Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Highly Efficient Bifunctional Heterogeneous Catalyst for Morphological Control of Discharged Products in Na-air Battery

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S1 Experimental

***Synthesis of Co_3O_4* nanowires**

Pure carbon cloth supported-Co_3O_4 was prepared via a template-free growth method. In a typical experiment, after degreased with acetone, the carbon cloth (3*4 cm^2) was then rinsed with deionized water and absolute ethanol for 30 min respectively. Then the pure carbon cloth was placed standing against the wall of the Teflon-lined autoclave (100 ml).

Co_3O_4 nanowires were directly deposited on the carbon cloth by a solvothermal method. In a typical synthesis, 0.7485g $Co(NO_3)_2 \cdot 6H_2O$, 0.0635g NH_4F and 0.2574g $CO(NH_2)_2$ were dissolved into 60ml deionized water under vigorous magnetic stirring. The pink solution was then transferred into a Teflon-lined stainless autoclave for reaction. The autoclave was sealed and maintained at 120℃ for 5.5h. After cooling down to room temperature, the product was collected, washed, vacuum dried and then annealed at 250℃for 3h.

Electrochemical measurements and Physical characterization

The assembly of the cell has been described in detail in our recent work [22]. 0.05M $Fe(C_5H_5)_2$ in 1M $NaClO_4$/1,2-dimethoxyethane (DME) was used as the electrolyte. Charge-discharge measurements were performed at room temperature with a Land BT 1-40 battery test system. Field-emission scanning electron microscopy (FESEM, Cambridge S-360) was employed to study the morphology of the air cathodes. Field-emission transmission electron microscopy (FETEM) and selected-area

electron diffraction measurements (SAED) were carried out in a 200 kV side entry JEOL 2010 TEM. All discharge/charge capacities were calculated based on the weight of Co_3O_4 nanowires (0.5 mg cm^{-2}), which was examined by electrobanlance (BP211D, Sartorius).

Table S1. Cyclic performance of Na-air batteries reported recently

Battery System	Discharge Product	Air Electrode	Discharge Capacity / mAh g^{-1}	Current Density / mA g^{-1}	Cycle Number	Reference
Na-O_2	Na_2O_2	DLC	1050-2100	1/10 C	20	1
Na-O_2	Na_2O_2	GNS	1150	75	3	2
Na-O_2	Na_2O_2	NGNS	1150	75	3	2
Na-O_2	Na_2O_2	GNS	1200	300	10	3
Na-O_2	Na_2O_2	CF_x	1000	200	6	4
Na-O_2	$Na_2O_2.2H_2O$	CNT	1000	500	7	5
Na-O_2	Na_2O_2	$NiCo_2O_4$	1000	50	10	6
Na-O_2	NaO_2	GDL	64	200 μAcm^{-2}	80	7
Na-O_2	NaO_2	Ketjenblack	1666	200 μA cm^{-2}	60	7
Na-O_2	NaO_2	VACNT	750	67	130-140	8
Na-O2	Na_2O_2	CNT+ NaI	1000	500	150	9
Na-O2	Na_2O_2	CNT + ferrocene	1000	500	230	10
Na-O_2	NaO_2	GDL-MWCNT	500	100	60	11
Na-O_2	Na_2CO_3	OMC	500	100	20	12
Na-O_2	$Na_2O_2{\cdot}2H_2O$	B-OLC	1000	0.3mA/cm^2	120	13
Na-O_2	Na_2O_2	3D N-GA	500	100	100	14
Na-O_2	NaO_2 Na_2O_2	NC-750	500	200	66	15
Na-O_2	Na_2O_2	Co_3O_4/C	1000	500	570	This work

Reference

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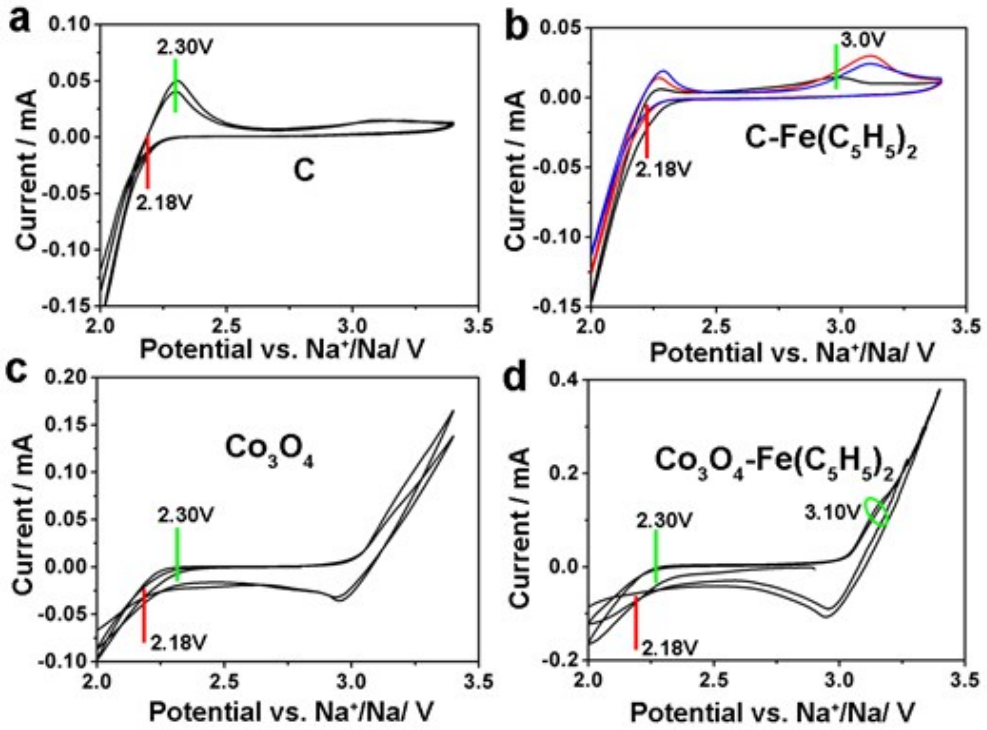

