Supporting Information (SI)

Titanium dioxide nanoparticle sandwiched separator for Na-O_2 battery with suppressed dendrites and extending cycle life

Hao Yang, Jianchao Sun, Hang Wang, Jing Liang and Haixia Li*

Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education) and Collaborative Innovation Center of Chemical Science and Engineering, College of Chemistry, Nankai University, Tianjin 300071, China

***Corresponding Author:** liangjing@nankai.edu.cn

This PDF file includes: Materials, Methods, Fig.S1 to S11 and Table S1 to S2.

Table of contents

Table S1 A summary of electrochemical performances of Na-O_2 batteries·····6

Fig. S1 The first cycle of Na-Cu batteries with different separators·····7

Fig. S2 XRD patterns of glass fiber before and after discharge-charge·····8

Fig.S3 Optical photograph, SEM images and EDX elemental mapping images of the sodium dendrites in glass fiber·····9

Fig. S4 SEM images of glass fiber, PP and PVDF sandwiched separator·····10

Fig. S5 Galvanostatic cycling of Na-Cu batteries·····11

Fig. S6 Optical photograph of pristine and sodiated PP-TiO_2-PP separator·····12

Fig. S7 Ti 2p XPS spectra of TiO_2 nanoparticles packed in separators·····13

Fig. S8 The line-scan during EDS analysis for the sodiated TiO_2 nanoparticles··14

Fig. S9 Regions of sodiated TiO_2 selected for EDS spectroscopy·····15

Table S2 Atomic concentrations of Ti, O and Na determined by EDS·····16

Fig. S10 Coulombic efficiencies of Na−O_2 battery·····17

Fig. S11 Discharge-charge curve of Na-O_2 battery·····18

Experimental section

Materials

Titanium dioxide (TiO_2, rutile) and silicon dioxide (SiO_2) were supplied by Aladdin. The solvent, diethylene glycol dimethyl ether (DEGDME), was also purchased from Aladdin. Prior to use, it was treated to remove water by Na metal and reduced pressure distillation, and then stored with activated 4 Å molecular sieves (beads 8-12mesh, J&k) in glove box (H_2O and O_2<0.1 ppm). $NaSO_3CF_3$ (anhydrous, Aladdin) was dried under vacuum at 80 °C for 10 hours. The polypropylene (PP) separators are Celgard 2400, and specification of conductive carbon black is TIMCAL Super P li.

Methods

Preparation of sandwiched separators

The PP-TiO_2-PP sandwiched separator was prepared as followed. TiO_2 nanoparticles and polyvinylidene difluoride (PVDF) were dispersed in N-methyl-2-pyrrolidone (NMP) to make a slurry (mass ratio of TiO_2:PVDF is 9:1). The slurry were coated on the side of the PP separator. And then the slurry coated separator was dried in a vacuum oven at 50 °C for 24 h. Finally, the two TiO_2 coated separators was pressed together. The other sandwiched separators with different fillers (SiO_2 or PVDF) were prepared using the same method.

Electrode fabrication

The cathode of Super P on carbon paper without any binder was prepared using a spraying method. The slurry containing 35 mg Super P in 20 mL ethanol was obtained by sonicating for one hour. Then the uniform slurry was spraying onto one piece of carbon paper (10×10 cm^2) with a power gas of high-pressure air at 100 °C. The

obtained carbon cathode was dried in a vacuum oven at 80°C overnight. The loading of Super P is 0.33 mg/cm^2. The TiO_2 electrode was prepared by admixing TiO_2 nanoparticles, Super P and (PVDF) binder at a weight ratio of 6:3:1. The mixture was spread and pressed on a copper foil as working electrodes, and dried in vacuum at 100°C for 12 h.

