Supporting Information

Ambient Hydrolysis Deposition of TiO$_2$ in Nanoporous Carbon and the Converted TiN/Carbon Capacitive Electrode

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Experimental section:

CMK-3 was prepared by a nanocasting method following the well-established procedure in the literature by employing SBA-15 as a hard template.[1]

The AHD Process:

Step I: Surface functionalization

Typically, CMK-3, 0.3 g, was added to a freshly-prepared aqueous solution of $(NH_4)_2S_2O_8$, (1.0 M) and H_2SO_4, (2.0 M) (30 ml). The mixture was stirred at 60 °C for 6 hrs. Then, the oxidized CMK-3 (C-APS) was filtered, rinsed with deionized water and dried overnight in an oven at 80 ℃.

Step II: Water loading

Degassed C-APS, 50 mg, was loaded into a plastic syringe in a glovebox. The carbon-containing syringe was warmed up in an oven at 80 ℃ before water loading to prevent water condensation on the syringe side wall and the external surface of C-APS particles. A narrow-mouth bottle of 500 ml volume that contains water 100 ml was heated in an oven at 80 ℃. We used the warmed-up carbon-containing syringe to take in a certain volume of water-vapor/air mixture for a desired amount of water loading. The needle of the syringe was sealed after water loading. Then, the syringe was shaken by a vortex mixer for 5 mins at 80°C in order to enable good contact of water vapor with C-APS before the syringe was kept in an oven at 60 ℃ for half an hour. For the reference level of water loading, a vial containing C-APS was 'soaked' in water-vapor/air mixture in a larger narrow-mouth bottle that contained water in an oven at 80 ℃.

Step III: Hydrolysis deposition of TiO_2

Water-loaded C-APS samples were soaked for an hour in a dilute solution of titanium tetraisopropoxide (TTIP) in 1, 3 dioxolane (DOXL) (5 vol%). The product was collected by

filtration in a glovebox. Samples were heated at 250 ℃ under nitrogen before N_2 sorption measurements and nitridation.

Nitridation of C-TiO$_2$-100

Samples were heated in a tube furnace at 850 ℃ for 6 hrs under NH_3 with a flow rate of 54 cc/min.

Formation of activated carbon

Carbon microfiber of 2 g (Osaka Gas Co., Ltd) was heated in quartz tube furnace at 910 ℃ under CO_2 with a flow rate of 100 ml/min for 18 hrs.

Boehm titration procedure

The amount of surface functional groups was determined using Boehm titration. In Boehm titration, the following assumptions were made to distinguish between the carbon–oxygen functionalities based on their acidity: NaOH is the strongest base and it neutralizes all Brønsted acids, including phenols, lactonic and carboxylic groups, while $NaCO_3$ neutralizes carboxylic and lactonic groups and $NaHCO_3$ neutralizes only carboxylic acid groups. Briefly, C-APS, 0.2 g, was dispersed in 20 ml of 0.05 M $NaHCO_3$ solution and the mixture was stirred for 48 hrs. The solution was then allowed to remain quiescent for 24 hrs. The aliquot (neutralized with 0.05 M conc. HCl) of 5 ml was back titrated against standardized NaOH solution using phenolphthalein as indicator.

Characterization methods:

X-Ray diffraction (XRD) patterns were collected using a Rigaku Ultima IV Diffractometer with Cu Kα irradiation (λ= 1.5406 Å). Nitrogen sorption measurements were performed on a Micromeritics TriStar II 3020 analyzer at 77.4 K. The samples were outgassed at 250 ℃ under N_2 for 12 hrs prior to the N_2 sorption measurements. X-ray Photoelectron

Spectroscopy (XPS) measurements were performed in a Physical Electrons Quantera Scanning ESCA Microprobe with a focused monochromatic Al Kα X-ray (1486.6 eV) source for excitation. The X-ray beam used was a 25 W, 100 μm X-ray beam spot at the sample. The binding energy (BE) scale was calibrated using the Cu $2p_{3/2}$ feature at 932.62 ± 0.05 eV and Au 4f at 83.96 ± 0.05 eV. The ion gun used in this system was a standard Quantera ion gun, and the sputter depth profiles were acquired using a 1 KeV argon-ion beam rastered over a 3 mm x 3 mm area. To minimize charging artifacts, the XPS data were collected with 1 eV, 20 μA electrons and low-energy Ar^+ ions. The morphology was examined by field emission scanning electron microscopy (FESEM) using an FEI NOVA 230 high resolution SEM with an energy-dispersive X-ray (EDX) attachment. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded by an FEI Titan 80-300 TEM. High angle annular dark field scanning TEM (HAADF-STEM) measurements were carried out on an FEI Titan 80-200 microscope coupled with a HAADF detector and an EDX spectrometer.

