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Electronic Supplementary Information

Carbon-coated $CoSe_2$ Nanoparticles Confined in N-doped Carbon Microboxes for Enhanced Sodium-Ion Storage

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Experimental Section

Synthesis of Co-Co PBA microcubes. Co-Co PBA microcubes were synthesized through a surfactant-mediated precipitation method. In a typical synthetic procedure, 79.7 mg of cobalt(Ⅱ) acetate tetrahydrate was dissolved in 40 mL of deionized water to form solution A. 66.4 mg of potassium hexacyanocobaltate(Ⅲ) and 1.4 g polyvinylpyrrolidone (PVP K30, Mw=30,000) were dissolved in 40 mL of deionized water under magnetic stirring for 1 h to form clear solution B. Then, solution A was slowly added into solution B under continuous magnetic stirring. After stirring for another 3 min, the obtained mixed solution was aged for 24 h at room temperature. The precipitate was collected by centrifugation, washed with deionized water and ethanol for six times and dried at 70 ^{o}C overnight.

Synthesis of Co-Co PBA@PDA microcubes. In a typical synthetic procedure, 40 mg of as-prepared Co-Co PBA microcubes were dispersed in a Tris-buffer solution (50 mL, 10 mM) with the assistance of magnetic stirring and ultrasonication for 30 min. Then 5 mg of dopamine hydrochloride was added. The mixture was stirred at room temperature for 5 h. The resultant product was collected by centrifugation, washed with deionized water and ethanol for four times and dried at 70 ^{o}C overnight.

Synthesis of DCC-Co microcubes. In a typical synthetic procedure, 40 mg of Co-Co PBA@PDA microcubes were spread in a porcelain boat and transferred into a sealed tube furnace. Argon atmosphere was applied at room temperature for 30 min, then vacuum was achieved via a constant running vacuum pump. The powder was heated at 550 ^{o}C for 3 h with a ramping rate of 2 ^{o}C min^{-1} in vacuum.

Synthesis of DCC-CoSe$_2$ microcubes. In a typical synthetic procedure, 20 mg of as-prepared DCC-Co microcubes and 60 mg of Se powder were mixed by grinding with a mortar and pestle, and transferred into a glass thin-neck bottle (50 mL of volume). The bottle containing the mixed precursors is attached to a constant running vacuum pump. Then the bottleneck is slowly heated and softened by a butane torch, finally sealed together and cooled down to room temperature. The sealed vacuum bottle was heated at 350 °C for 3 h with a ramping rate of 2 °C min^{-1} in a tube furnace.

Synthesis of P-CoSe$_2$ microcubes. The synthetic procedure is similar with that of the DCC-CoSe$_2$ microcubes, but without the coating of PDA layer on Co-Co PBA microcubes.

Synthesis of S-CoSe$_2$ microcubes. In a typical synthetic procedure, 40 mg of Co-Co PBA microcubes and 60 mg of Se powder were uniformly mixed by grinding with a mortar and pestle. Then, the mixture was transferred to a porcelain boat and heated at 350 °C for 3 h with a ramping rate of 2 °C min^{-1} in argon atmosphere.

Synthesis of Co$_3$O$_4$ microcubes. In a typical synthetic procedure, 100 mg of Co-Co PBA microcubes were annealed at 500 °C in air for 2 h in a tube furnace, with a ramping rate of 2 °C min^{-1}.

Synthesis of Co$_3$O$_4$@PDA microcubes. In a typical synthetic procedure, 40 mg of Co$_3$O$_4$ microcubes were dispersed in a Tris-buffer solution (50 mL, 10 mM) with the assistance of magnetic stirring and ultrasonication for 30 min. Then 15 mg of dopamine hydrochloride was added. The mixture was stirred at room temperature for 5 h. The resultant product was collected by centrifugation, washed with deionized water and ethanol for four times and dried at 70 °C overnight.

Synthesis of CoSe$_2$ microcubes. In a typical synthetic procedure, 20 mg of as-prepared Co$_3$O$_4$ microcubes and 60 mg of Se powder were mixed by grinding with a mortar and pestle, and transferred into a glass thin-neck bottle (50 mL in volume). The bottle containing the mixed precursors is attached to a constant running vacuum pump. Then the bottleneck is slowly heated and softened by a butane torch, finally sealed together and cooled down to room temperature. The sealed vacuum bottle was heated at 350 °C for 3 h with a ramping rate of 2 °C min^{-1} in a tube furnace.

