Se/N co-doped carbon nanorods for potassium ion storage

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Experimental Section

Material synthesis

Chemicals: 1,3,5-benzenetricarboxylic acid ($C_9H_6O_6$, 99%), manganous acetate tetrahydrate ($C_4H_6MnO_4$), polyvinylpyrrolidone (PVP), selenium (Se-powder, 99.99%), ethanol and ultrapure water were used. All starting materials were obtained from commercial suppliers and used without further purification.

Synthesis of Mn-BTC: 1,3,5-benzenetricarboxylic acid (0.09 g) was dissolved in ethanol (5 ml) in a beaker, stirring a few minutes, and 5 ml of water was added, marked as solution A. And manganous acetate tetrahydrate (0.049 g) and polyvinylpyrrolidone (0.3 g) were fully dissolved in the mixed solution of ultrapure water (5 ml) and 5 ml ethanol in another beaker to form solution B. The solution A was slowly added into the solution B. After 24 h later, the product was thoroughly washed by ultrapure water and ethanol several times. Ultimately, the powder was dried in an oven at 60 °C overnight.

Synthesis of CRs: The white Mn-BTC was placed in ceramic boat and annealed at 600°C in N_2 atmosphere with a heating rate of 10 °C min^{-1} and kept for 2 h. And then, the resulting MnO was etched by HCl. After that washed by ultrapure water and ethanol several times and dried in an oven at 60 °C overnight. The resulting sample is denoted as CRs.

Synthesis of SeCRs: The re-prepare CRs and puper selenium powder were placed in ceramic boats respectively (mass ratio of 1:2) and annealed at 600 °C in N_2 atmosphere with a ramp rate of 3 °C min^{-1} and kept for 2 h. The resulting sample is named as SeCRs.

Synthesis of SeNCRs: The re-prepare SeCRs was placed in ceramic boat and annealed at 600 °C in NH_3 atmosphere with a heating rate of 10 °C min^{-1} and kept for 2 h. The resulting sample is denoted as SeNCRs.

Material characterization

The crystal structures of all samples were determined with an X-ray diffractometer (Rigaku Co, Japan, D/MAX-γA) equipped with Cu-Ka radiation. The morphologies of the as-prepared samples were investigated using scanning electron microscopy

(SEM, JEOL JSM-6700 M) with a voltage of 200 kV and transmission electron microscopy (TEM, Hitachi H-800) using an accelerating voltage of 200 kV. High resolution transmission electron microscopy (HRTEM, JEOL-2011) was further performed to investigate the structure. The electronic states of all elements in samples were investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250). The Raman spectrum was obtained using a Confocal Laser MicroRaman Spectrometer (Via-Reflex/inVia-Reflex).