Electrochemical Measurements:

A two-electrode cell configuration was used to measure the electrochemical performance of samples. Electrodes were composed of 90 wt% active mass and 10 wt% poly(vinylidene fluoride) binder. The materials were slurry-cast from a cyclopentanone suspension onto a carbon-fiber paper current collector (Model: 2050A). The electrodes were dried at 120 ℃ under vacuum for 12 hrs and then cut into 10 mm disks. The active mass loadings are ~1 mg/cm^2. Then, two identical (by weight and size) electrodes were assembled in coin-type cells that use polypropylene films as the separator and a CH_3CN solution of 1.0 M ammonium tetrafluoroborate (NH_4BF_4) as the electrolyte. Cyclic voltammetry (CV), galvanostatic charge/discharge, and EIS were carried out on a VMP-3 multi-channel workstation at room

temperature. CV and charge/discharge profiles were collected in a voltage window from 0 to 2.5

V. EIS was carried out with the potential amplitude of 10 mV at the frequency range of 200 kHz

to 10 mHz. The voltage drop at the beginning of discharge (V_{drop}) is used to estimate the

equivalent series resistance, R_{ESR}, at a constant current of I with the formula of $R_{ESR} = V_{drop}/(2I)$.
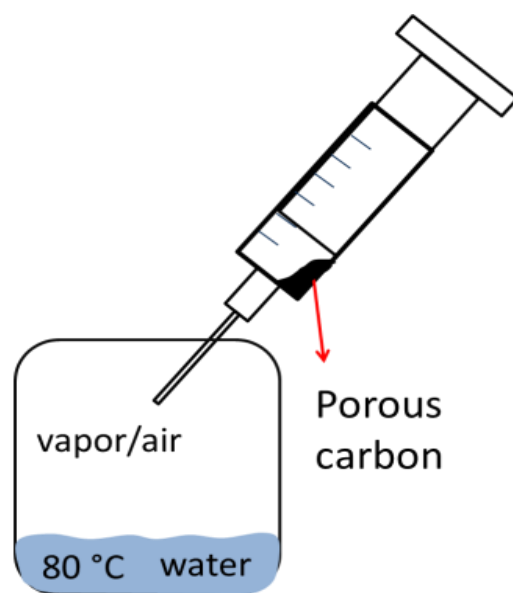
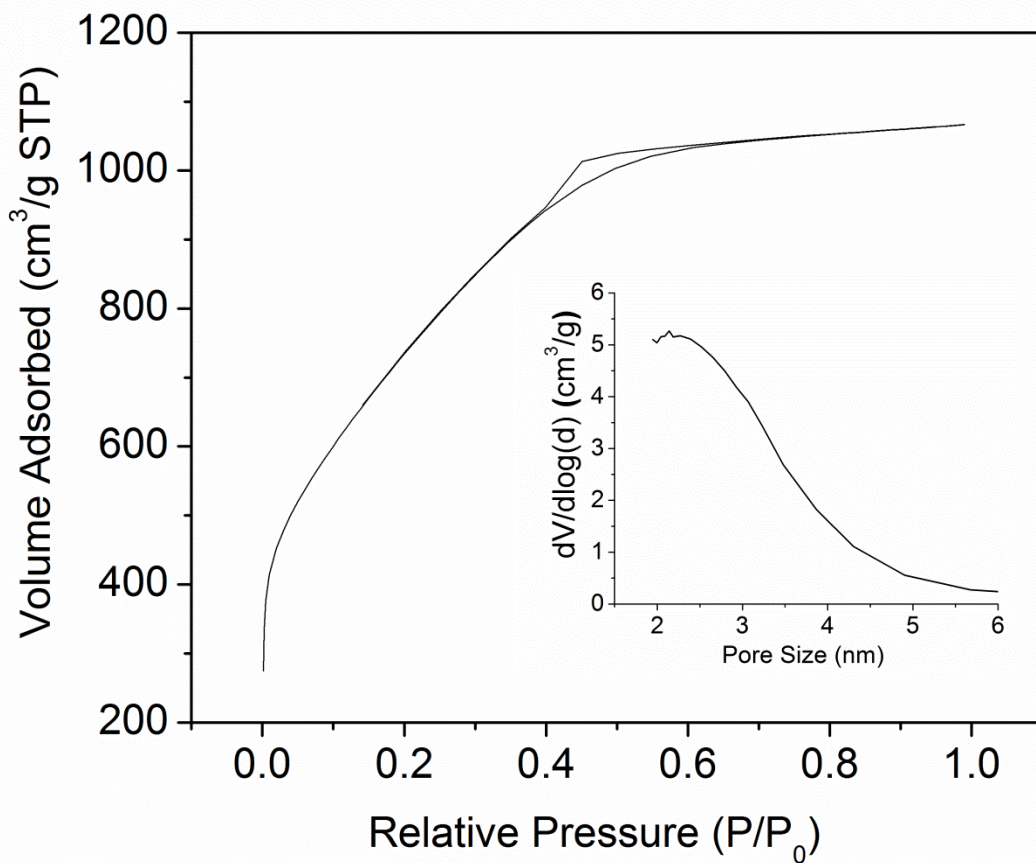**Fig. S1.** Schematic showing water-loading by a porous-carbon-containing syringe.

