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Supporting Information for

Hollow Ni-NiO nanoparticles embedded in porous carbon nanosheets as a hybrid anode for sodium-ion batteries with an ultra-long cycle life

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Materials and methods

Materials synthesis: 0.582 g (2 mmol) $Ni(NO_3)_2 \cdot 6H_2O$, 1.8 g $C_6H_{12}O_6$ and 14 g NaCl were dissolved in 40 ml deionized water. The solution was dried at 80 °C for 24 h and then ground to fine powders. After that, the powders were calcinated at 750 °C for 2 h under Ar atmosphere, forming Ni/C/NaCl. Then, Ni/C/NaCl was annealed in air at 300 °C for 4 h, obtaining Ni-NiO/C/NaCl. At last, Ni-NiO/PCNs was obtained by dissolving NaCl with deionized water. To optimize the annealing condition, other temperature and time (200 °C-4 h, 300 °C-2 h and 300 °C-6 h, and 400 °C-4 h) were also tested. In order to optimize the carbon content in Ni-NiO/PCNs, 4 mmol and 6 mmol $Ni(NO_3)_2 \cdot 6H_2O$ were also used to fabricate the hybrid samples in this work. Moreover, for comparisons, Ni/PCNs and Ni-NiO/C composites were synthesized by removing NaCl directly from Ni/C/NaCl and by carbonizing the mixture of $Ni(NO_3)_2 \cdot 6H_2O$ and $C_6H_{12}O_6$ without adding NaCl as a template, respectively.

Materials characterization: The morphology and microstructure of the specimens were characterized by a FESEM (JSM-6700F, JEOL, 15 keV) and a TEM (JEM-2100F, JEOL, 200 keV). XRD measurements were carried out on a D/max2500pc diffractometer using Cu Kα radiation. XPS was performed on an ESCALAB 250 system. TGA was carried out on an SDT Q600 instrument. Raman spectra were recorded on a micro-Raman spectrometer (Renishaw) with a laser source of 532-nm excitation wavelength. The specific area and pore size distribution were determined by nitrogen adsorption and desorption using a Micromeritics ASAP 2020 analyzer.

Electrochemical measurements: The electrochemical measurements were conducted on coin-type half cells (CR2025) with a Na foil as both the counter and reference electrode, glass fiber (GF/D) as the separator and 1.0 M $NaClO_4$ in the

mixture of ethylene carbonate and dimethyl carbonate (1:1 w/w) as the electrolyte, which were assembled at room temperature in an argon-filled glove box ([O_2] < 1 ppm and [H_2O] < 1 ppm). The working electrode was fabricated by mixing active materials (Ni-NiO/PCNs or Ni-NiO/C), conductive material (Super P) and binder of polyvinylidene fluoride (PVDF) with a weight ratio of 8:1:1 with N-methyl-2-pyrrolidone (NMP, Aladdin Reagent, AR) as the solvent. The mixture was stirred for 5 h and then uniformly pasted on Cu foil. After vacuum drying at 110 °C for 12 h, the electrode disks with a diameter of 12 mm were punched and weighed. The mass loading of active materials in each electrode is 0.5-0.8 mg. CV measurements were carried out on an Ivium-n-Stat electrochemical workstation (Ivium Technologies) within the potential range of 0.01-3.0 V (*vs.* Na^+/Na). EIS tests were performed with an amplitude of 10 mV in the frequency range of 100 kHz to 10 mHz. Galvanostatic charge-discharge cycling tests were performed using a LAND CT2001A battery testing system. In order to elucidate the reaction mechanism of Ni-NiO/PCNs during the charge/discharge process, after electrochemical tests, the electrodes were disassembled from the cells in an argon-filled glove box ([O_2] < 1 ppm and [H_2O] < 1 ppm) and were then rinsed with dimethyl carbonate to remove the residual electrolyte before *ex-situ* characterization.