Synthesis of CoSe$_2$@C microcubes. The synthetic procedure is similar with that of the CoSe$_2$ microcubes, except for using Co$_3$O$_4$@PDA microcubes instead of Co$_3$O$_4$ microcubes as precursor.

Synthesis of Na$_3$V$_2$(PO$_4$)$_3$ cathode material. 40 mL of water is first heated to 75 °C. Then, 459.3 mg of V$_2$O$_5$ and 945.5 mg of oxalic acid are added into the heated water to obtain a uniform solution and stirred for 10 min. Then, 398.2 mg of Na$_2$CO$_3$ is added and stirred for another 10 min. Finally, 866.9 mg of $NH_4H_2PO_4$ is added to the solution and stirred for 10 min. The mixed solution is aged for 3 h and then dried under 80 ^oC over night. The dried sample is collected and annealed at 800 ^oC in argon atmosphere for 8 h with a ramping rate of 5 ^oC min^{-1}.

Materials Characterizations. The XRD patterns were recorded on the EMPYREAN PANnalytical (Cu Kα radiation, λ = 1.540598 Å). The morphologies and structures of the samples were characterized by scanning electron microscopy (SEM, HITACKI SU8010) and transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN FEI). X-ray photoelectron spectroscopy (XPS) was performed on Thermo Fisher Scientific Escalab 250Xi. Elemental analysis was carried out using energy-dispersive X-ray spectroscopy (EDS) attached to TEM and SEM.

Electrochemical Measurements. The samples were mixed with Super P and polyvinylidene fluoride (PVDF) at the weight ratio of 7:2:1 in N-methyl pyrrolidone (NMP) to form a slurry, which was uniformly coated on a copper foil. After vacuum drying at 80 ^oC for 10 h, the electrodes were assembled into 2032-type coin cells in a glovebox (MIKROUNA) filled with ultra-high-purity argon. The mass loading of the electrode materials on copper foil was about 1 mg cm^{-2}. In the coin cells, Na metal foil and glass microfiber (Whatman, GF/D) were used as the anode and separator, respectively, and the electrolyte was 1 M $NaCF_3SO_3$ in diglyme. For the assembly of full cells, the mass ratio of anode material and cathode material is 1:6. The mass loading of cathode material is about 10% excessive in terms of reversible capacity. The specific capacity is calculated based on the mass loading of DCC-$CoSe_2$ on anode. Cyclic voltammetry (CV) was tested with an electrochemical workstation (Biologic) at a scan rate of 0.1 mV s^{-1} in the voltage range of 0.5-2.9 V (vs. Na/Na^+) for $CoSe_2$ half cell. The galvanostatic charge/discharge performances of the electrodes were tested in a battery test incubator at 27 ^oC using a NEWARE battery tester, in a voltage range of 0.5-2.9 V (vs. Na/Na^+) for $CoSe_2$ half cell, 2.6-4.0 V (vs. Na/Na^+) for $Na_3V_2(PO_4)_3$ half cell, and 0.5-2.9 V for DCC-$CoSe_2$/$Na_3V_2(PO_4)_3$ full cell. The electrochemical impedance spectroscopy (EIS) measurement was carried out using electrochemical workstation (Biologic) in a frequency range from 20 kHz to 20 MHz.

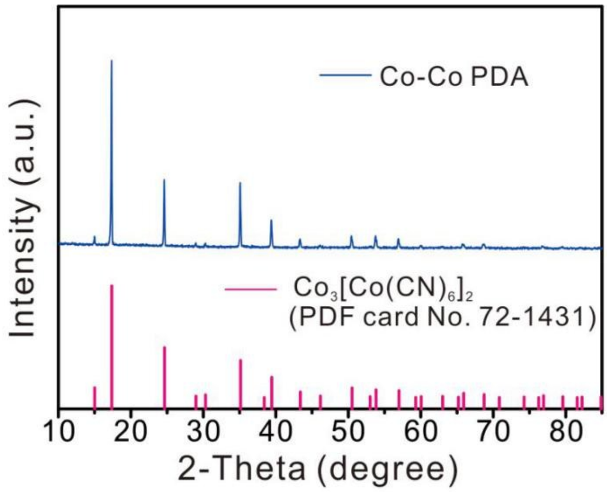

Fig. S1 XRD pattern of the Co-Co PBA microcubes.