Fig. S2. N_2 isotherms of the CO_2 activated carbon. Inset: pore size distribution.
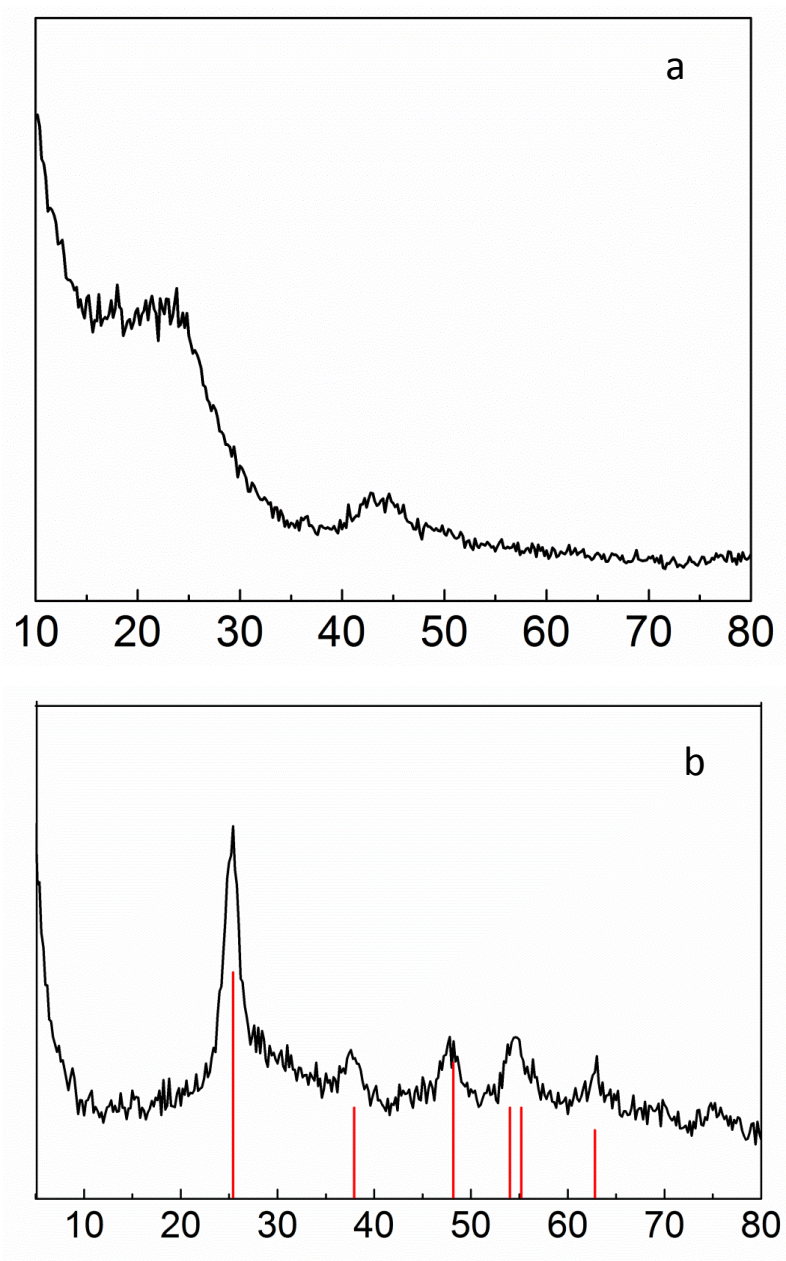