Supplementary Figures

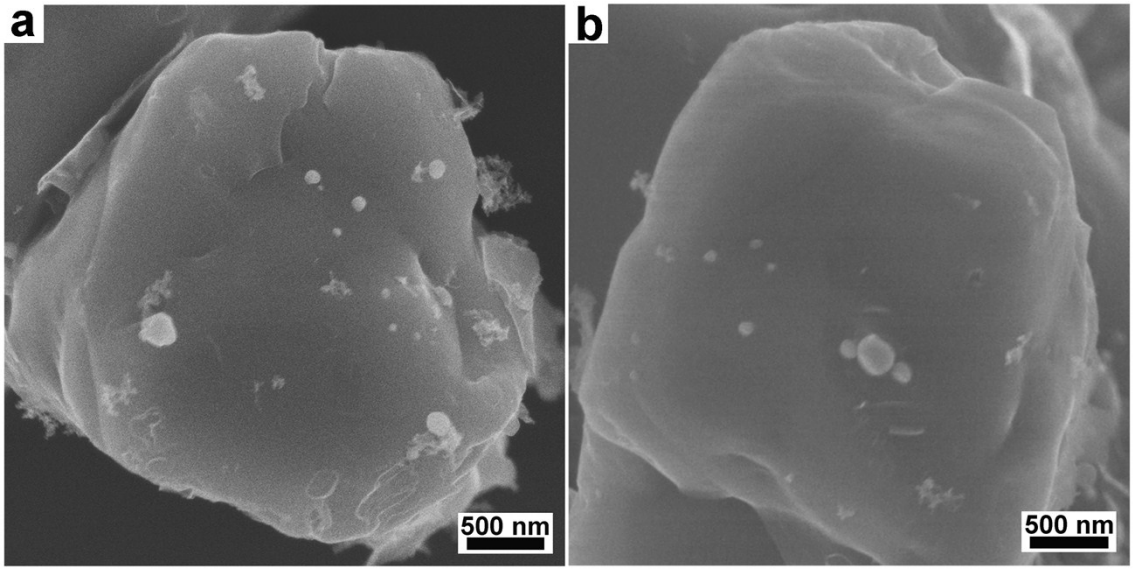

Fig. S1 FESEM images of (a) Ni/C/NaCl and (b) Ni-NiO/C/NaCl.

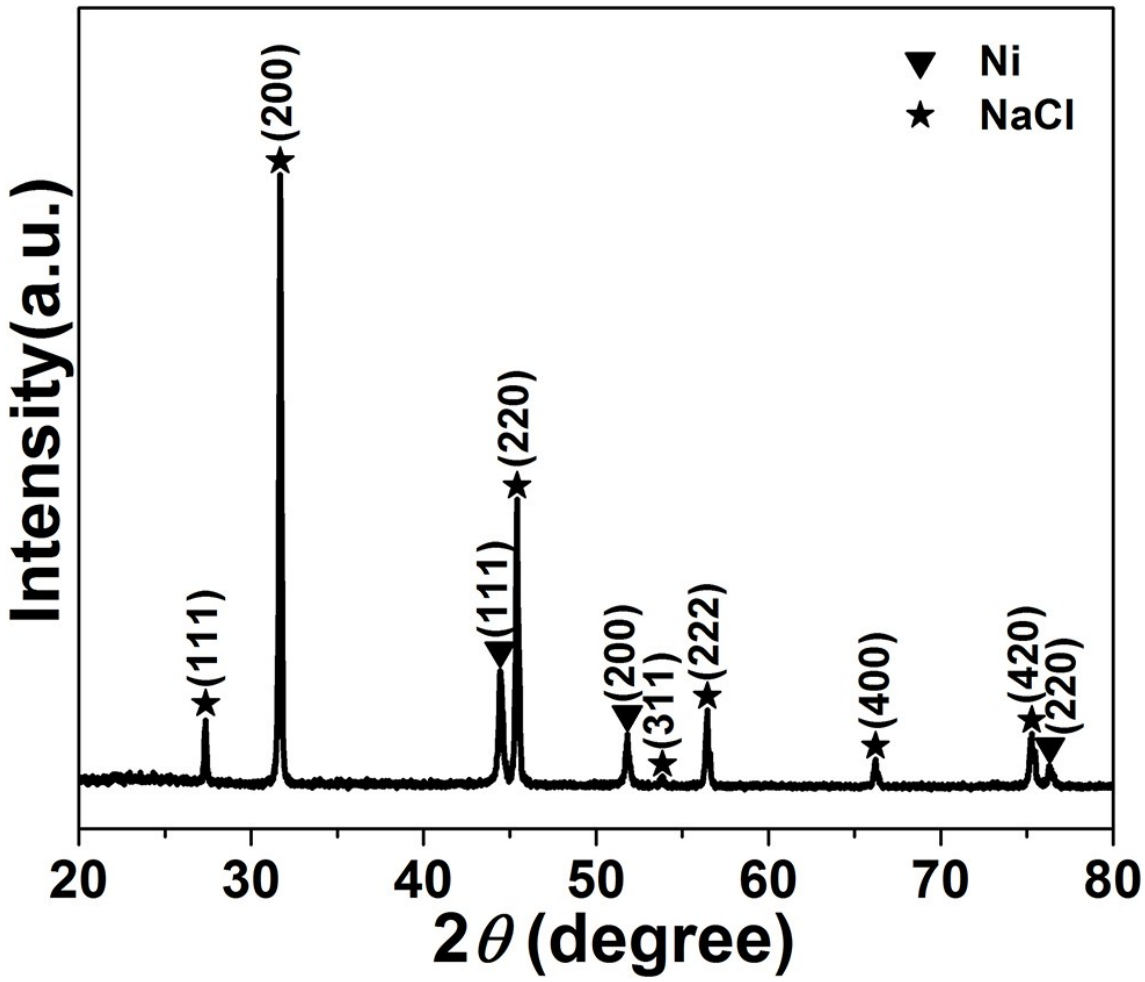

Fig. S2 XRD pattern of Ni/C/NaCl.