Electrochemical measurements

All the electrochemical measurements were characterized employing half coin cells (CR2032). As-synthesized sample, conductive carbon black and polyvinylidene fluoride (PVDF) binder were mixed in N-methylpyrrolidone (NMP) at a mass ratio of 8:1:1, and as-obtained mixture was magnetically stirred to form a homogeneous slurry. The homogenous slurry was obtained and was pasted on a Cu foil and dried at 80 °C overnight under vacuum conditions. After the solvent was completely evaporated, the coated copper foil was punched into a round sheet with a diameter of 14 mm and used as the working electrode. The electrolyte was 3 M KFSI in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in volume). The galvanostatic charge-discharge tests was measured by the Neware CT3008 W instrument within a voltage window of 0.01-3.0 V. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on CHI760E electrochemical workstation.
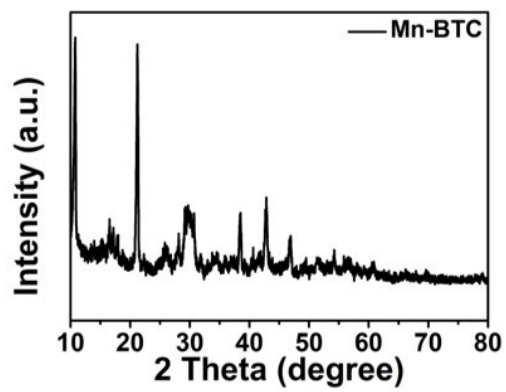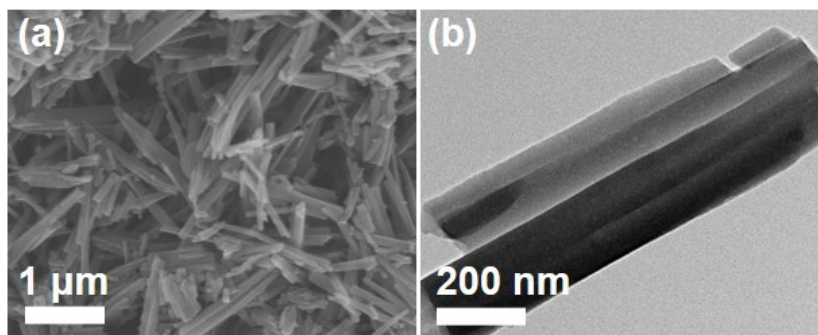
Figure S1. XRD pattern of Mn-BTC.

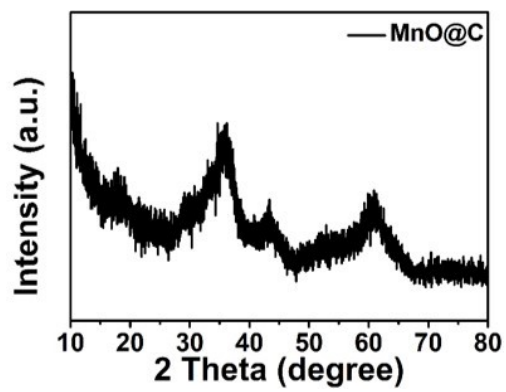**Figure S2.** (a) SEM and (b) TEM images of Mn-BTC.

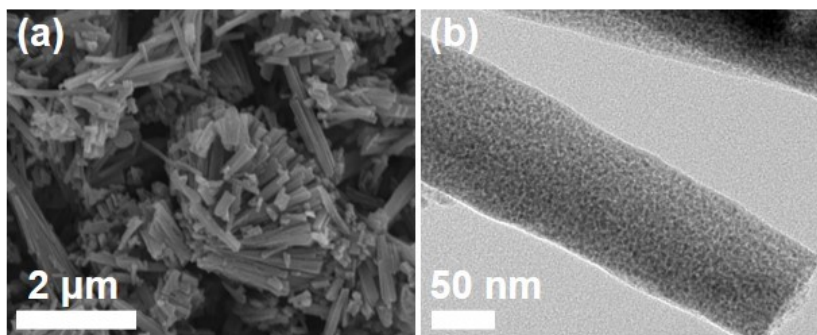**Figure S3.** XRD pattern of MnO@C.

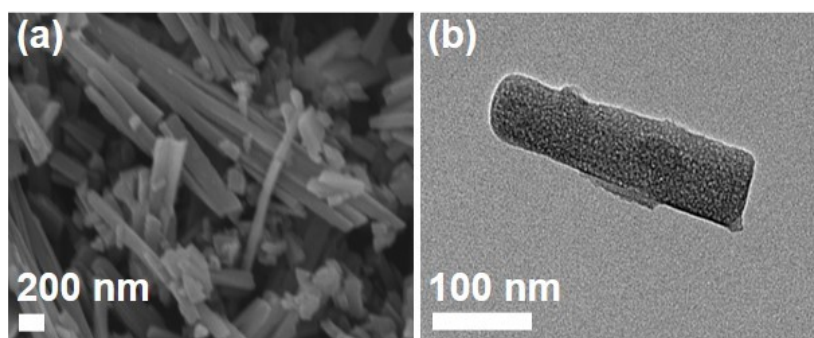**Figure S4.** (a) SEM and (b) TEM images of MnO@C.