Battery assembly

Na-Cu batteries were assembled by using Na anode (ϕ=10 mm) and Cu cathode (ϕ=10 mm) with various separators respectively. Na-O_2 batteries were assembled using Na anode, different separators and Super P cathode. The above batteries are the coin-type CR-2032 cells and assembled in an argon-filled glove box. Especially, the cathode cases of Na-O_2 batteries were predrilled with seven homogenously distributed holes to allow the diffusion of O_2, and the Na-O_2 batteries were put into an oxygen-filled glove box. Before electrochemical testing, all the batteries are rested for 10 h, and the electrolyte is 0.5M $NaSO_3CF_3$ in DEGDME.

Characterization

X-Ray diffraction (XRD) analysis between 20-70° was performed on a Rigaku MiniFlex600 with Cu-Kα radiation (λ = 1.54178 Å) with a rate of 4°/min. The morphology and structure were observed by field-emission scanning electron microscopy (SEM, JEOL JSM7500F) and transmission electron microscopy (TEM, Philips Tecnai-F20). Raman spectroscopy was measured with a Thermo-Fisher Scientific (excitation wavelength, 532 nm). X-ray photoelectron (XPS) spectroscopy was measured in a Versa Probe PHI 5000 system (Al Kα radiation of 1486.6 eV).

Electrochemical testing

Galvanostatic discharge/charge tests were measured on a LAND battery-test instrument (CT2001A). Electrochemical impendence spectra (EIS) were performed on a Parstat 2273A potentiostat/galvanostat workstation (AMETEK Company) in the

frequency of 100 mHz to 100 kHz. Cyclic voltammetry was conducted on a CHI660B electrochemical workstation at a scan rate of 1 mV/s.

Improved Content	Current Density	Specific Capacity	Electrode Loading	Cycles	Ref.
Cathodes: $CaMnO_3$/C	200 mA g^{-1}	1000 mA h g^{-1}	-	80	[1]
Cathodes: N-doped carbon	200 mA g^{-1}	500 mA h g^{-1}	0.5 mg cm^{-2}	66	[2]
Cathodes: B-doped carbon	3000 mA g^{-1}	1000 mA h g^{-1}	0.6 mg cm^{-2}	125	[3]
Cathodes: N-doped graphene	100 mA g^{-1}	500 mA h g^{-1}	1 mg cm^{-2}	100	[4]
Anode: Na@r-GO	200 mA g^{-1}	200 mA h g^{-1}	0.6 mg cm^{-2}	20	[5]
Anode: Sodiated carbon	20 mA g^{-1}	-	9.7 mg cm^{-2}	40	[6]
Concentrated Electrolyte	0.05 mA cm^{-2}	0.15 mA h cm^{-2}	-	150	[7]
Separator: Nafion-Na^+	0.16 mA cm^{-2}	0.96 mA h cm^{-2}	-	118	[8]
Separator: PP-TiO_2-PP	200 mA g^{-1}	1000 mA h g^{-1}	0.33 mg cm^{-2}	137	This work
	0.066 mA cm^{-2}	0.33 mA h cm^{-2}			

Table S1 A summary of electrochemical performances of Na-O_2 batteries in recent years.