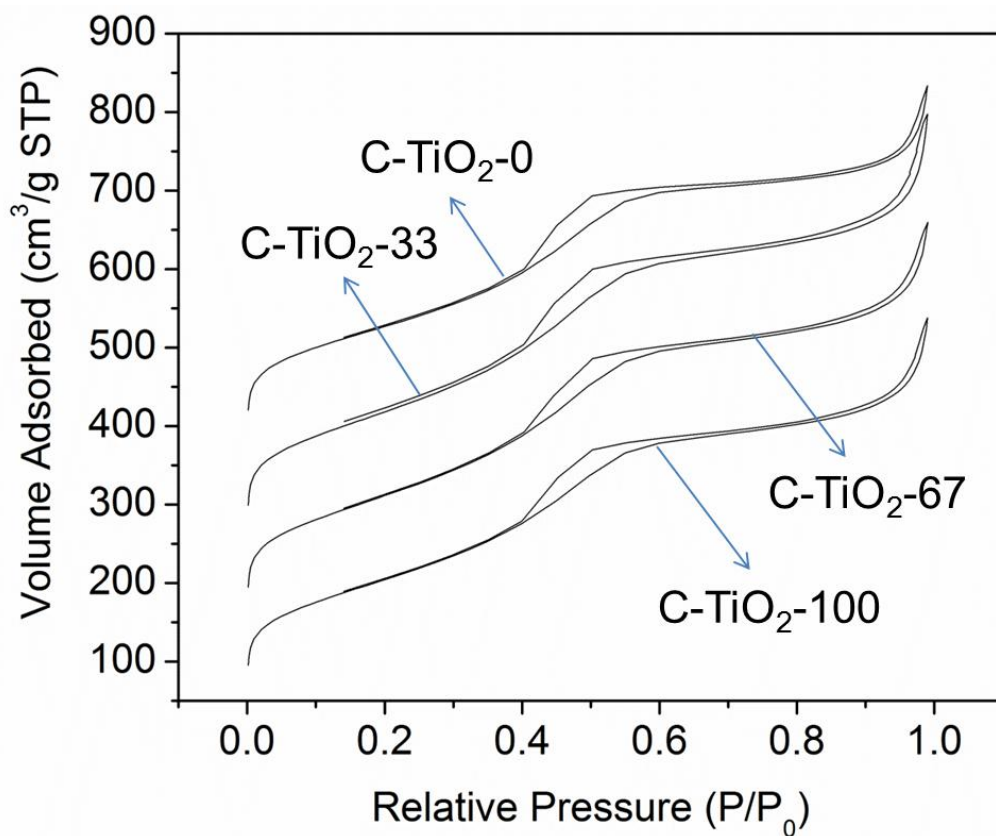**Fig. S3.** XRD patterns of a) C-TiO$_2$-100 and b) bulk TiO$_2$ powder.