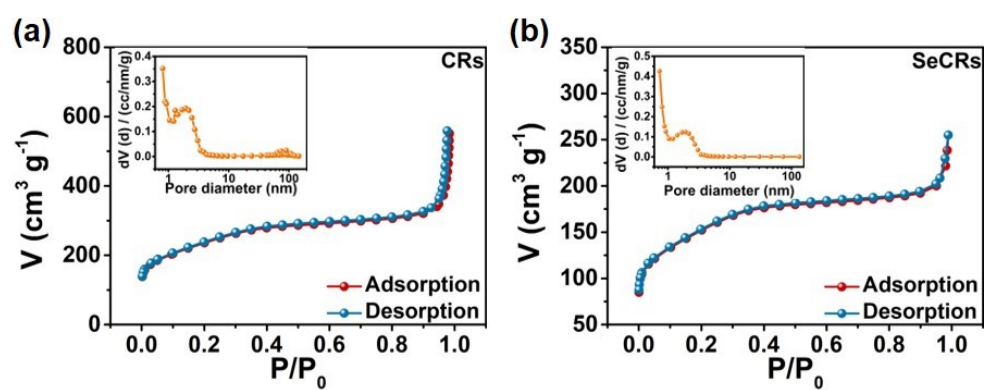**Figure S5.** (a) SEM and (b) TEM images of CRs.

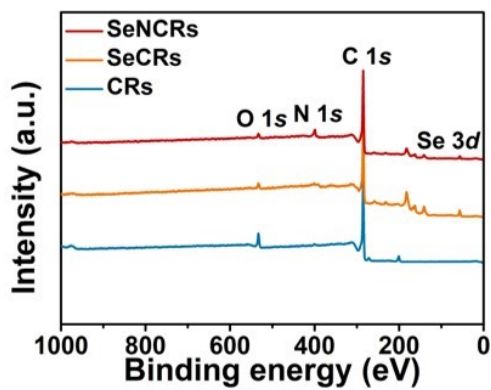**Figure S6.** N_2 adsorption isotherms and the corresponding pore size distribution of (a) CRs and (b) SeCRs.

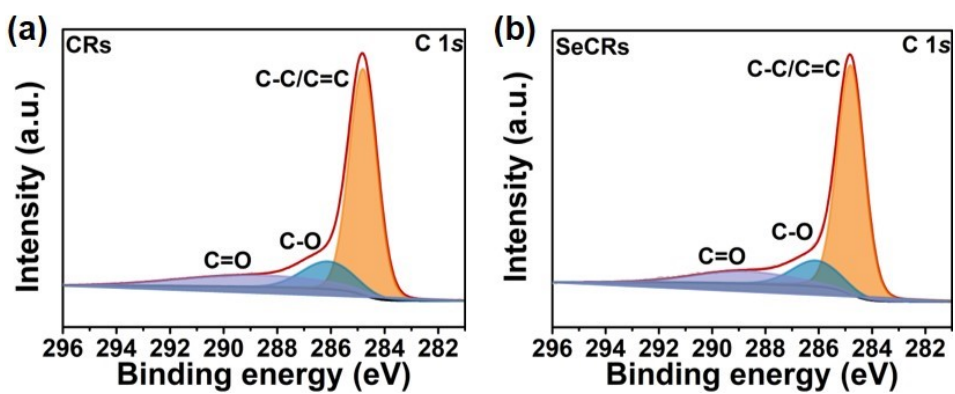**Figure S7.** The XPS survey spectra.