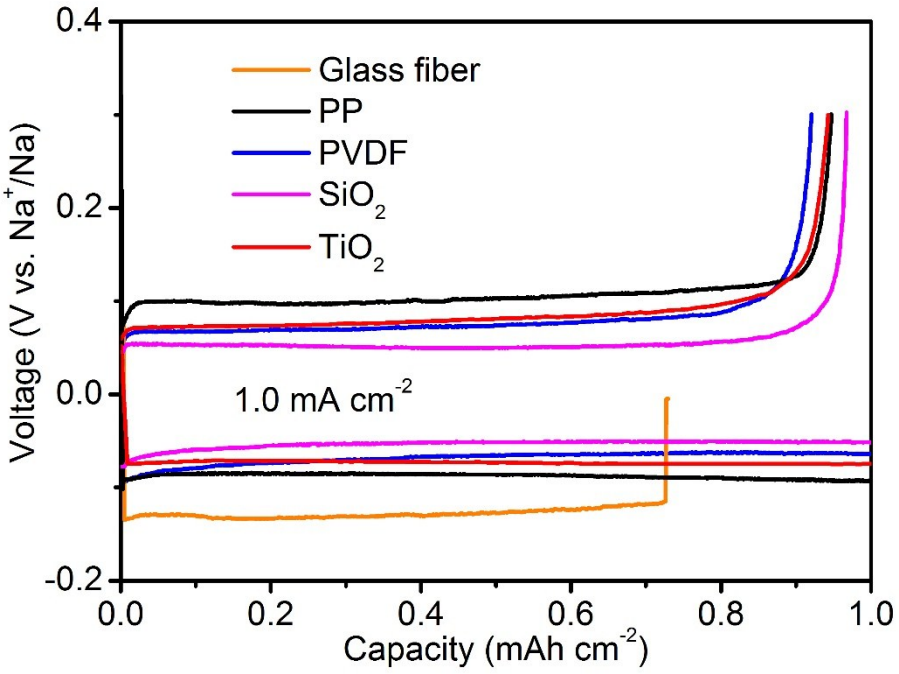

Fig. S1 The first cycle of Na-Cu batteries with different separators at the current density of 1.0 mA cm^{-2} for a specific capacity of 1 mA h cm^{-2}.

We used a program of 1 h of discharge followed by a compound procedure controlling charge process (a time limit of 1 h or a voltage limit of 0.3 V). The purpose of this setting is to prevent decomposition of electrolyte.

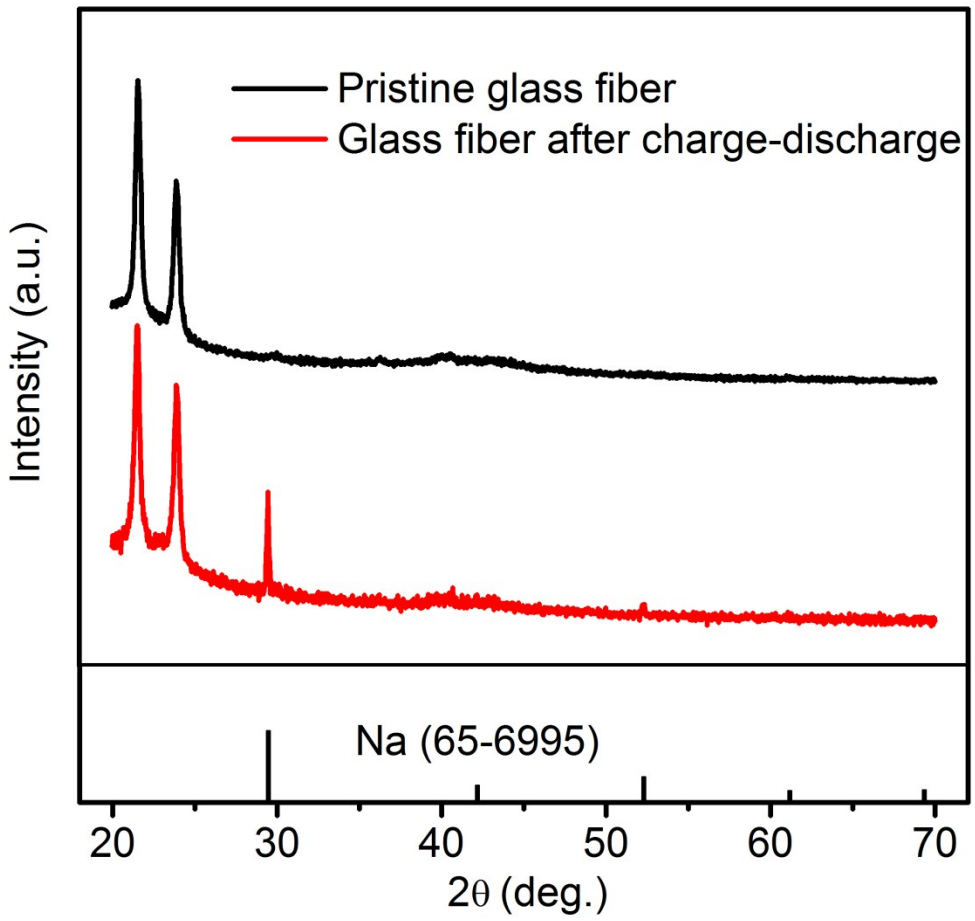

Fig. S2 XRD patterns of glass fiber before and after discharge-charge.