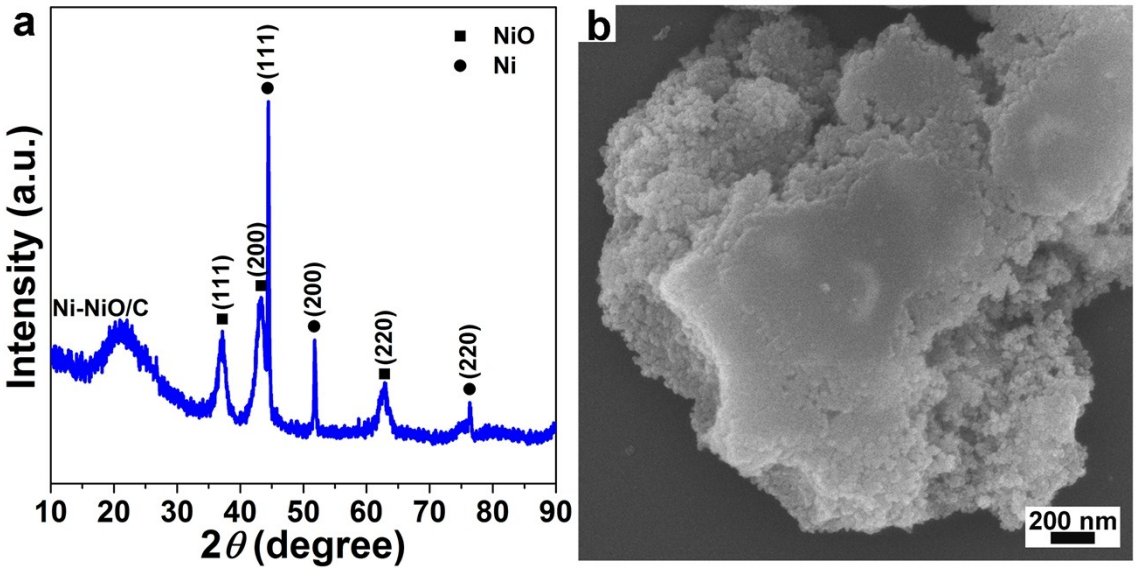

Fig. S3 (a) XRD pattern and (b) FESEM image of Ni-NiO/C.

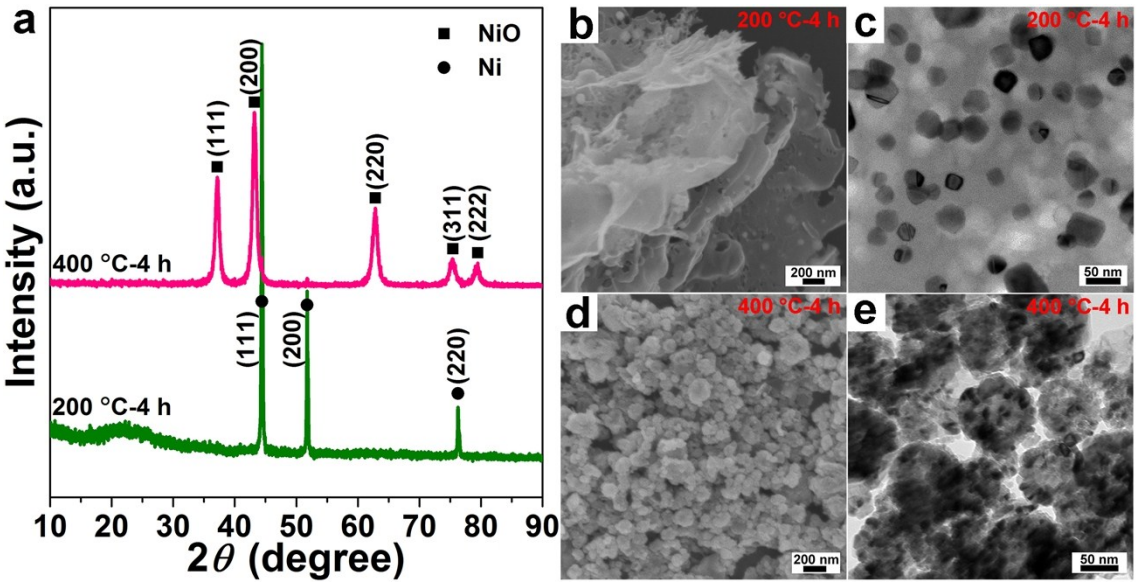

Fig. S4 (a) XRD patterns of final products through annealing at 200 °C and 400 °C for 4 h. (b) FESEM and (c) TEM images of the product at 200 °C-4 h. (d) FESEM and (e) TEM images of the product at 400 °C-4 h.