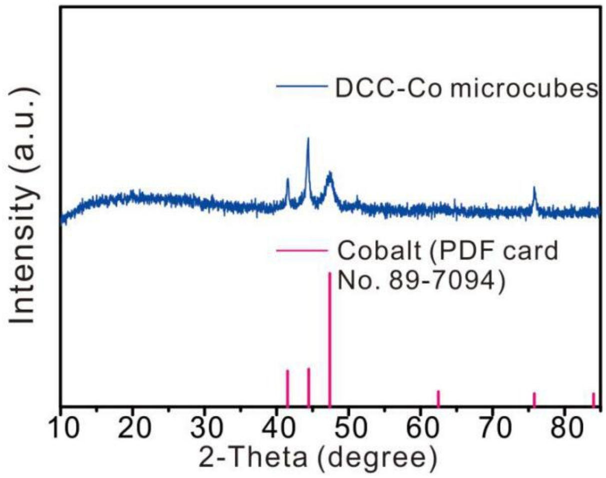

Fig. S2 XRD pattern of the DCC-Co microcubes.

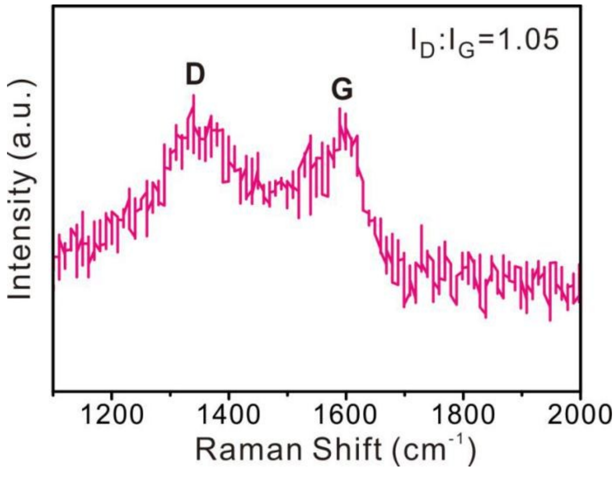

Fig. S3 Raman spectrum of the DCC-Co microcubes

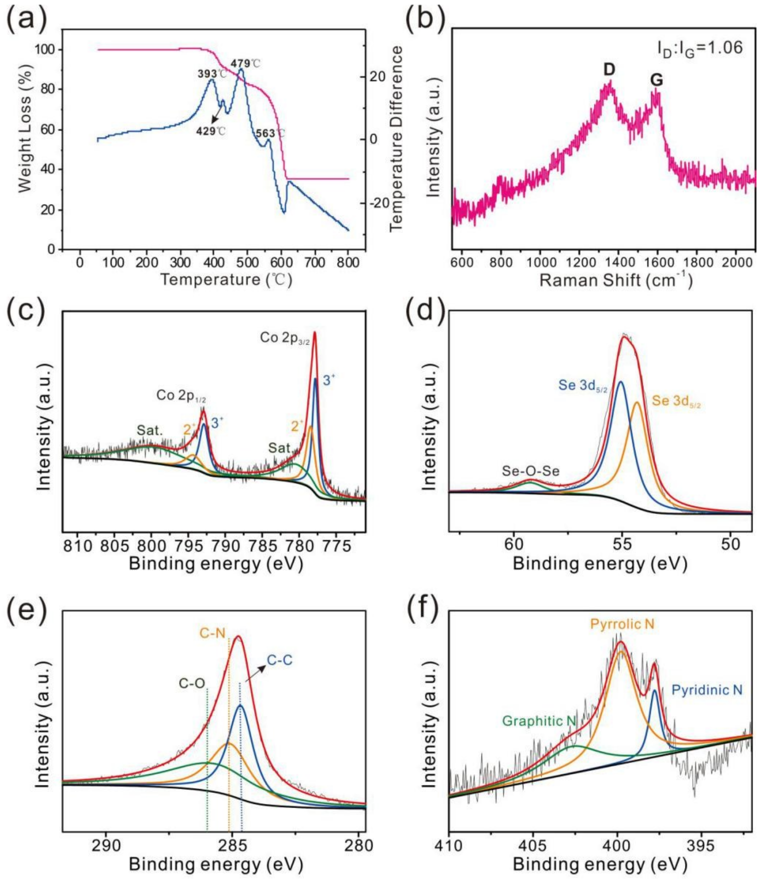

Fig. S4 (a) Thermogravimetric analysis and (b) Raman spectrum of the DCC-$CoSe_2$ microcubes; (c) Co 2p, (d) Se 3d, (e) C 1s, and (f) N 1s XPS spectra of the DCC-$CoSe_2$ microcubes.