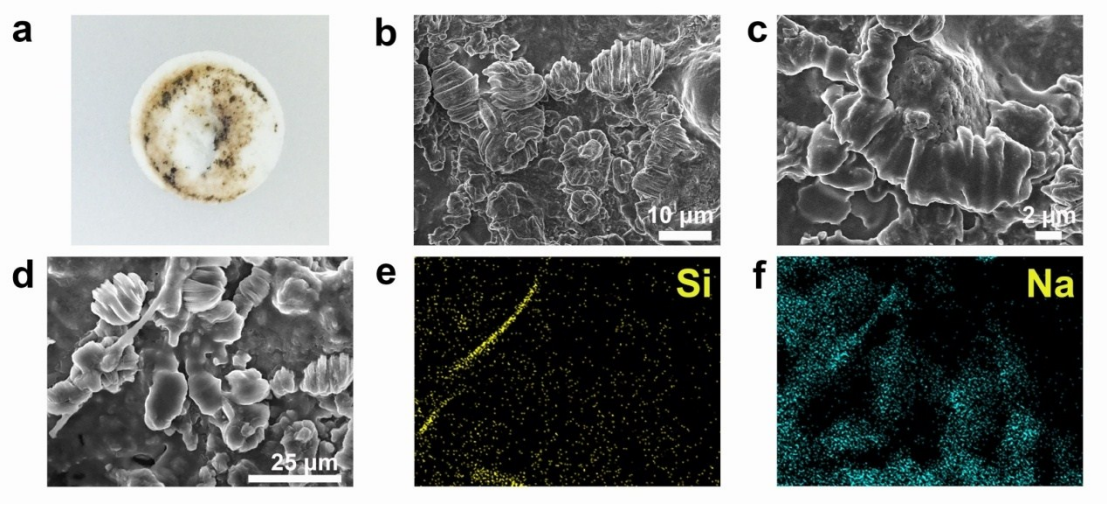

Fig. S3 (a) Optical photograph, (b-d) SEM images and (e, f) EDX elemental mapping images of the sodium dendrites in glass fiber.