Fig. S4. N_2 isotherms of TiO_2/carbon nanocomposites. C-TiO_2-67, C-TiO_2-33 and C-TiO_2-0 are moved upward by 100, 200, and 300 cm^3/g STP, respectively, for a better comparison of the curves.
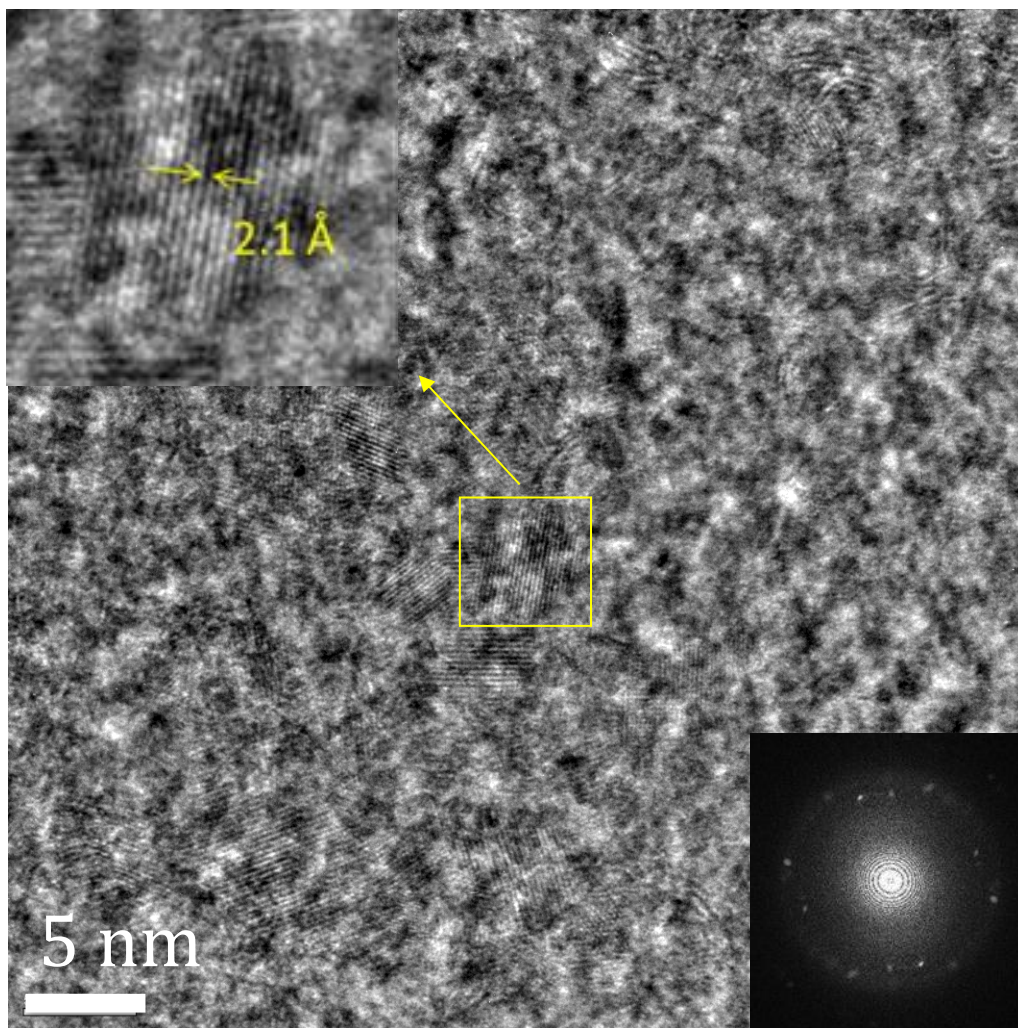
Fig. S5 HRTEM images of C-TiN, corresponding selected