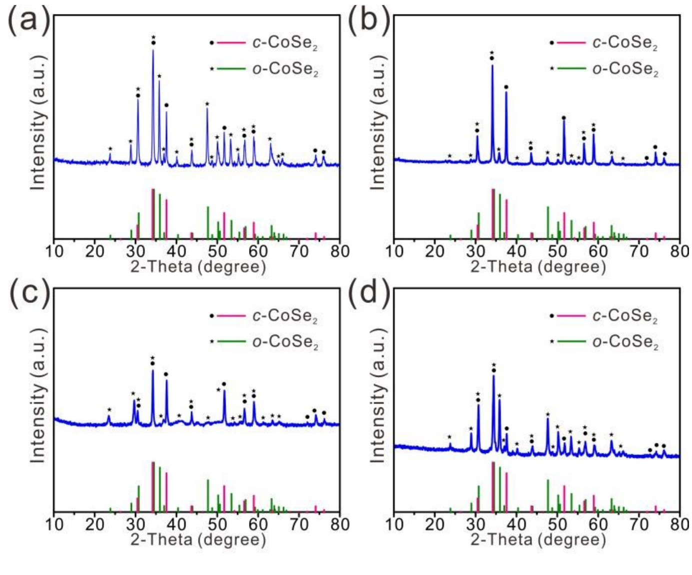

Fig. S5 XRD patterns of the P-$CoSe_2$ (a), S-$CoSe_2$ (b), $CoSe_2$ (c), and $CoSe_2$@C (d) microcubes.

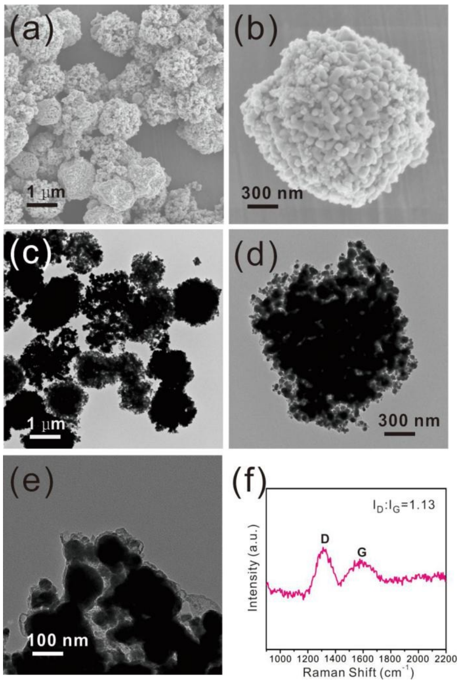

Fig. S6 (a,b) SEM images, (c-e) TEM images, and (f) Raman spectrum of the P-$CoSe_2$ microcubes.

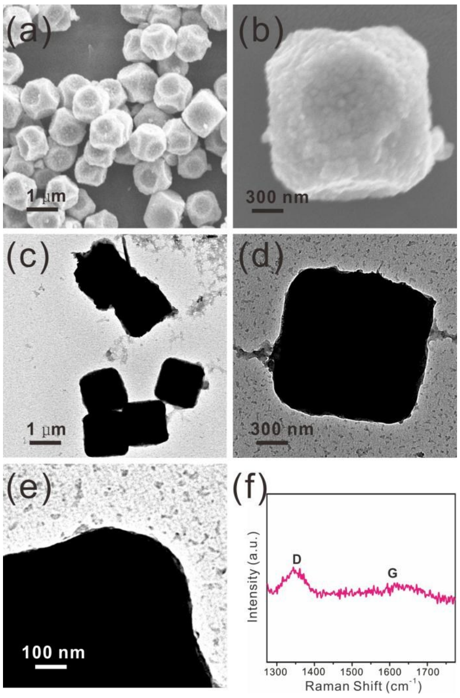

Fig. S7 (a,b) SEM images, (c-e) TEM images, and (f) Raman spectrum of the S-$CoSe_2$ microcubes.