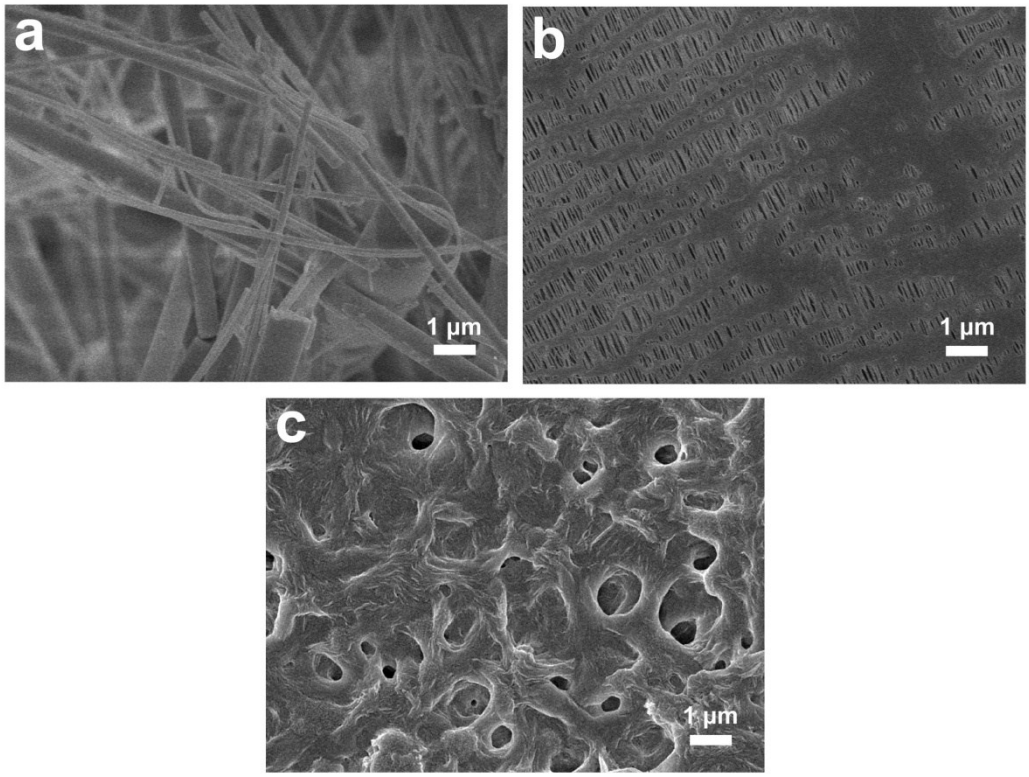

Fig. S4 (a-c) SEM images of glass fiber, PP and PVDF sandwiched separator respectively.

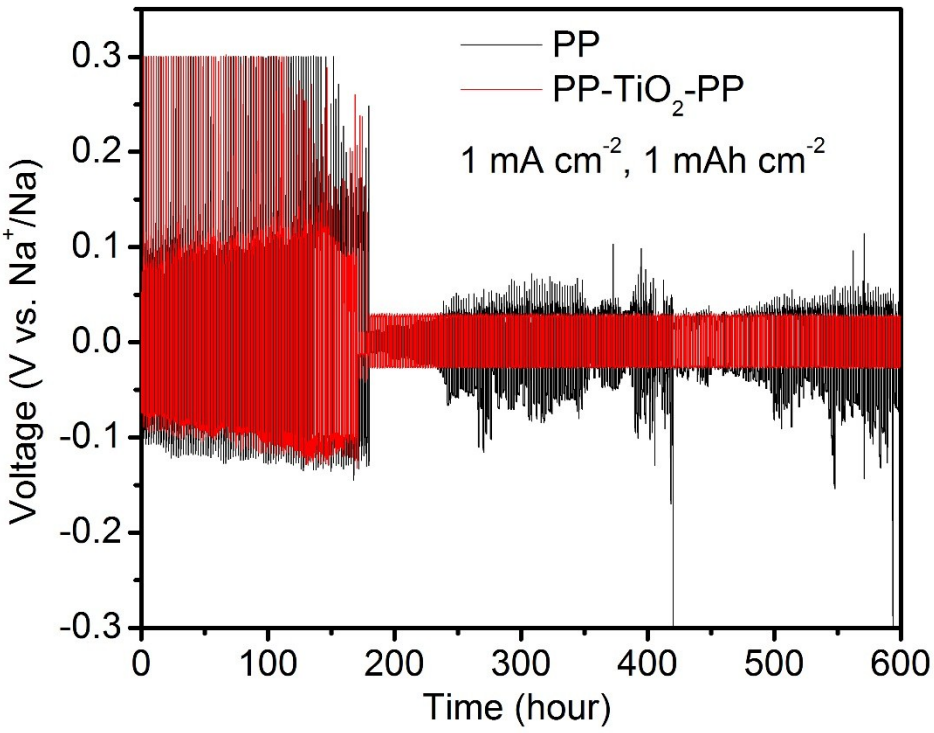

Fig. S5 Galvanostatic cycling of sodium-copper batteries with PP separators or PP-TiO_2-PP separators. The current density was fixed at 1 mA cm^{-2} with each cycle set to 2 h.