Figure S1. The CV curves of SABs with (a) carbon air electrode in pristine electrolyte (b) carbon air electrode in ferrocene-containing electrolyte (c) Co_3O_4 NWs/C air electrode in pristine electrolyte (d) Co_3O_4 NWs/C air electrode in the ferrocene-containing electrolyte between 2.0 and 3.4 V at a scanning rate of 0.1 mV/s.

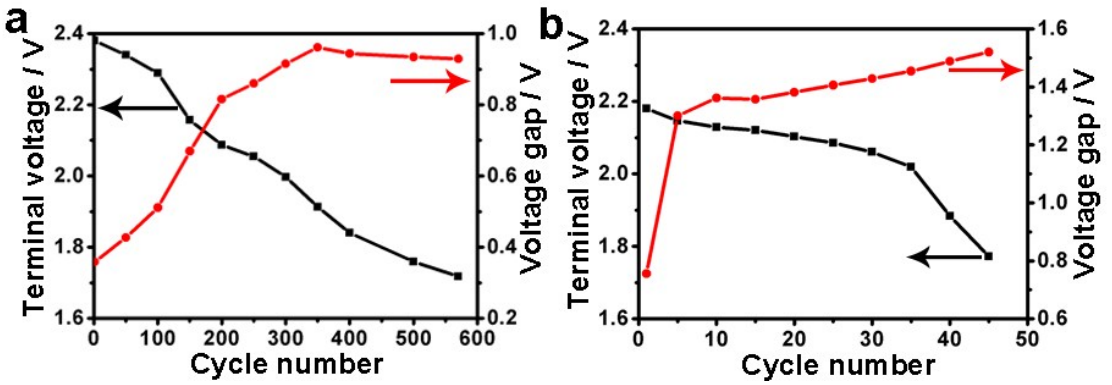

Figure S2. Terminal discharge voltage (the black line) and voltage gap (the red line) Co_3O_4 NWs/C air electrodes using (a) 0.05 M ferrocene-containing electrolyte; (b) pristine electrolyte during galvanostatic discharge and charge at 500 mA h g^{-1} as a function of cycle number.

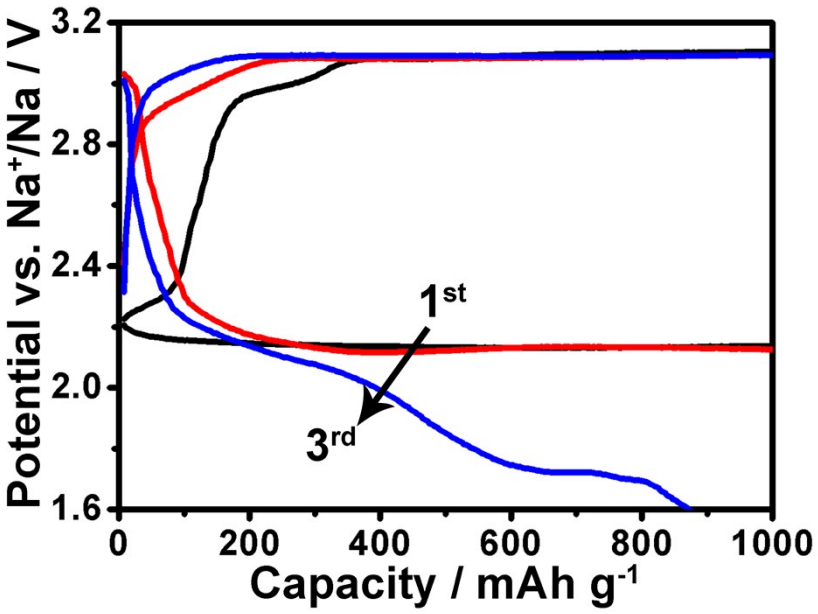

Figure S3. Cyclic performance of pure C air electrodes using 0.05 M ferrocene-containing electrolyte (the capacity was limited to 1000 mAh g^{-1}) at the current density of 500 mA g^{-1}.