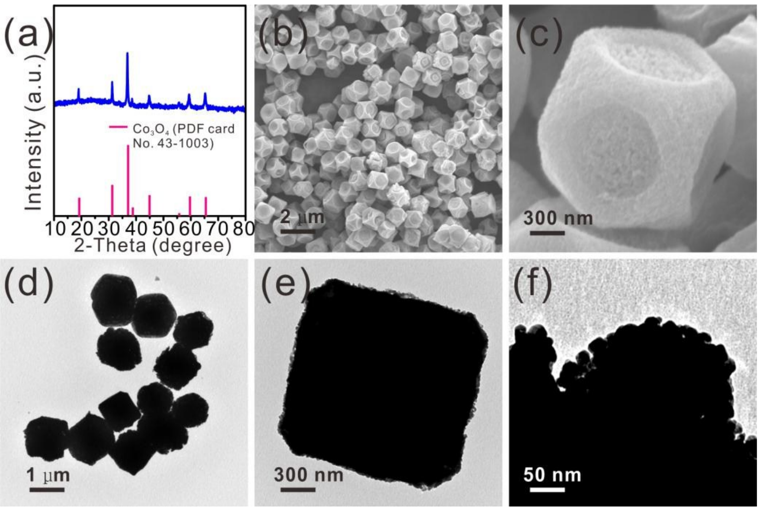

Fig. S8 (a) XRD pattern, (b,c) SEM images, and (d-f) TEM images of the Co$_3$O$_4$ microcubes.

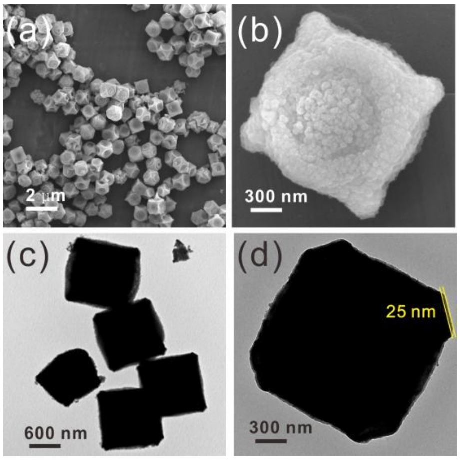

Fig. S9 (a,b) SEM images and (c,d) TEM images of the Co$_3$O$_4$@PDA microcubes.

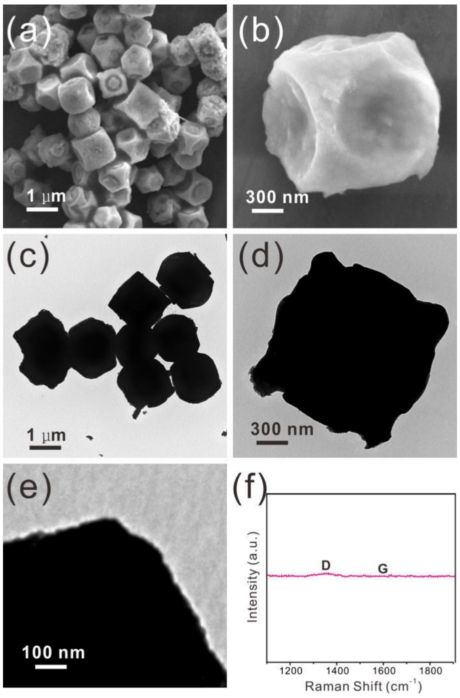

Fig. S10 (a,b) SEM images, (c-e) TEM images, and (f) Raman spectrum of the $CoSe_2$ microcubes.