The first 180 hours shows normal discharge-charge cycle of Na-Cu batteries. However, metallic sodium accumulated on the copper electrode because of limited Coulombic efficiency, and then the batteries evolved into Na-Na batteries after cycling 180 hours. According to the whole cycling curves, the battery with PP-TiO_2-PP separators shows better stability.

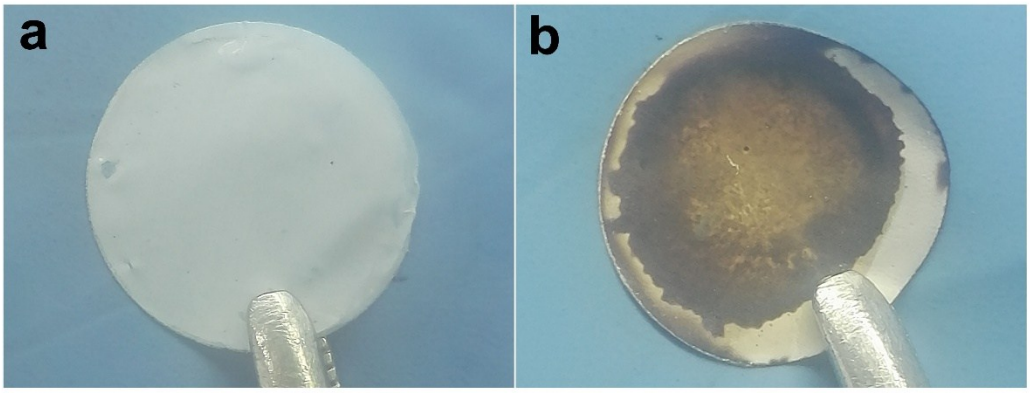

Fig. S6 Optical photograph of (a) pristine and (b) sodiated PP-TiO_2-PP separator.

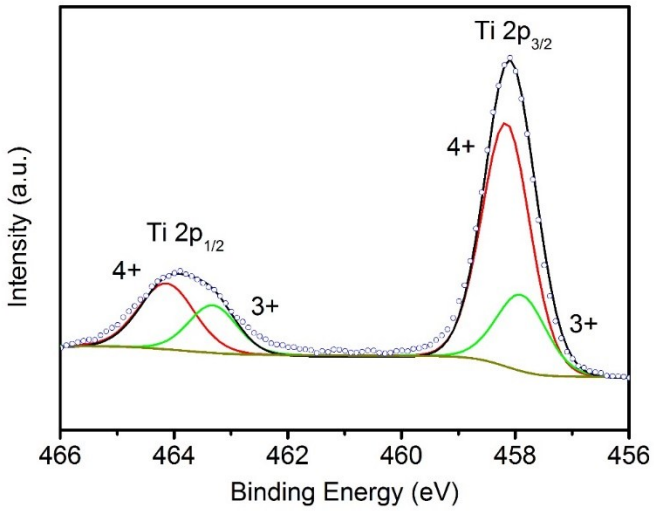

Fig. S7 Ti 2p XPS spectra of TiO_2 nanoparticles packed in separators.