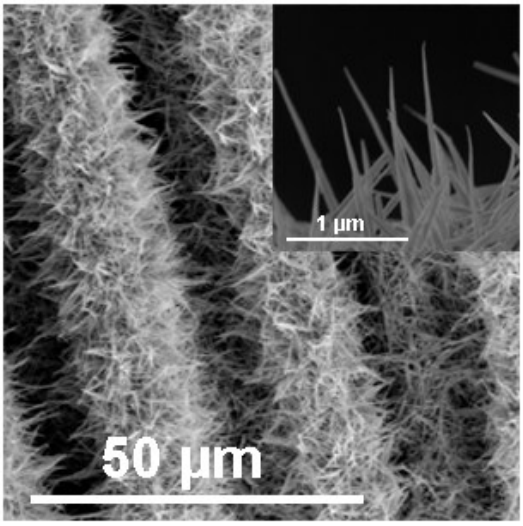

Figure S4. SEM images of Co_3O_4 nanowires/C

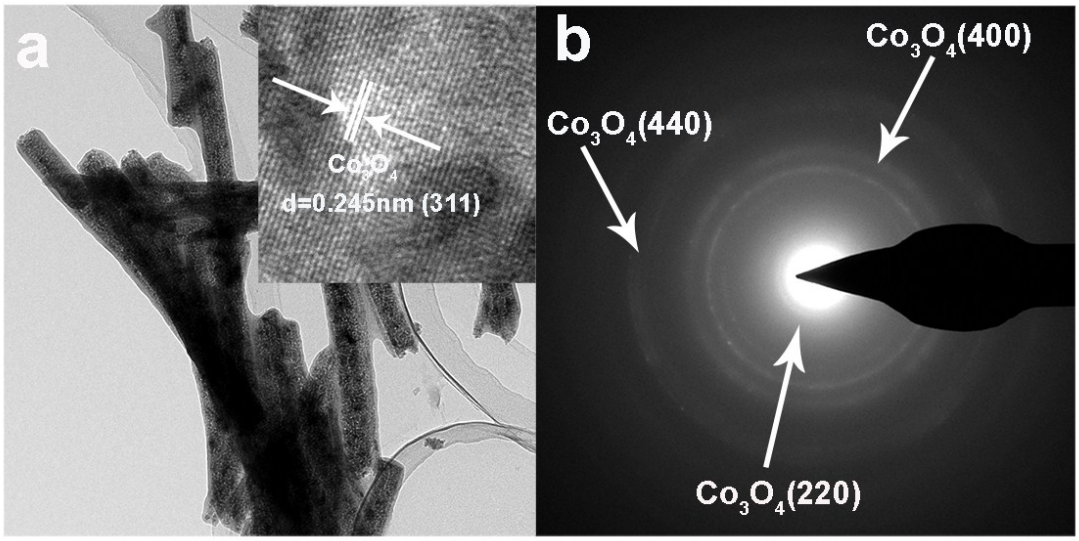

Figure S5. High resolution TEM images of the Co_3O_4 nanowires/C in the ferrocene containing electrolyte (a) after charging to 3.3 V at the current density of 500 mA g^{-1} and (b) corresponding SAED patterns.

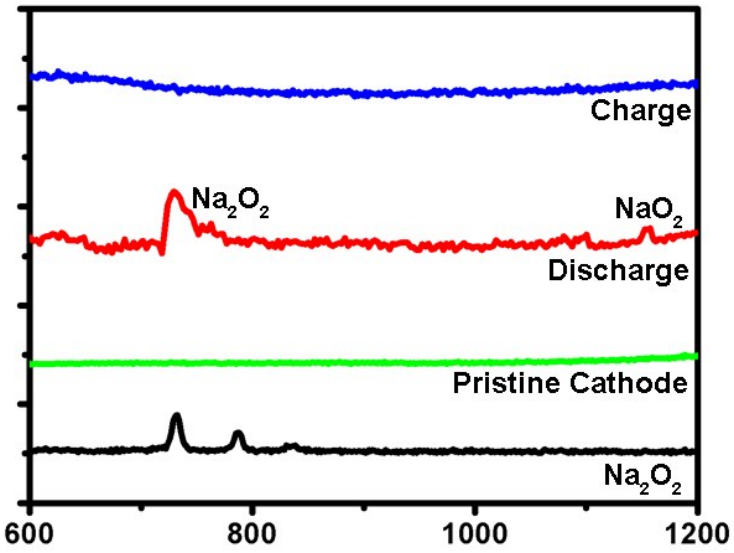

Figure S6. Raman spectra of the pristine cathode and electrodes after being discharged to 1.8V and charged to 3.3V in ferrocene-containing electrolyte, respectively.

To test the Raman spectra of discharge product, we use the carbon cathode instead of Co_3O_4 NWs/C cathode.