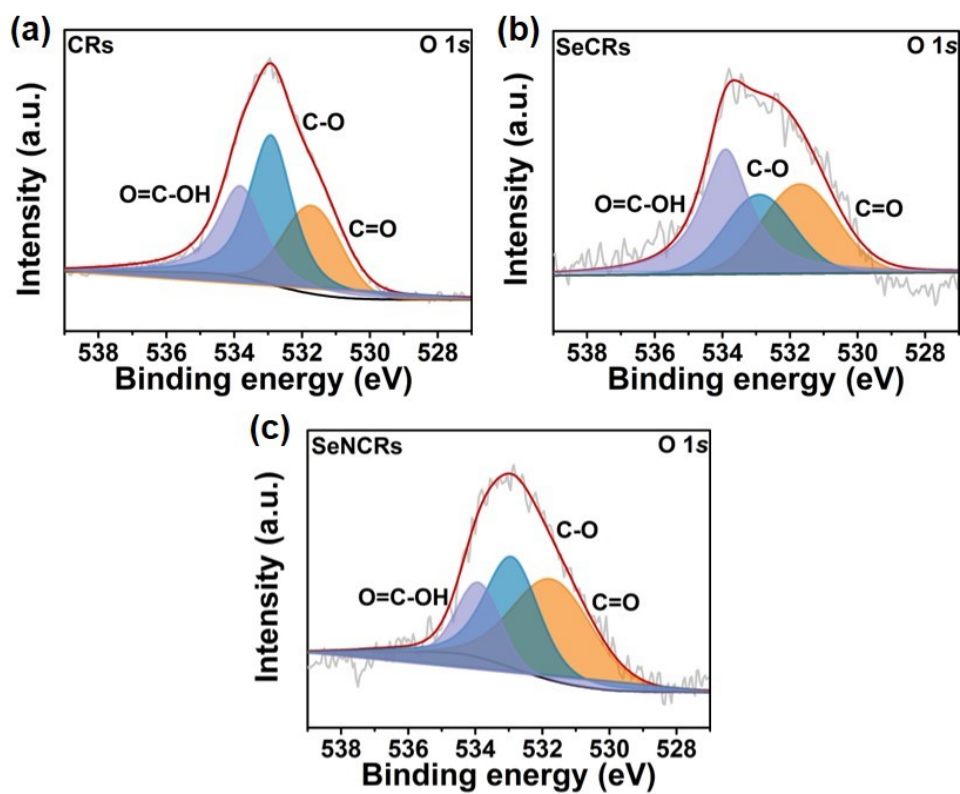**Figure S8.** High-resolution C 1*s* XPS of (a) CRs and (b) SeCRs.

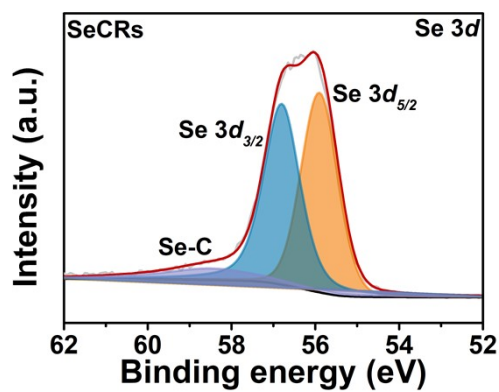**Figure S9.** High-resolution O 1*s* XPS of (a) CRs, (b) SeCRs and (c) SeNCRs.

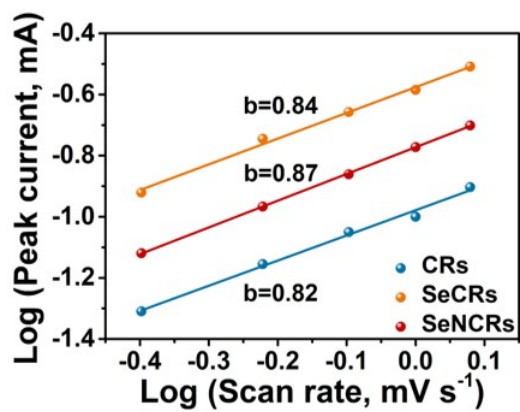

Figure S10. High-resolution Se 3*d* XPS of SeCRs.