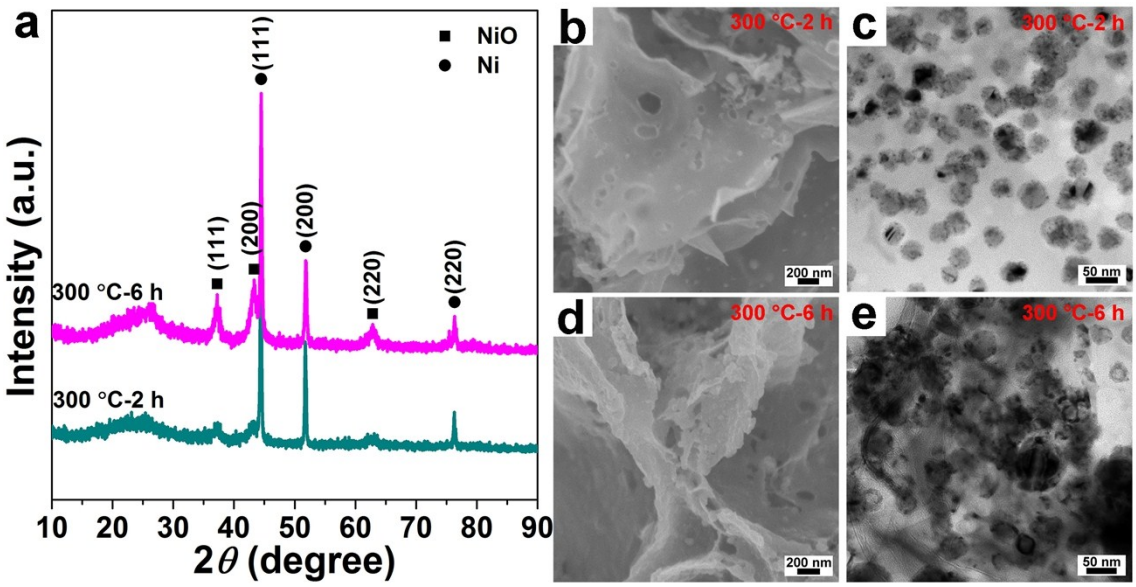

Fig. S5 (a) XRD patterns of final products through annealing at 300 °C for 2 h and 6 h. (b) FESEM and (c) TEM images of the product at 300 °C-2 h. (d) FESEM and (e) TEM images of the product at 300 °C-6 h.