area electron diffraction (inset bottom right) and an enlarged image of a representative TiN particle with a d-spacing of 2.1 Å (inset top left).
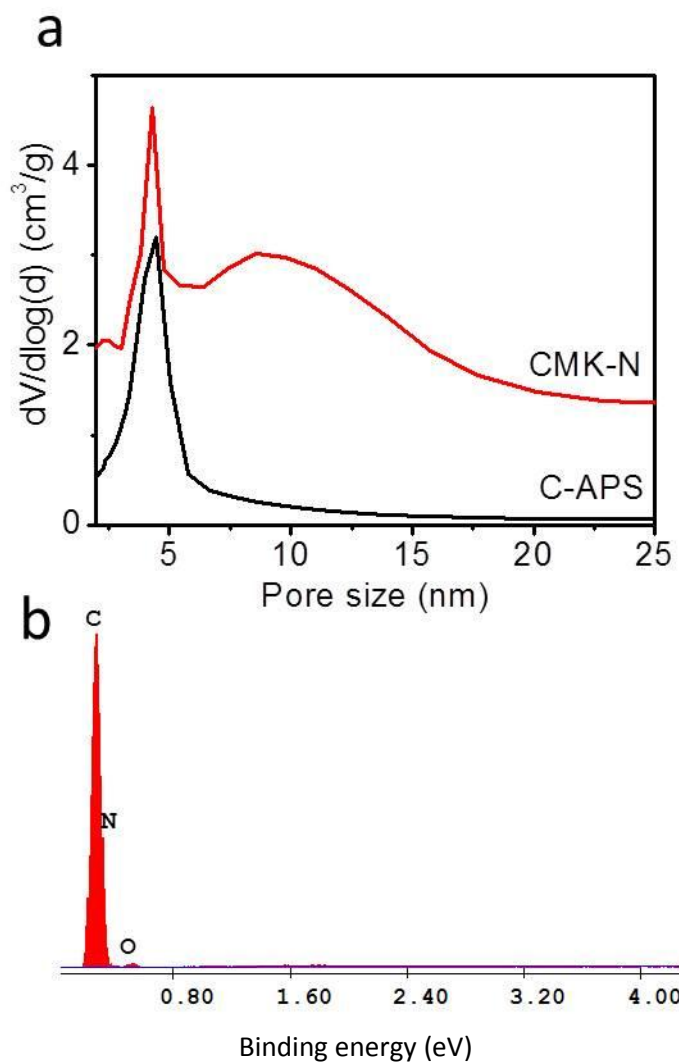
Fig. S6 a) Pore size distribution profiles of C-APS and CMK-N. b) EDX analysis for CMK-N.