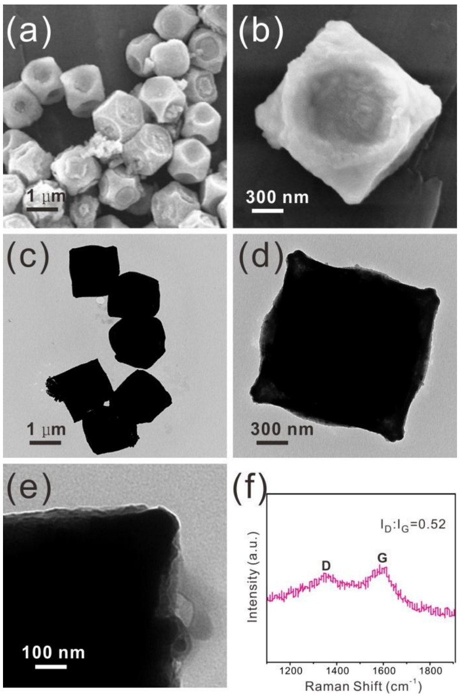

Fig. S11 (a,b) SEM images, (c-e) TEM images, and (f) Raman spectrum of the $CoSe_2$@C microcubes.

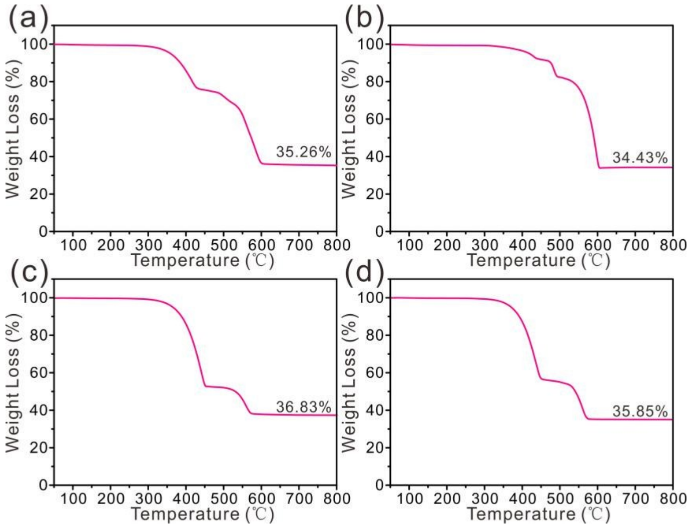

Fig. S12 Thermogravimetric analysis of the P-$CoSe_2$ (a), S-$CoSe_2$ (b), $CoSe_2$ (c), and $CoSe_2$@C (d) microcubes.

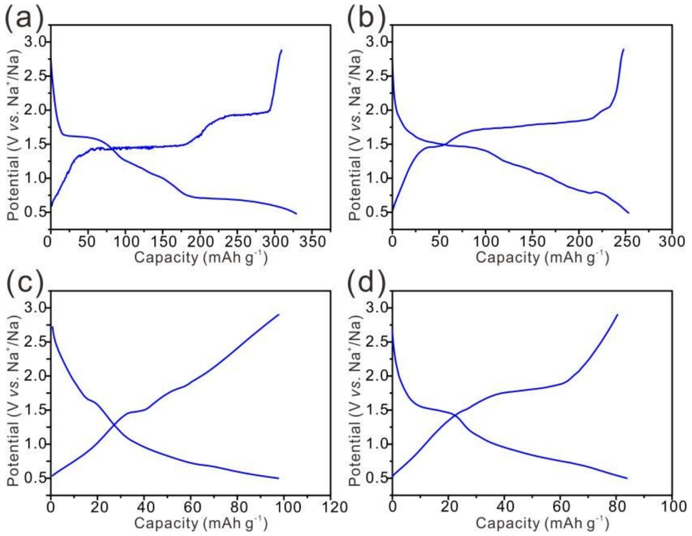

Fig. S13 Typical discharge/charge voltage profiles of the P-$CoSe_2$ (a), S-$CoSe_2$ (b), $CoSe_2$ (c), and $CoSe_2$@C (d) microcubes at a current density of 100 mA g^{-1}.