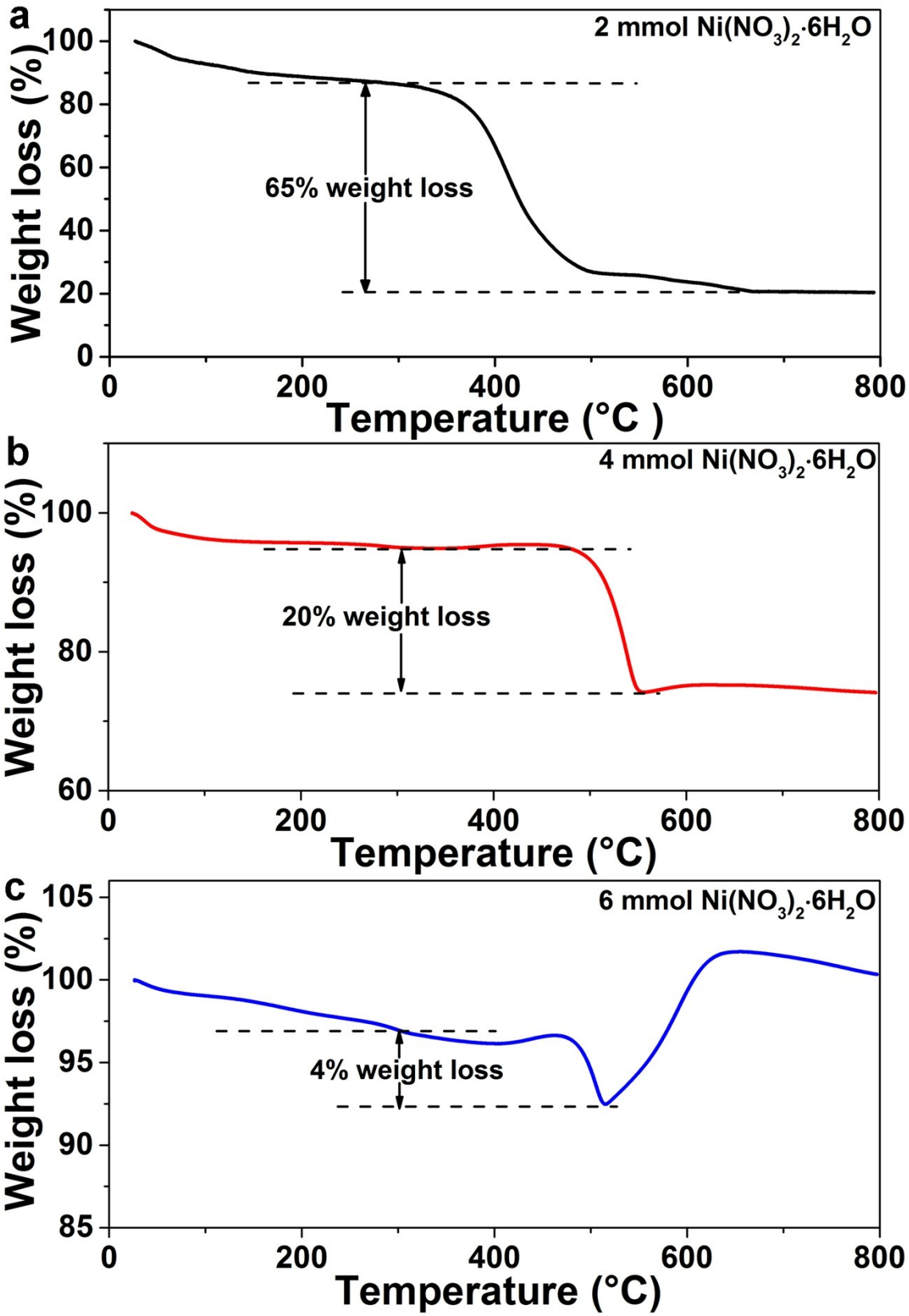

Fig. S6 TGA profiles of final products fabricated with (a) 2 mmol (*i.e.* Ni-NiO/PCNs), (b) 4 mmol and (c) 6 mmol $Ni(NO_3)_2 \cdot 6H_2O$.

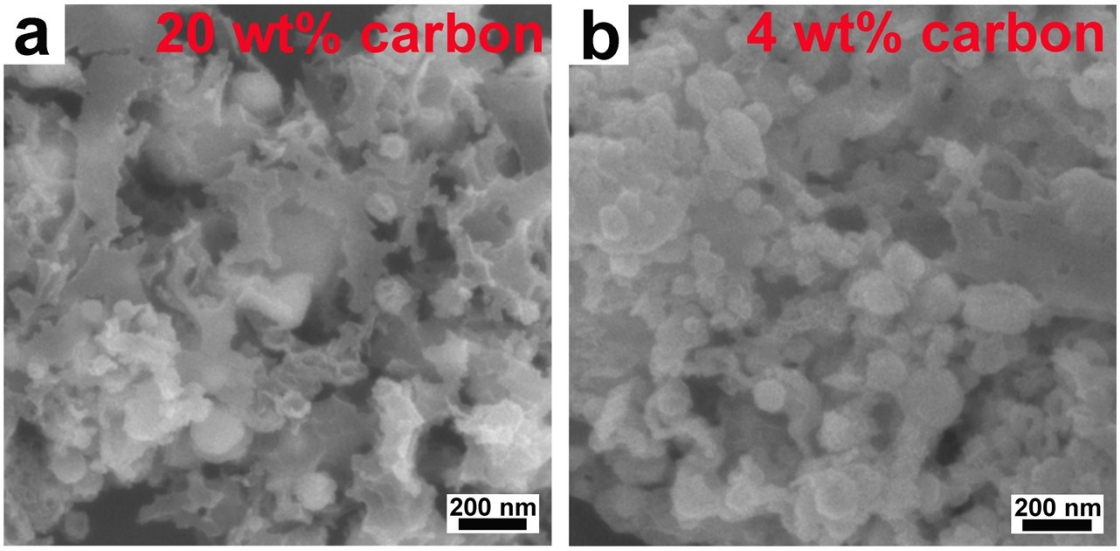

Fig. S7 FESEM images of the products with (a) 20 wt% and (b) 4 wt% carbon.

