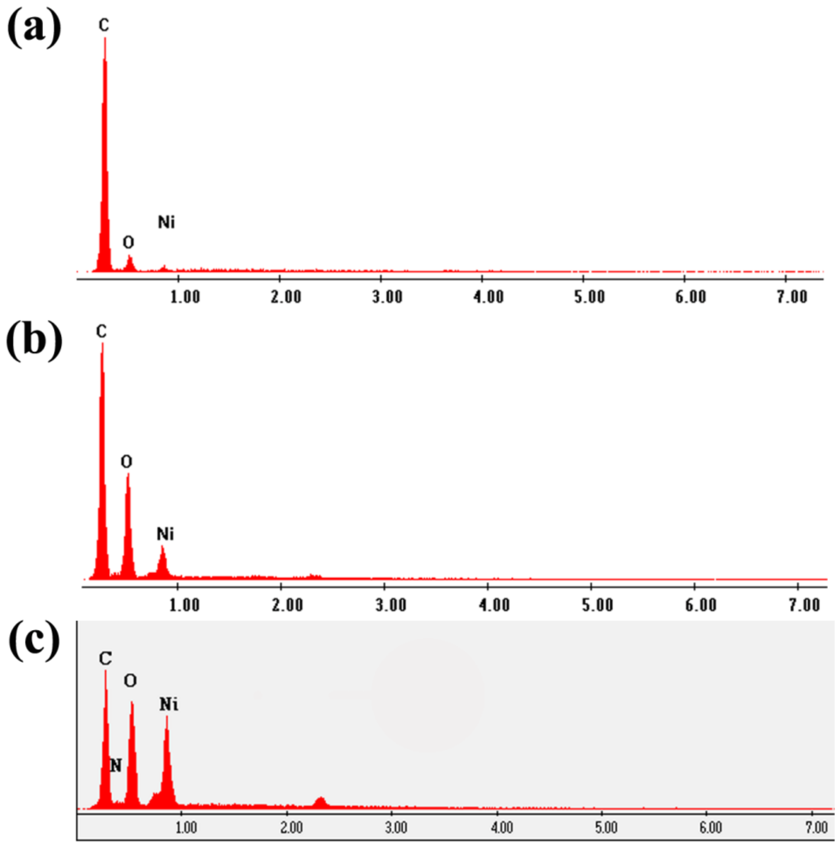

Fig. S4 Energy-dispersive X-ray spectroscopy of the $Ni(OH)_2$-CFG composite with different reaction time 1 h (a), 3 h (b), and 6 h (c).

To determine the formation mechanism of hierarchical porous structure, we made a series of control experiments at 1 h, 3 h, and 6h. As we assumed, the hierarchical porous nickel hydroxide densely covers on the graphene layer with continuous porous channels, which is beneficial for excellent electrochemical performance. With increasing the reaction time (1 h, 3 h, and 6 h), the contents of nickel and oxygen elements in Fig. S4 increased gradually which is in accordance with the SEM images in Figure 3. Nickel hydroxide grows on the graphene layer to form the vertical and cross-linked network for excellent performance.

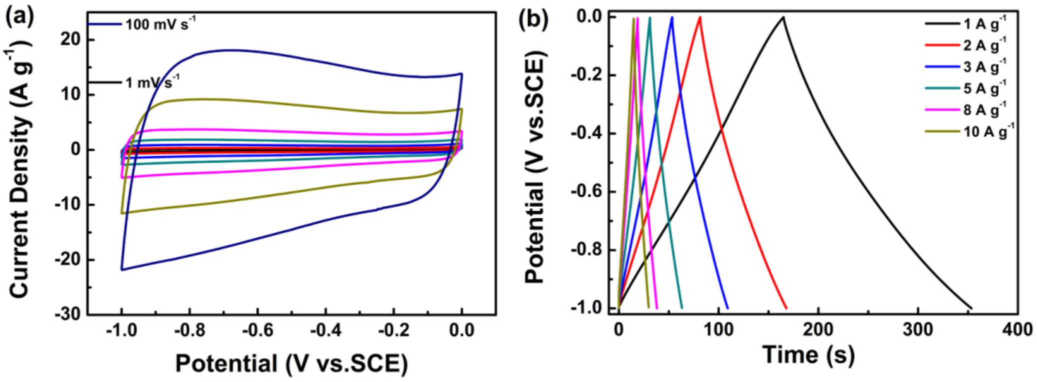

Fig. S5 (a) CV curves of AC at different scan rate with the potential ranged from -1.0 to 0 V in 2 M NaOH aqueous solution electrolyte. (b) GCD curves of AC at different current densities from 1 to 10 A g^{-1}.

CV curves of AC (shown in Fig. S5a) exhibit the excellent rate performance. Even at high scan rate of 100 mV s^{-1}, it still maintains the rectangular CV curves, which is beneficial for the asymmetric supercapacitor. Figure S5b gives the GCD curves at different current densities. Almost no IR drop can be seen at 10 A g^{-1}, which contributes to the good conductivity in the electrode materials.