Supporting Information

High-performance Na-O₂ Battery Enabled by Oriented NaO₂ Nanowires as Discharge Products

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Experimental

Synthesis of high-spin electrocatalyst: In brief, 1.2 g of CoCl₂.6H₂O was dissolved into 38 ml of ethylene glycol as solvent and reducing agent. When the homogeneous red solution was obtained, 0.5 g of polyvinylpyrrolidone (PVP) was added very slowly to the solution. 10 ml of NaOH solution (5 M) of deionized water and ethylenediamine were added drop wise under strong agitation. After one hour of stirring, the solution was transferred into the 100 ml warm Teflon-lined autoclave and maintained at 473 K for 24 h. Then the autoclave was cooled to room temperature and the precipitates were separated from the solution by centrifugation. After washing the precipitates with pure ethanol, the powder was dried at 333 K for one night in the vacuum oven. In the next step, about 100 mg of this powder was loaded in the alumina boat, while the high temperature permanent magnet (AlNiCo with energy product of (BH) max \approx 4 MG.Oe and working temperature up to 823 K) was installed at the bottom of the alumina boat. Then the boat with loaded cobalt powder in contact with AlNiCo permanent magnet was put in the muffle furnace and was heated to 773 K with the heating rate of 278 K / min. The process was followed with keeping the sample at 773 K for 120 min and then the sample was cooled in the air. The control sample was prepared with the same way except the use of external magnetic field.

 $Na-O_2$ battery assembling and electrochemical measurement: Catalyst, super P carbon (SPC) and Polyvinylidene fluoride (PVDF) as binder were mixed in 3:6:1 ratio. The mixture was dispersed in N-Methyl-2-pyrrolidone (NMP) and sonicated for three hours to make uniform ink. Then the ink was sprayed to the nickel foam as 3D gas diffusion layer (GDL). For

spraying the Argon was used as carrier gas and the output flow of material was controlled to form the one side coated GDL. It should be noted that with drop casting method the ink wets the both sides of nickel foam but with spray method only one side will be wetted by the mixture of catalyst, carbon and binder. All the material which are used as ink in cathode side of the battery have low electric conductivity so with drop casting method the electric conductivity between current collector and GDL is lower than the GDL which is fabricated by spraying. To dry the deposited layer, GDL was kept in the oven at 333 K for 48 hours. After drying the GDL was punched to disks with 10 mm in diameters and used as cathode of half-cell. The mesh coin case No.2032 was employed for assembling and the pure Na pills prepared in the argon filled glove box by cutting and pressing from Na block. 0.5 M NaSO₃CF₃ tetraethylene glycol dimethyl ether (TEGDME) used as electrolyte and glass fibre (Whatman) was installed between Na pill and DGL as a membrane. All assembling was performed in the Ar gas filled glove box with water content less than 0.01 ppm. After assembling and pressing the battery, they were put in the oxygen filled glove box with water content less than 0.1 ppm for one day aging. Galvanostatic charge/discharge was measured in a potential window of 1.5-3.5 V vs. Na/Na⁺ with a multichannel battery testing (LAND CT 2001A) system. The atmosphere for testing battery was the oxygen filled glovebox with water content less than 0.1 ppm and the specific capacity was reported per total mass of the catalyst and SPC, which is about 0.6-0.8 mg cm⁻². (The 2D area was considered as the apparent flat area of DGL disk)

Sample preparation for Raman spectroscopy and XRD characterization: As discharged products of Na-O₂ battery are very sensitive to the atmosphere, for Raman spectroscopy and

XRD characterization of discharged products, special instrument and strategy were employed. The XRD were performed in a *semi-in situ* way. For this purpose the air electrode was prepared in the similar way of battery assembling section. After mixing the carbon, catalyst and binder with the same ratio the mixture was rolled and punched in 8 mm diameter round. After drying the punched material overnight at 70 °C the No.2032 coin case with lateral window (hole diameter: 5mm) was used for assembling the battery with same electrolyte and membrane that was used for Na-O₂ battery before. The charge/discharge was performed in the same oxygen filled glovebox with water content less than 0.1 ppm and after each step the battery removed from the testing clamp in the glovebox and the lateral window was covered and sealed by Kapton tape before XRD measurement. For Raman spectroscopy the battery was assembled in a similar way and placed in the sealed module with lateral thin-glass window. This module was assembled in the same oxygen filled glovebox with water content less than 0.1 ppm and then was employed for Raman spectroscopy.