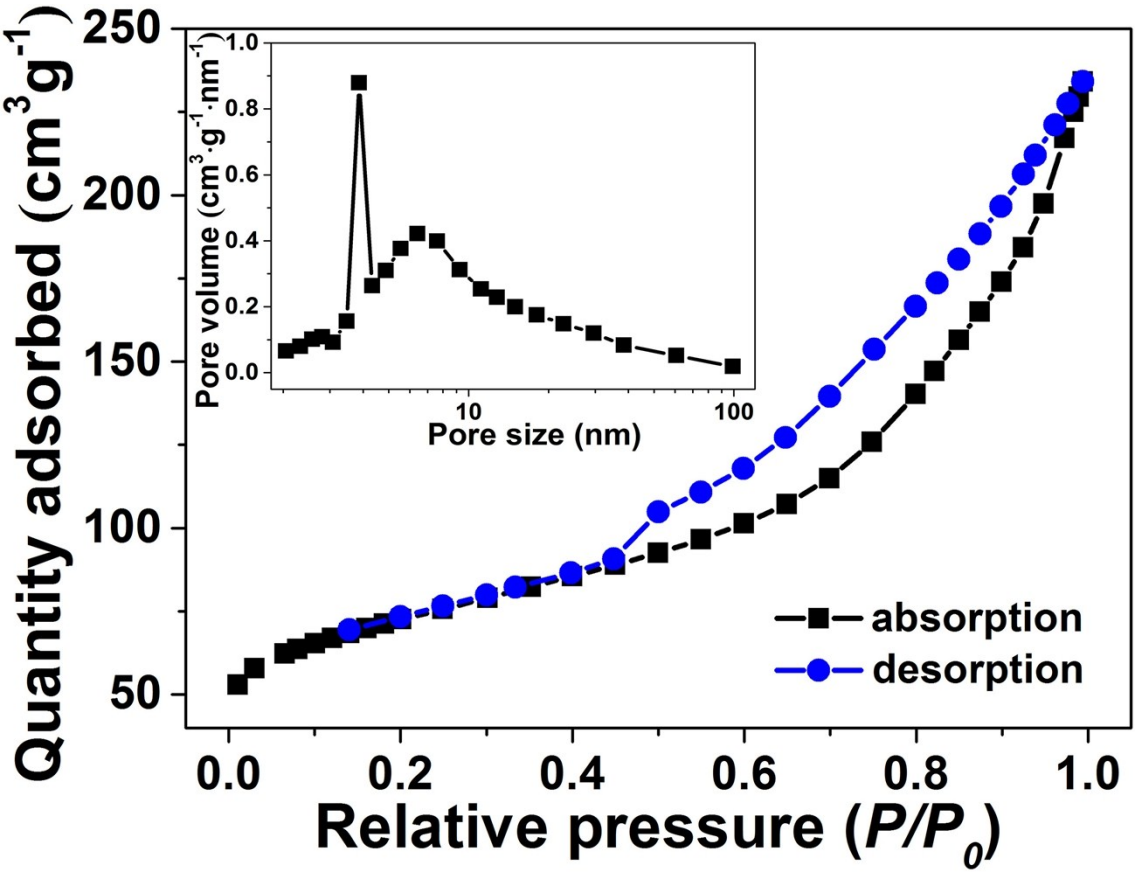

Fig. S8 N_2 adsorption/desorption isotherms and pore size distribution (the inset) of Ni-NiO/C.

