Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

Figure S1: Morphology of low carbon-content reference sample (a, b) and the carbon-coated reference sample (c, d). (a) The low-magnification TEM image indicates the particle size of the sample is about 3~5 μm. (b) The high-magnification image for the red square of (a) demonstrates the solid nature of the material. (c) The low-magnification TEM image indicates the particle size of the carbon coated sample is about 3~5 μm. (d) The high-magnification image for the red square of (c) demonstrates the existence of surface carbon layer and solid nature of the material.

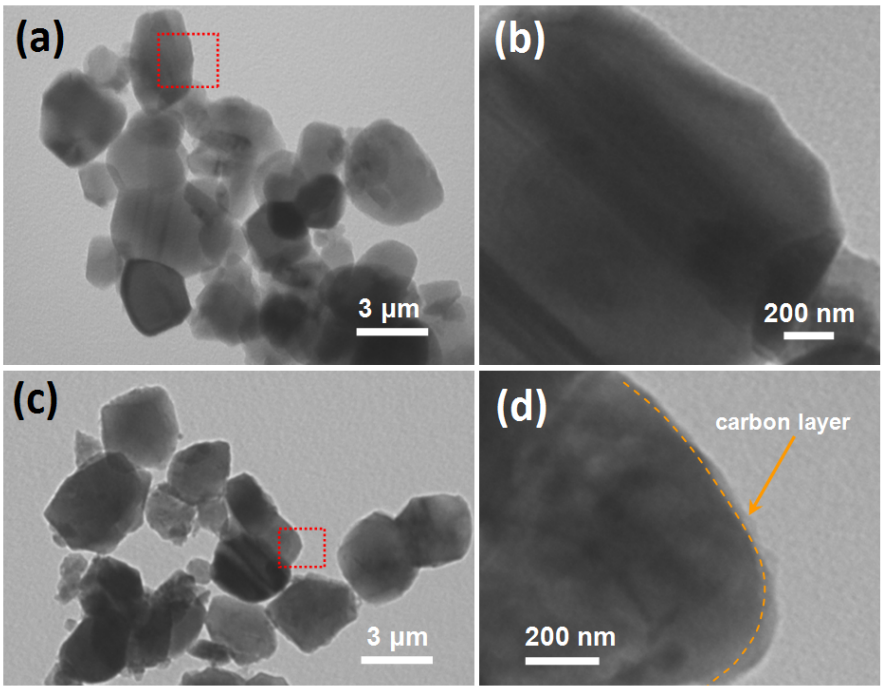

Figure S2: Linear behavior of the transient voltage changes (E) vs. ($\tau^{1/2}$) during the titration process demonstrates the validity of simplified equation (2) in our study.

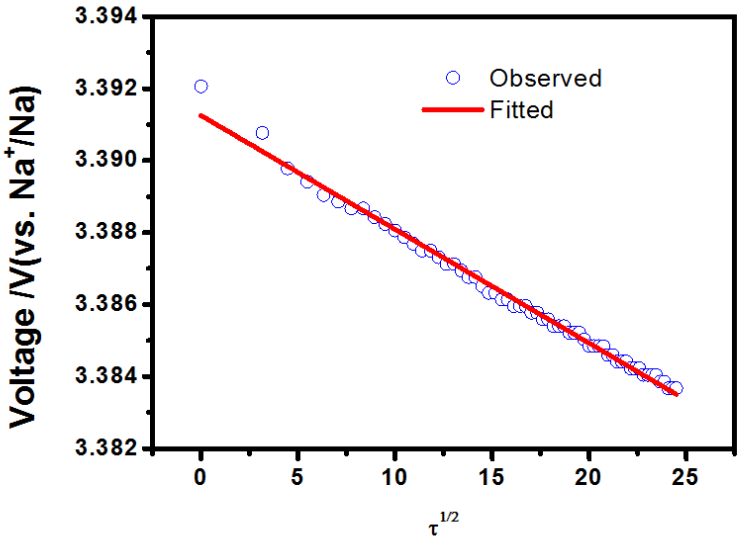

Figure S3: Cycling properties of the honeycomb-structured microball and the microsized nanoporous sample at the 20 C rate.

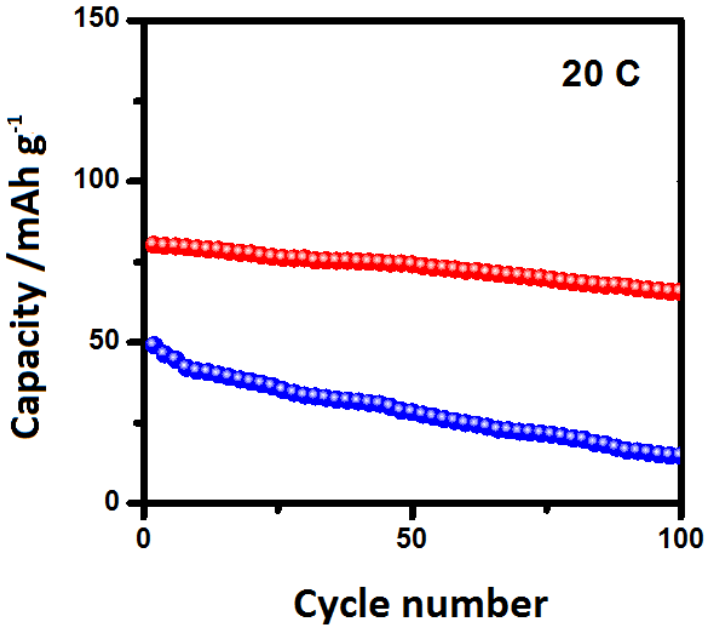

Table S1: Atomic parameters of carbon coated reference sample refined from the XRD data. (a=8.7211(3) Å, c=21.8126(2) Å)

Atom	**Wyckoff site**	***x***	***y***	***z***
Na1	6b	0	0	0
Na2	18e	0.6403	0	1/4
V	12c	0	0	0.1476
P	18e	0.2864	0	1/4
O1	36f	0.1783	0.9622	0.1912
O2	36f	0.1910	0.1631	0.0843

Table S2: Atomic parameters of low carbon-content reference sample refined from the XRD data. (a=8.7190(4) Å, c=21.8112(3) Å)

Atom	**Wyckoff site**	***x***	***y***	***z***
Na1	6b	0	0	0
Na2	18e	0.6359	0	1/4
V	12c	0	0	0.1472
P	18e	0.2850	0	1/4
O1	36f	0.1791	0.9661	0.1904
O2	36f	0.1918	0.1654	0.0834