Characterization: To measure the crystalline structure advance D8 X-ray diffractometer with a non-monochromated Cu Kα X-ray source was employed. Morphological study was investigated by field emission scanning electron microscope (JEOL-7100F), transmission electron microscope (TEM) and high resolution TEM. (HRTEM, JEM-2100F STEM/EDS) X-ray photoelectron spectroscopy (XPS) in CAE mode, Al: mono (step size of survey spectra: 1 eV and step size of narrow-spectra: 0.1 eV) with resolution of 0.3 eV was employed for comparison of binding energy. Magnetic property of samples was measured at room temperature with Physical Property Measurement System (PPMS-9: Quantum Design, San Diego, CA, USA). Electron paramagnetic resonance (EPR) was recorded at room temperature with Bruker-EMX-10/12 EPR spectrometer system. Raman spectra were gained using a Renishaw IN VIA micro-Raman spectroscopy system with laser wavelength of 633 nm.



Figure S1. (a) Schematic synthesis process of high-spin electrocatalyst. (b) XRD pattern of synthesized high-spin electrocatalyst with corresponding PDF card No.00-001-1152. (c) SEM morphology and inset TEM image of catalyst nanoparticles. (d) TEM image of finger-shaped dendrite on catalyst nanoparticle with the inset image from the surface of nanoparticles with higher magnification. (e, f, g) EDX mapping of finger-shaped dendrite and proportional maps of cobalt and oxygen.



Figure S2. Magnetic measurement of: (a) pure cobalt sample, which is synthesized by solvothermal method. (b) Co_3O_4 which is oxidized at 773 K with external magnetic field (EMF). (c) Co_3O_4 which is oxidized at 773 K without EMF (control sample).



Figure S3. The electronic structure of: (a) superoxide ion. (b) Co^{2+} in low spin (L.S.) and high spin (H.S) states. (c). Co^{3+} in low spin (L.S.) and high spin (H.S) states. (Crystal structure of Co_3O_4 , tetrahedral and octahedral states of Co^{2+} and Co^{3+} from Ref. 1)

Table S1. Comparison of charge/discharge potential, combined overpotential and cycling number related with morphology and chemical composition of discharged products in previous reports of $Na-O_2$ battery with this work.

Ref.	morphology of discharged product	chemical composition of discharged product	charge potential (V)	discharge potential (V)	combined overpotential (mV)	cycling numbers
2	micro-cubic	NaO ₂	~2.30	~2.20	100	1
3	micro-cubic	NaO ₂	~2.50	~2.10	400	10
4	nanoparticle	NaO_2/Na_2O_2	~2.45	~2.00	450	~20
5	nanoparticle	NaO ₂	~2.45	~2.20	250	~100
б	micro-cubic	NaO ₂	~2.35	~2.23	120	20
this work	nanowire	NaO ₂	~2.33	~2.27	60	120
			~2.55	~2.31	240	~300



Figure S4. (a) Charge/discharge curves of Na-O₂ battery with normal Co_3O_4 electrocatalyst. (b, c) SEM image from discharge products of Na-O₂ battery with normal Co_3O_4 electrocatalyst. (d) EDS mapping from discharge products of Na-O₂ battery with normal Co_3O_4 electrocatalyst.



Figure S5. EDS mapping of NaO_2 layer on the surface of catalyst and nanowires growth from the surface



Figure S6. XPS spectra of Na from discharged product of Na-O₂ battery



Figure S7. Schematic illustration of NaO_2 nanowire growth in $Na-O_2$ battery. The synergistic phenomena of spin-spin interaction, direct oxygen reduction and magnetogyration provides the oriented linear directions for NaO_2 nanowires growth.

Supplementary Text

Unpaired electrons in the superoxide and high-spin (HS) $\operatorname{Co}^{2+}/\operatorname{Co}^{3+}$ are in the vicinity of each other. Thus, the interaction between these unpaired electrons will be considerable as their quantum spin is not isolated. In this way the interaction between the embryo of NaO₂ as discharge products of Na-O₂ battery and unpaired electron of HS $\operatorname{Co}^{2+}/\operatorname{Co}^{3+}$ in catalyst have similar behavior. This interaction cannot form the unit molecules but can orient the linear direction during the moments of NaO₂ formation. So it is anticipated the spin polarization (it is entirely different with polarization of electron spins by inducing the external magnetic field) can happen between the superoxide in NaO₂ and HS $\operatorname{Co}^{2+}/\operatorname{Co}^{3+}$ in catalyst, which can delocalized the spin density between them.