Figure S11. The plots of log(i)-log(v) for the b-value determination from CV scans of CRs, SeCRs and SeNCRs.
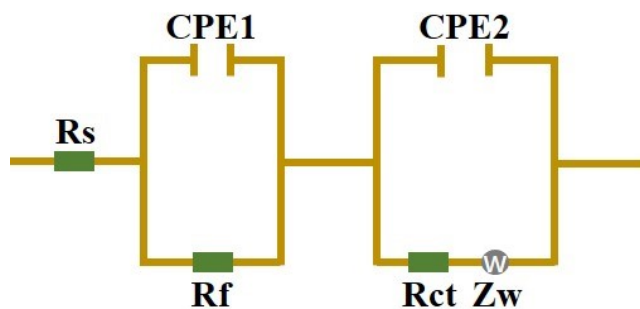

Figure S12. The equivalent circuit model of electrochemical impedance spectroscopy.
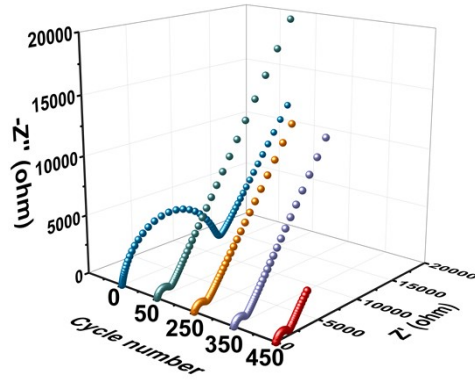
Figure S13. EIS curves of SeNCRs after different cycles from the 0 to 450 th cycles.
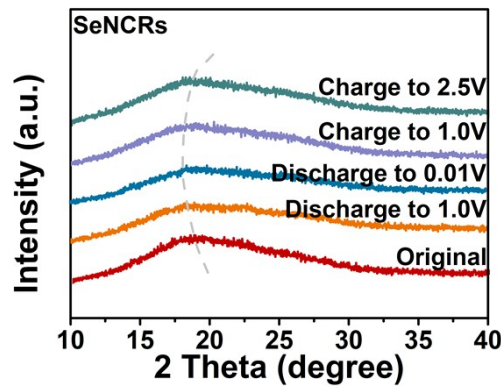

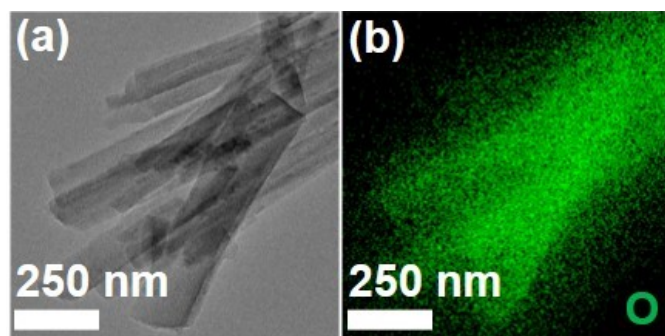**Figure S14.** *Ex-situ* XRD patterns of the SeNCRs.

Figure S15. (a) and (b) EDS mapping images of SeNCRs after discharge/charge process.

Table S1. Specific surface area and pore size of CRs, NCRs and SeNCRs.

Samples	Specific surface area (m^2g^{-1})	Pore diameter (nm)
CRs	829.9	5.7
SeCRs	533.8	3.0
SeNCRs	876.2	4.2

Table S2. Element composition of different samples from the XPS test.

Samples	Se(at%)	O(at%)	N(at%)	Pyridinic-N (%)	Pyrrolic-N (%)	Graphitic-N (%)
SeCRs	4.53	1.1	-	-	-	-
SeNCRs	1.81	0.94	5.14	31.1	42.5	26.4