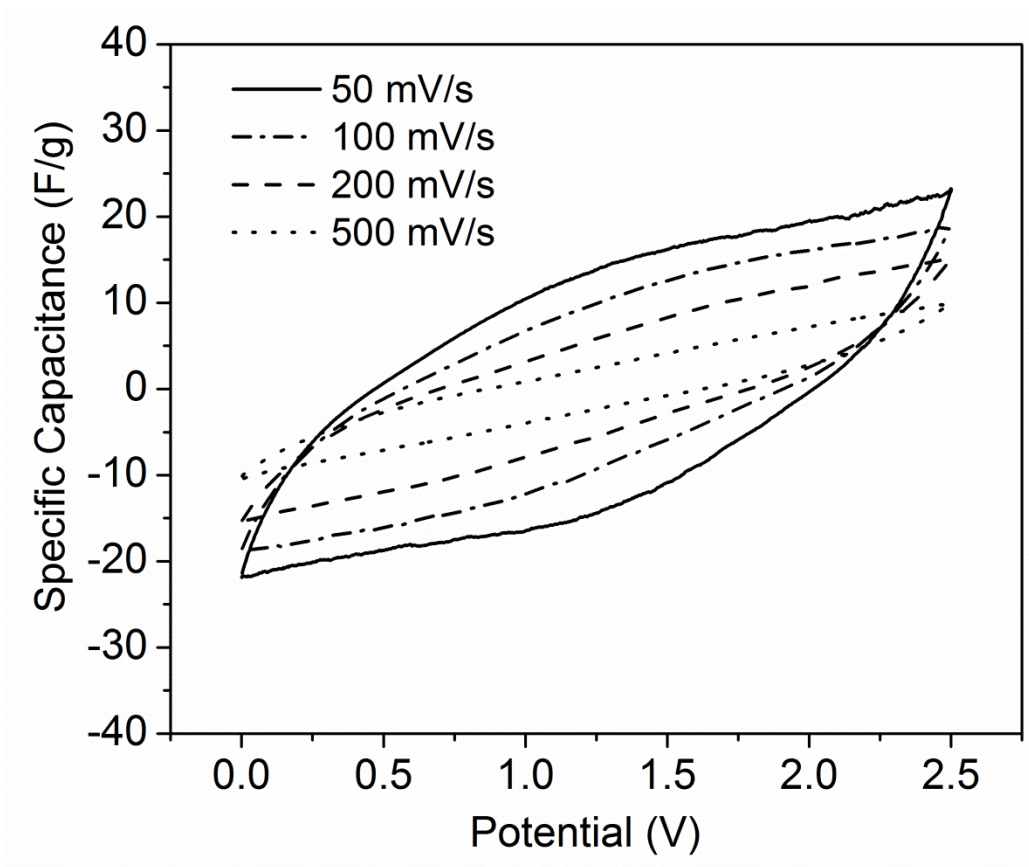
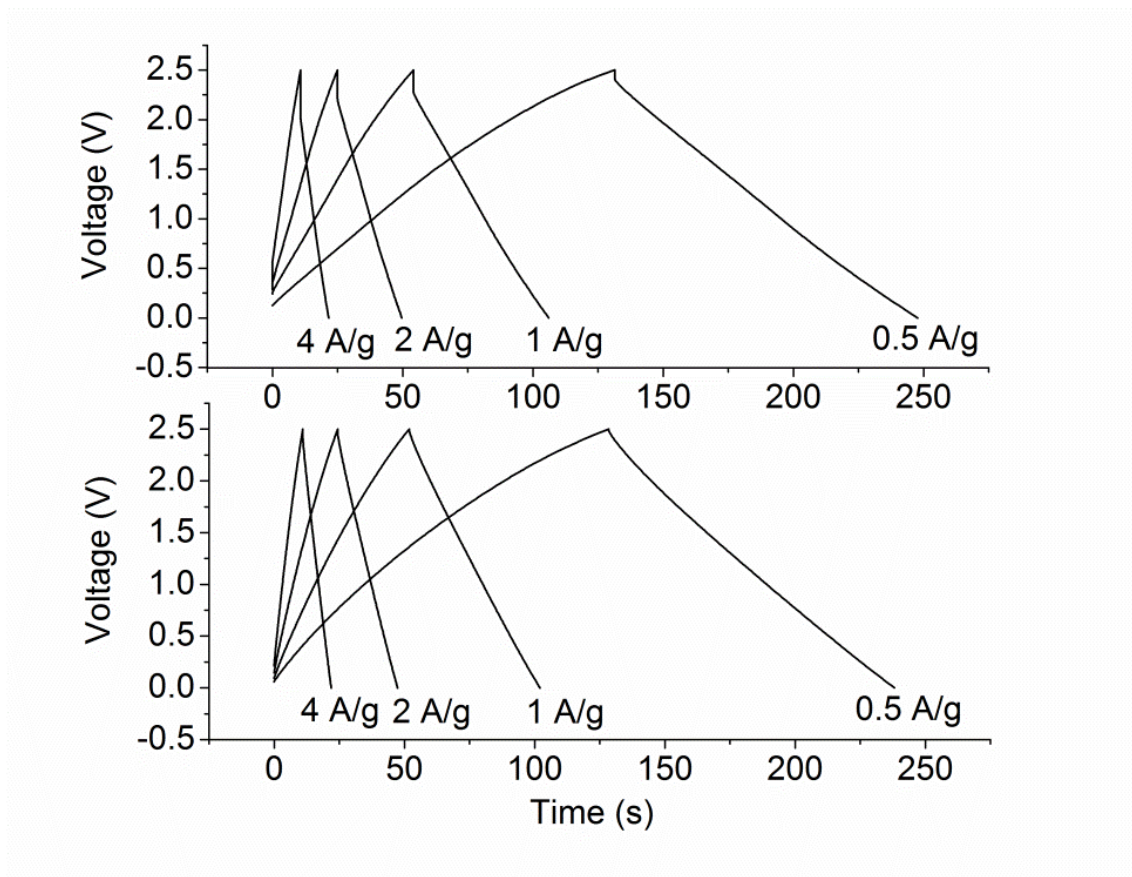**Fig. S7.** CV curves of CMK-N at different scanning rates.

Fig. S8. Galvanostatic charge/discharge profiles at different current rates.

[1] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* 1998, **279,** 548-552.