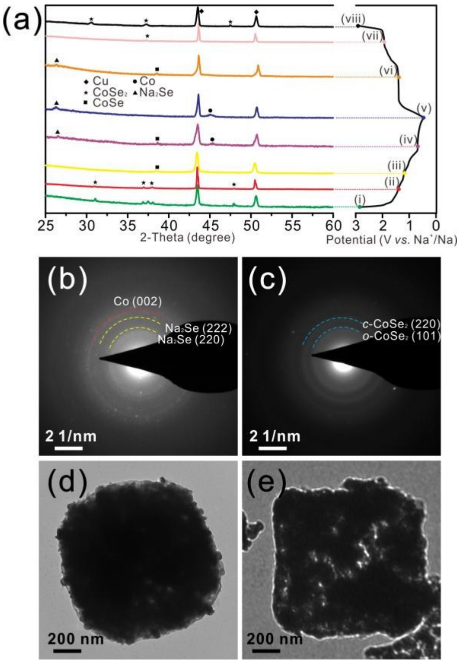

Fig. S14 (a) *Ex* situ XRD patterns of the DCC-$CoSe_2$ microcube electrode at different discharge and charge states. (b-e) SAED patterns and corresponding TEM images of the DCC-$CoSe_2$ microcube electrode discharged to 0.5 V (b,d) and charged to 2.9 V (c,e).

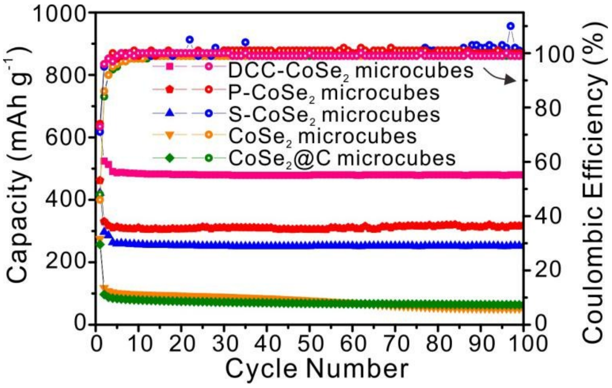

Fig. S15 Cycling performances of the DCC-$CoSe_2$, P-$CoSe_2$, S-$CoSe_2$, $CoSe_2$, and $CoSe_2$@C microcube electrode at a current density of 0.1 A g^{-1}.

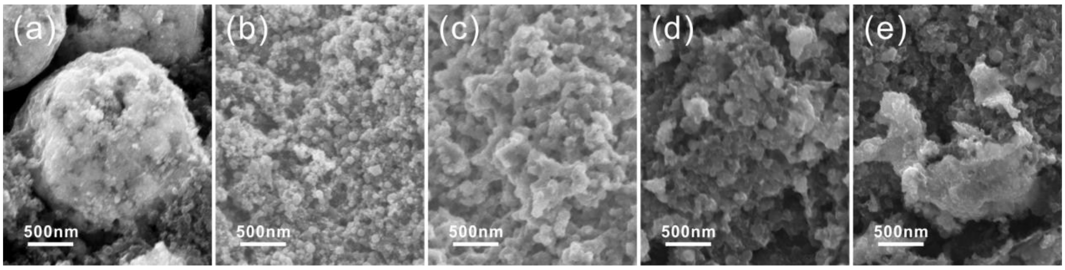

Fig. S16 SEM images of the DCC-$CoSe_2$ (a), P-$CoSe_2$ (b), S-$CoSe_2$ (c), $CoSe_2$ (d), and $CoSe_2$@C (e) microcube electrode after 100 cycles at a current density of 5 A g^{-1}.

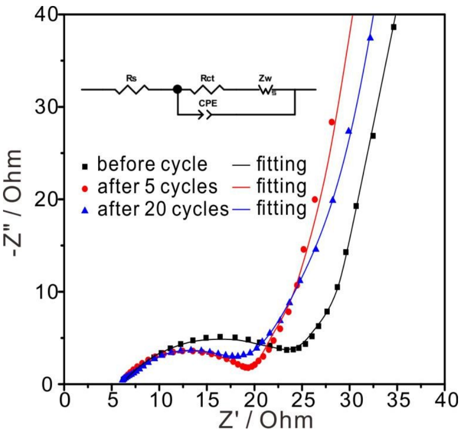

Fig. S17 EIS plots and the fitting results of the DCC-$CoSe_2$ microcube electrode after different cycles at a current density of 1 A g^{-1}.