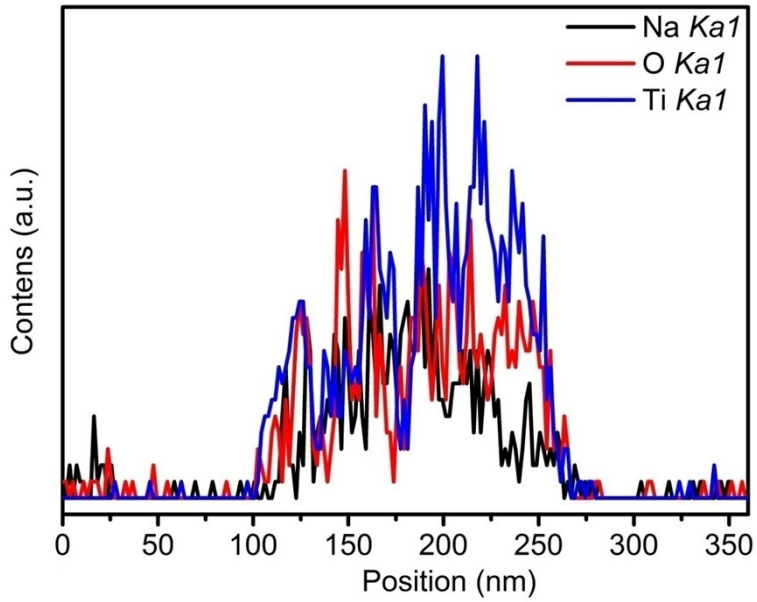

Fig. S8 The line scan EDS analysis for the sodiated TiO_2 nanoparticles after cycles.

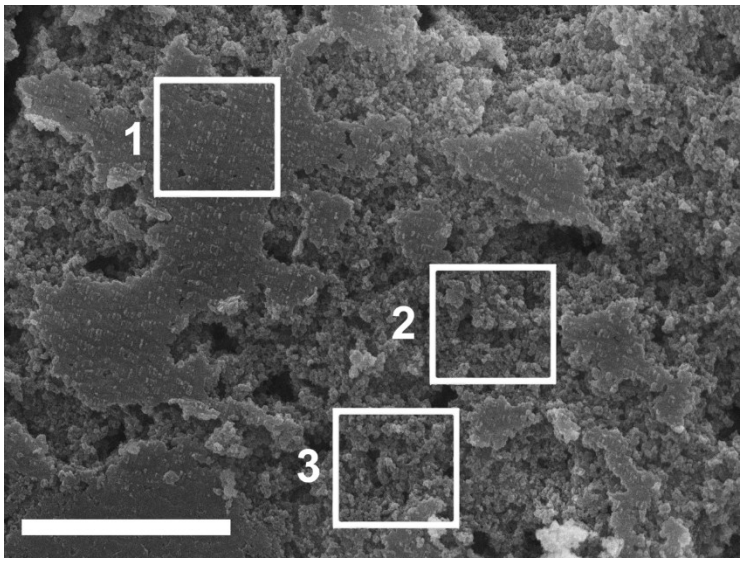

Fig. S9 Regions of sodiated TiO_2 selected for EDS spectroscopy. The white scale bar is 5 μm.

Region	Ti (At. %)	O (At. %)	Na (At. %)
1	25.91	62.50	11.59
2	26.98	65.48	7.55
3	31.56	60.35	8.09
Average	28.15	62.78	9.08

Table S2 Atomic percent of Ti, O and Na determined by EDS on areas selected in the Fig. S9.