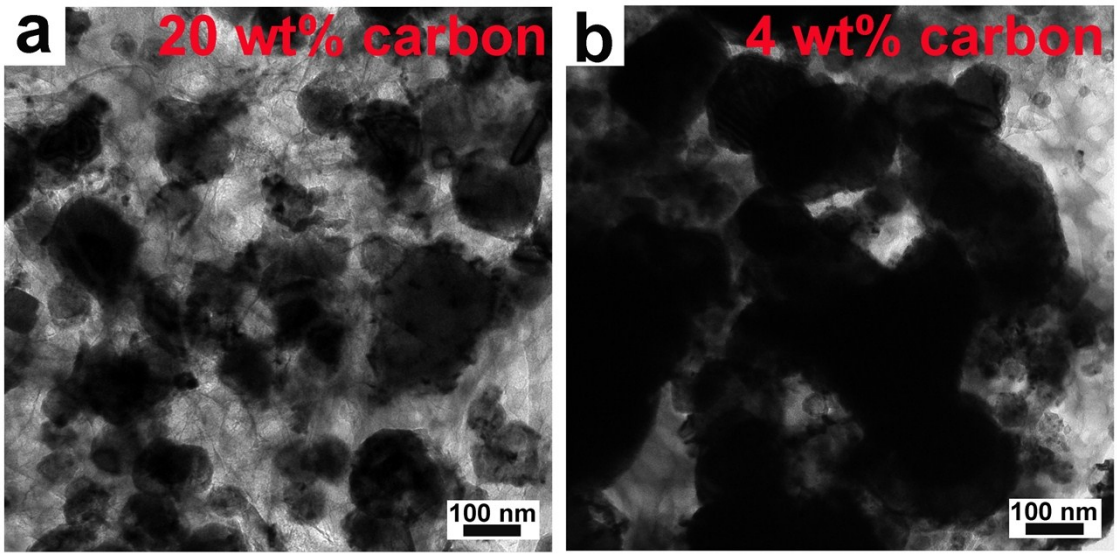

Fig. S9 TEM images of the products with (a) 20 wt% and (b) 4 wt% carbon.

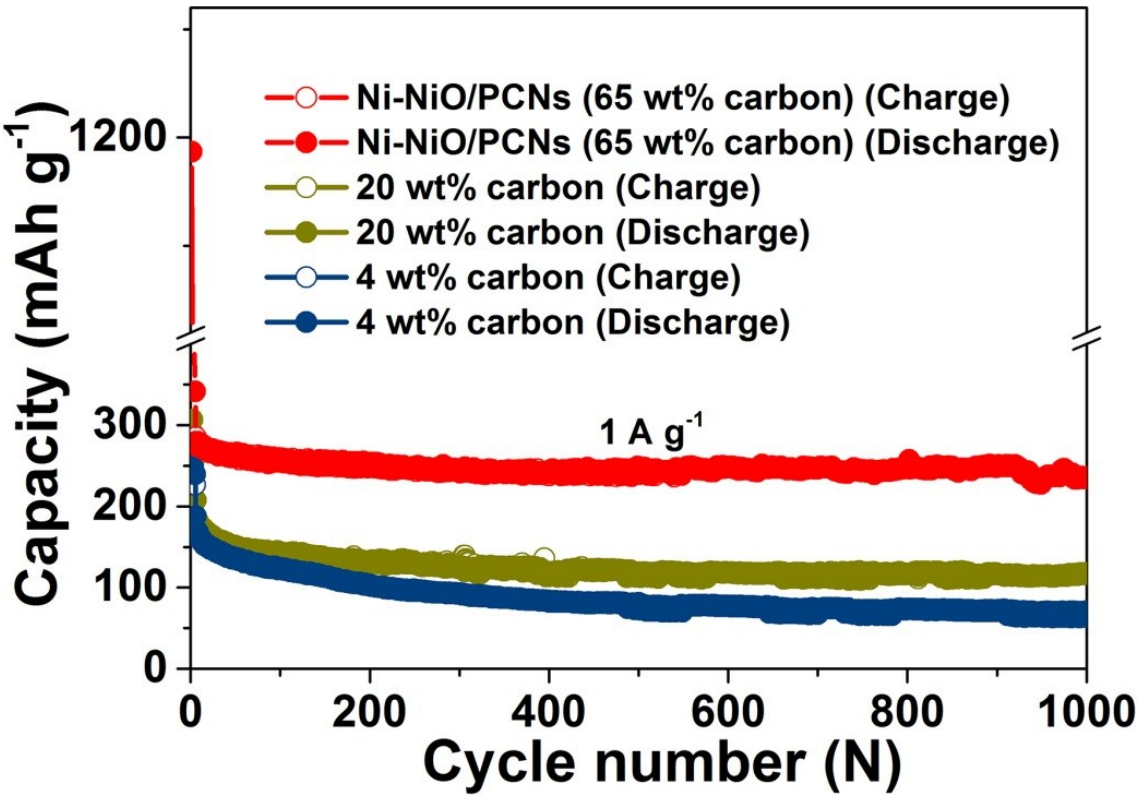

Fig. S10 Cycling performances of Ni-NiO/PCNs (65 wt% carbon) and final products with 20 wt% and 4 wt% carbon.

