**Supporting Information**

**The synergistic effect of carbon coating and CNTs compositing on the hard carbon anode for sodium ion batteries**

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**Experimental section**

*Chemicals*

Formaldehyde solution (37 wt% in $H_2O$ containing 10-15 wt% methanol) and carbon nanotubes were purchased from Sigma-Aldrich Co. Resorcinol, toluene, ethanol, Pluronic F127 and hydrochloric acid (HCl, 35-38 wt%) were purchased from Sinopharm Chemical Reagent Co. Deionized water was used in all experiments.

*Preparation of hard carbon materials*

Mesoporous carbon（ME）and Mesoporous carbon with carbon nanotubes (ME-CNT) were prepared by similar soft-templated methods [21]. 2.2 g of resorcinol and 2.2 g of F127 were dissolved in 9 mL of EtOH and 9 mL of HCl aqueous solution (3.0 M). Then the solution was added 2.6 g formaldehyde (37 wt%). The MPC-CNT requires an additional 5 wt% of carbon nanotubes. After stirring for about 11 min at room temperature, the clear mixture turned turbid. The polymer-rich gel phase was obtained by centrifugation at 9500 rpm for 4 min after the mixture was stirred for 40 min. The gel was then loaded on a large PTFE board, dried at room temperature overnight, and subsequently cured at 80 ℃ and 120 ℃ for 24 h. The dried gels were subsequently carbonized at 1400 ℃ for two hours with under argon (1 L/min) at the heating rate of 4 ℃/min. In this work,

As for the carbon-coated ME-CC and ME-CNT-CC, the black powders were placed in a graphite crucible and then put into a tube furnace, carbonized at 800 ℃ for 5 h in

a mixed atmosphere of argon and toluene, and naturally cooled to obtain a final carbon coating materials (labeled as ME-CC and ME-CNT-CC, respectively).

*Basic physicochemical characterization*

The structures of the samples were determined by X-ray diffraction (XRD) on a diffractometer (Bruker D2) with Cu radiation ($\lambda = 0.15406$ nm). Raman spectra were measured by a Micro-Raman spectrometer (Renishaw in-Via Basis) using an argon laser with a wavelength of 532 nm. The morphologies of the samples were characterized by a SEM (Hitachi S4800 and SU5000). The pore size distributions and surface areas of the samples were obtained by the nitrogen adsorption/desorption apparatus (Quantachorme Autosorb-iQ3).

*Electrochemical measurements*

All the battery performances were conducted in CR2032 coin cells employing 1 M $NaClO_4$ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v:v) as the electrolyte. The working electrode was prepared by spreading the mixed slurry of active material and sodium alginate binder in water solvent with a weight ratio of 9.5:0.5 onto Cu foil, and then dried at 100 ℃ in vacuum for 10 hours. The mass loading of the electrode was controlled at around 1 mg/cm. All the cells were assembled in a glove box. The charge and discharge measurements were carried out at different current densities in the voltage range of 0-3.0 V (*vs*. $Na^+/Na$) on a Land CT2001A battery test system. CV measurements (the potential range of 0-3.0 V *vs*. $Na^+/Na$) and electrochemical impedance spectroscopy (EIS, frequency range from 100 kHz to 0.1 Hz) of coin cells were performed on a Solartron 1470E Analytical electrochemical workstation.