Delocalization of unpaired electron in "d" layer of transition metals (here HS Co^{2+}/Co^{3+}) to Na s-state is affected by large distance between them. Oxygen usually in perovskite-like structure is intervening ion with complete occupied shell but here the superoxide ions with unpaired electrons in Na-O₂ battery has similar condition with anisotropic solution. In this way the interim chain of Co-O-Na during the formation of NaO₂ embryo just can be influenced by super transfer hyperfine (SHF) interactions and the NaO₂ embryo can be delocalized in linear direction. The presence of HS electrocatalyst with high quantity of uncompensated electrons provides the considerable provisional interaction at the moment of NaO₂ formation. This interim interaction can be enough to conduct the discharge products toward the nanowire shaping. We use the calculation of dipole interaction to describe the mechanism but it should be noticed that NaO₂ formation just relied on the provisional state of this coupling interaction and forces. In fact, the behavior of NaO₂ embryo and cobalt cations follows the spin-spin interaction generally. In this way, the spin-spin interaction and related calculation can elucidate the energy and most possible direction for this interaction. As discussed in the main text, the HS electrocatalyst provides a high density region of unpaired electron of cobalt cations on the surface of catalyst particles. If the resultant of the magnetic moments of all these unpaired electrons of HS catalyst be considered as C spins and the magnetic moment of NaO_2 embryo because of unpaired electron of superoxide be considered as N spins, then the spin-spin interaction of these two (C-N) moments can be calculated.

When the battery is working, the electric current is flowing between the anode and cathode. Passing the current between cathode materials and discharged products (eddy current is neglected) provides a weak magnetic field that can be calculated by *Biot-Savart* law. In this condition the spin-spin interaction between C and N is related to the distance and the angle between the connected line of C and N and induced magnetic field. (Figure S8)



Figure S8. Spin –spin interaction in the presence of electric current and induced magnetic field.

The energy between N and C can be derived from following equation.

$$E=J_{CN}.I_{C}.I_{N}$$
(1)

Where E is spin-spin interaction energy, I_C and I_N is resultant spin vectors of HS Co^{2+}/Co^{3+} and NaO₂ embryo respectively and J_{CN} is scalar coupling constant. It means more unpaired electrons in the catalyst provide the higher interaction energy with NaO₂ embryo. The current between catalyst and discharge products induces a weak magnetic field (B₀) but the important point is that the J_{CN} is scalar constant and not related to the amount of the field. In fact, the angle and distance between C and N determines the amount of this energy. The spin-spin interaction follows a Cosine equation as below:

Scalar coupling constant =
$$-\frac{\mu_0}{4\pi} \cdot \frac{\gamma_C \gamma_N \hbar}{r_{C-N}^3} \cdot \frac{1}{2} (3 \cos^2 \theta_{C,N} - 1)$$
 (2)

Where μ_0 is magnetic field constant, r_{C-N} is the distance between the center of C and N, the gyromagnetic ratio of C and N is shown by γ , \hbar is reduced planck's constant and θ is the angle between the connected line of two spins and magnetic field. It can be seen that the magnitude of this interaction is proportional to the inverse third power of the distance between the catalyst and NaO₂ embryo (r_{C-N}) and it is related to the second order of cos θ .

If the hypothetical catalyst and embryo of NaO₂ be plotted in trigonometric coordinate system then the investigation of spin-spin interaction in different distance and angle can be facilitated. In this coordinate system the HS catalyst including the HS $\text{Co}^{2+}/\text{Co}^{3+}$ is considered on the center and the embryos of NaO₂ can get different r and θ on the unit circle area (Fig. S9). As the current between catalyst and discharge product make a magnetic field, this magnetic field is perpendicular to the current direction and is parallel with spins. The Cosine value is in the range of (-1, 1) and the maximum absolute values of equation can be obtained for the $\theta=0$, π radian. According to the trigonometric coordinate system the NaO₂ embryo will accumulate on the X-axes

(Cosine axes) and form a line of atoms in contact with each other. As mentioned in the main text the magnetogyration between the NaO_2 embryos help this linear formation to make a strong nanowire of NaO_2 molecules.⁷⁻⁹



Figure S9. Positioning of catalyst and discharge products of Na-O₂ battery in trigonometric coordinate system and illustration of nanowire formation along the θ =0, π (cosine axes).

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