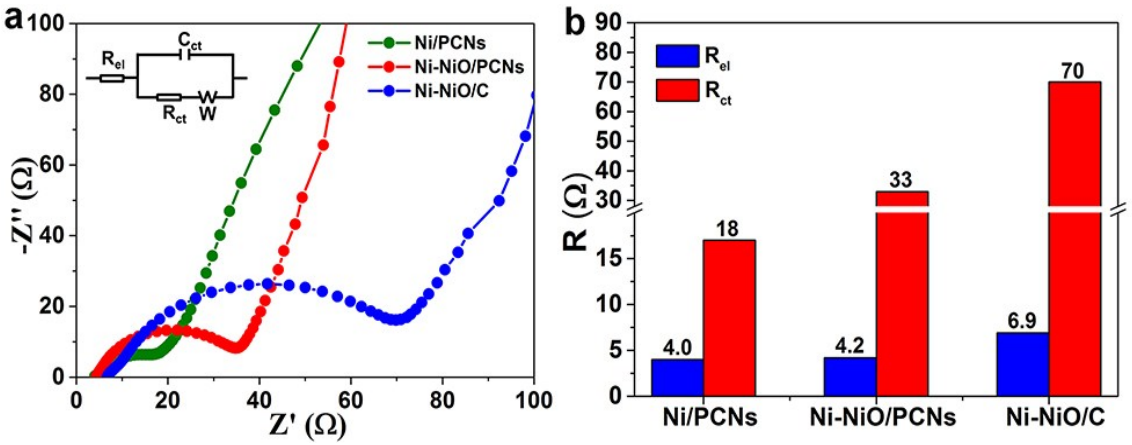

Fig. S11 (a) EIS of Ni/PCNs, Ni-NiO/PCNs and Ni-NiO/C electrodes in fresh SIBs, where the inset shows the equivalent circuit diagram. (b) R_{el} and R_{ct} values of Ni/PCNs, Ni-NiO/PCNs and Ni-NiO/C electrodes.

Supplementary Tables

Table S1. Part of the experimental data of higher initial charge capacities than theoretical capacities for electrode materials in SIBs reported in open literatures.

Electrode material	Theoretical capacity (mAh g^{-1})	Initial charge capacity (mAh g^{-1})	Ref.
α-Fe_2O_3@gum arabic	1007	1330	Ref. [50] of the text
graphene@Co_9S_8 quantum dots@mesoporous hollow carbon polyhedral matrix	544	750	Ref. [51] of the text
MoS_2@TiO_2	670	957	Ref. [56] of the text
N-rich hard carbon	372	445	Ref. [55] of the text
SnS nanosheet@graphene foam	1022	1147	Ref. [52] of the text
$CoSe_2$	494	548	Ref. [57] of the text
$NiSe_2$ nanofiber	495	575	Ref. [58] of the text
Sb/graphene	660	700	Ref. [41] of the text

Table S2. Comparisons of the cycling performance of Ni-NiO/PCNs electrode and recent reported experimental data of other metal oxides-based electrodes in SIBs.

Electrode material	Cycling performance (capacity@current desity, cycle life)	Ref.
Fe_2O_3@graphene nanosheets	161 mAh g^{-1}@1 A g^{-1}, 200 cycles	Ref. [19] of the text
Porous CuO arrays	290.6 mAh g^{-1}@0.2 A g^{-1}, 450 cycles	Ref. [25] of the text
Multi-walled carbon nanotubes@Fe_2O_3@C	272 mAh g^{-1}@0.16 A g^{-1}, 100 cycles	[1]
3D porous γ-Fe_2O_3@C	358 mAh g^{-1}@2 A g^{-1}, 1400 cycles	Ref. [17] of the text
Ultrafine MnO_2 nanocrystallites	209.1 mAh g^{-1}@0.15 A g^{-1}, 500 cycles	Ref. [24] of the text
NiO/Ni/graphene	232.2 mAh g^{-1}@1 A g^{-1}, 200 cycles	Ref. [18] of the text
Mesoporous Co_3O_4	416 mAh g^{-1}@0.09 A g^{-1}, 100 cycles	Ref. [26] of the text
Co_3O_4@N-doped carbon	175 mAh g^{-1}@1 A g^{-1}, 1100 cycles	Ref. [27] of the text
Hollow carbon@NiO	309 mAh g^{-1}@0.1 A g^{-1}, 50 cycles	Ref. [45] of the text
CuO/Cu_2O/graphitized porous C	302.9 mAh g^{-1}@0.05 A g^{-1}, 200 cycles	[2]
α-Fe_2O_3 nanorod/reduced graphene oxide nanosheet	332 mAh g^{-1}@0.2 A g^{-1}, 300 cycles	[3]
Ni-NiO/PCNs	235.4 mAh g^{-1}@1 A g^{-1}, 5000 cycles	this work

Notes and references

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2. A-Y. Kim, M. K. Kim, K. Cho, J.-Y. Woo, Y. Lee, S.-H. Han, D. Byun, W. Choi and J. K. Lee, *ACS Appl. Mater. Interfaces*, 2016, **8**, 19514-19523.
3. D. Kong, C. Cheng, Y. Wang, B. Liu, Z. Huang and H. Y. Yang, *J. Mater. Chem. A*, 2016, **4**, 11800-11811.