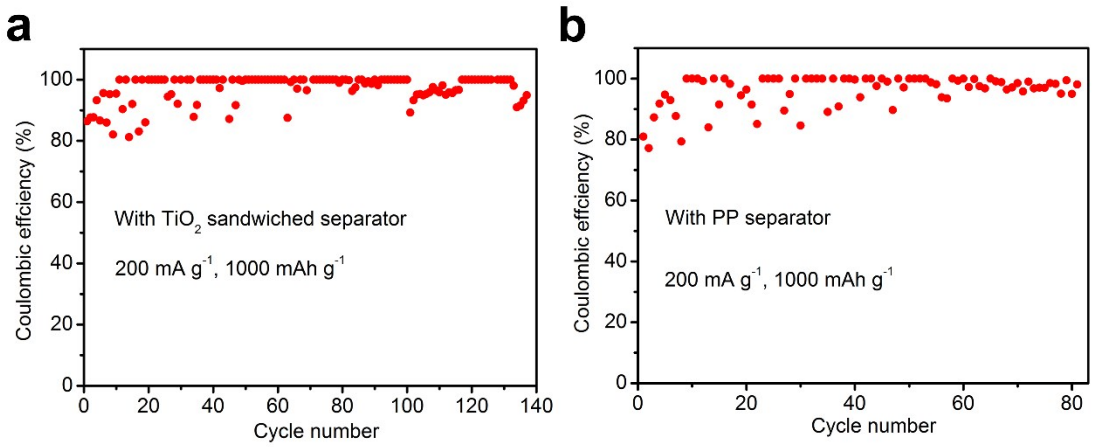

Fig. S10 Coulombic efficiencies of $Na-O_2$ batteries with TiO_2 nanoparticles sandwiched separator (a) and PP separator (b).

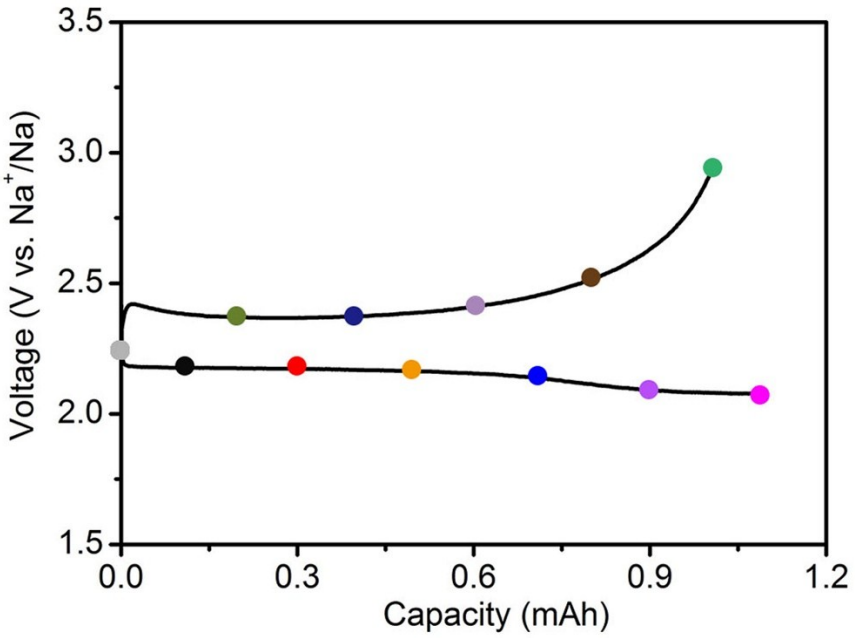

Fig. S11 Discharge-charge curve of Na-O_2 battery.

References

[1] Y. Hu, X. Han, Q. Zhao, J. Du, F. Cheng and J. Chen, *J. Mater. Chem. A*, 2015, **3**, 3320-3324.

[2] J. l. Ma and X.b. Zhang, *J Mater. Chem. A*, 2016, **4**, 10008-10013.

[3] C. Shu, Y. Lin, B. Zhang, S. B. Abd Hamid and D. Su, *J. Mater. Chem. A*, 2016, **4**, 6610-6619.

[4] S. Zhang, Z. Wen, J. Jin, T. Zhang, J. Yang and C. Chen, *J. Mater. Chem. A*, 2016, **4**, 7238-7244.

[5] A. Wang, X. Hu, H. Tang, C. Zhang, S. Liu, Y. W. Yang, Q. H. Yang and J. Luo, *Angew. Chem., Int. Ed.*, 2017, **56**, 11921-11926.

[6] C. L. Bender, B. Jache, P. Adelhelm and J. Janek, *J. Mater. Chem. A*, 2015, **3**, 20633-20641.

[7] M. He, K. C. Lau, X. Ren, N. Xiao, W. D. McCulloch, L. A. Curtiss and Y. Wu, *Angew. Chem., Int. Ed.*, 2016, **55**, 15310-15314.

[8] X. Bi, X. Ren, Z. Huang, M. Yu, E. Kreidler and Y. Wu, *Chem. Commun.*, 2015, **51**, 7665-7668.