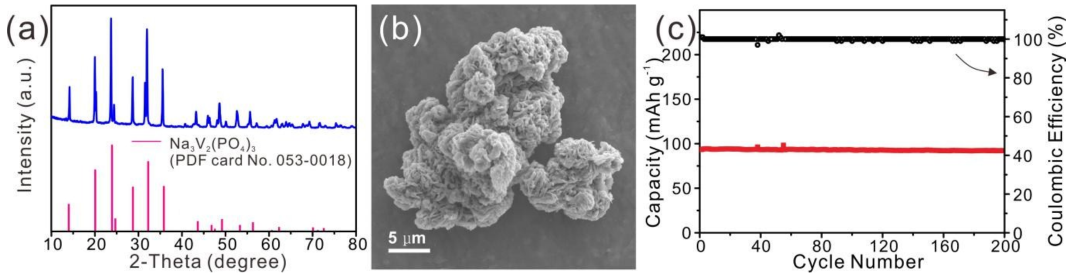

Fig. S18 (a) XRD pattern and (b) SEM image of the $Na_3V_2(PO_4)_3$ material. (c) Cycling performance of the $Na_3V_2(PO_4)_3$ material at a current density of 1 A g^{-1} with Na foil as counter electrode.

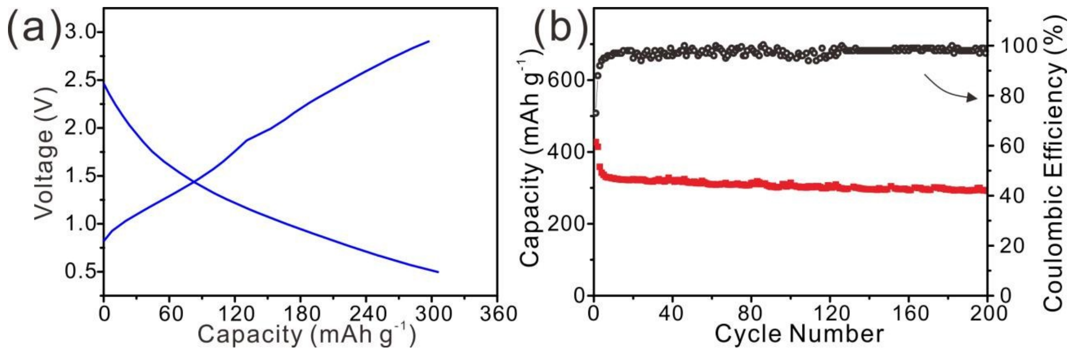

Fig S19 (a) The discharge/charge voltage profile for the first cycle and (b) cycling performance of the full cell assembled with the DCC-$CoSe_2$ microcube as anode material and the $Na_3V_2(PO_4)_3$ as cathode material at a current density of 0.5 A g^{-1}.

Table S1 Comparison of this work with reported $CoSe_x$-based anode materials for sodium storage

Materials	Reversible capacity (mAh g^{-1})	Cyclic stability	References
Dual-carbon confined $CoSe_2$ microcubes	**480 (0.1 A g^{-1})** **445 (5 A g^{-1})** **422 (10 A g^{-1})** **281 (20 A g^{-1})**	**94.5%** **(2000 cycles)**	**This work**
$CoSe_2$@C@CNT	323.3 (0.2 A g^{-1}) 295.1 (2 A g^{-1})	~95% (1000 cycles)	[1]
N-doped yolk-shell CoSe/C	594.1 (0.2 A g^{-1}) 361.9 (16 A g^{-1})	~96% (50 cycles)	[2]
Cu-doped $CoSe_2$ microboxes	492 (0.05 A g^{-1}) 185 (3 A g^{-1})	~94% (500 cycles)	[3]
Co_9Se_8/rGO	406 (0.2 A g^{-1}) 295 (5 A g^{-1})	98% (100 cycles)	[4]
Hollow $CoSe_2$ microsphere	521 (0.1 A g^{-1}) 446 (0.9 A g^{-1})	91% (40 cycles)	[5]
$CoSe_2$/N-doped CNT	482 (0.2 A g^{-1}) 368 (5 A g^{-1})	~87.6% (100 cycles)	[6]
$CoSe_2$/N-doped C framework	666 (0.2 A g^{-1}) 406 (10 A g^{-1})	~92.6% (500 cycles)	[7]
Urchin-like $CoSe_2$	434 (0.1 A g^{-1}) 354 (10 A g^{-1})	~98.6% (1800 cycles)	[8]

Supplementary references

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