# High-Performance Na-O<sub>2</sub> Batteries Enabled by Oriented NaO<sub>2</sub> Nanowires as Discharge Products

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Supporting Information

**ABSTRACT:** Na–O<sub>2</sub> batteries are emerging rechargeable batteries due to their high theoretical energy density and abundant resources, but they suffer from sluggish kinetics due to the formation of large-size discharge products with cubic or irregular particle shapes. Here, we report the unique growth of discharge products of NaO<sub>2</sub> nanowires inside Na–O<sub>2</sub> batteries that significantly boosts the performance of Na–O<sub>2</sub> batteries. For this purpose, a high-spin Co<sub>3</sub>O<sub>4</sub> electrocatalyst was synthesized via the high-temperature oxidation of pure cobalt nanoparticles in an external magnetic field. The discharge products of NaO<sub>2</sub> nanowires are 10–20 nm in diameter and ~10  $\mu$ m in length, characteristics that provide facile pathways for electron and ion transfer. With these nanowires, Na–O<sub>2</sub> batteries have surpassed 400 cycles with a fixed capacity of 1000 mA h g<sup>-1</sup>, an ultra-low over-potential of ~60 mV during charging, and near-zero over-potential during discharging. This strategy not only provides a unique way to control the morphology of discharge products to achieve high-performance Na–O<sub>2</sub> batteries but also opens up the opportunity to explore growing nanowires in novel conditions.



**KEYWORDS:** Na-O<sub>2</sub> battery, Na-air battery, discharge product, NaO<sub>2</sub> nanowire, unpaired electron

T he demand for "green" energy sources and storage is increasing. Metal-air batteries with high theoretical energy densities (3505 and 1105 Wh kg<sup>-1</sup> for Li-O<sub>2</sub> and Na-O<sub>2</sub> batteries, respectively) are considered the next generation of energy-storage systems. Although the energy density of Na-O<sub>2</sub> batteries is lower than that of Li-O<sub>2</sub> batteries, the charge-discharge polarization of Na-O<sub>2</sub> batteries is lower than that of Li-O<sub>2</sub> batteries, which causes better cycling performance. From a thermodynamic point of view, sodium peroxide (Na<sub>2</sub>O<sub>2</sub>) and sodium superoxide (NaO<sub>2</sub>) as discharge products of Na-O<sub>2</sub> battery, with  $E_0 = 2.33$  and 2.27 V; consequently, both are stable and possible (the Gibbs free energy values of Na<sub>2</sub>O<sub>2</sub> and NaO<sub>2</sub> are -449.7 and -437.5 kJ mol<sup>-1</sup>, respectively). Kinetically, the NaO<sub>2</sub> is more favored because of 1 $\overline{e}$  oxygen reduction.<sup>1-9</sup>

In the previous reports on  $Na-O_2$  batteries, the improvement of battery materials such as electrolyte, anode, and cathode materials is of interest, but the importance of the morphology of discharge products is rarely considered. Because of the direct role of the discharge product in the next charge and the related over-potential, the morphology of the discharge product might be more important than the morphology of the air electrode.<sup>3-14</sup> Thus, providing suitable conditions with which to optimize the morphology of discharge products inside the battery is theoretically a unique way for the control of oxygen reduction and evolution reactions (ORR and OER) to achieve high performance in  $Na-O_2$  batteries. For this purpose, understanding the electronic structure of  $NaO_2$  is a key point for optimizing the morphology.<sup>13</sup>

The discharge products in Na–O<sub>2</sub> batteries are usually reported in microcubic or microparticles, which have low conductivity and cause sudden death during charging because the pores clog.<sup>13,15</sup> Because the ionic conductivity and electronic conductivity of NaO<sub>2</sub> are higher than Na<sub>2</sub>O<sub>2</sub>, as with the hierarchical growth of nanosized NaO<sub>2</sub>, higherperformance Na–O<sub>2</sub> batteries are anticipated. In addition, this strategy can hinder the pore clogging of cathodes. Among nanoscale morphologies, the nanowires with one-dimensional (1D) morphology can provide the current pathways with which to facilitate the electrical transfer in comparison with particles. In addition, the ion diffusion length in nanowires is very short, which can improve the rate performance and decrease the diffusion time.<sup>16</sup>

NaO<sub>2</sub>, as a favorite product of Na–O<sub>2</sub> batteries with  $1\overline{e}$  transfer, has paramagnetic properties.<sup>5</sup> The combination of these two properties provides the proper conditions for the hierarchical growth of NaO<sub>2</sub> during the discharge. However, the

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Figure 1. (a) Comparison of magnetic hysteresis for the high-spin electrocatalyst and control samples. (b) EPR spectra of the electrocatalyst (red line), which is oxidized at 773 K under EMF, and the control sample (blue line), which is oxidized at 773 K without EMF; the g factor for each spectrum is measured with Win-EPR. (c) ZFC and FC curves for high-spin electrocatalyst. (d) ZFC and FC curves for the control sample. (e) The XPS spectra of cobalt and (f) the XPS spectra of oxygen for a comparison of high-spin electrocatalyst and control samples.

Co<sup>2+</sup> with a magnetic moment of 4.14  $\mu$ B in the tetrahedral sites of spinel Co<sub>3</sub>O<sub>4</sub> has catalytic properties. With consideration of all of these points, the interaction between Co<sup>2+</sup> in Co<sub>3</sub>O<sub>4</sub> and O<sub>2</sub><sup>-</sup> in NaO<sub>2</sub> during the charge and discharge of Na–O<sub>2</sub> battery should be effective.<sup>17–23</sup> Here, we show that the synthesis and employment of electrocatalyst with high-spin Co<sup>2+</sup> and Co<sup>3+</sup> result in the formation of NaO<sub>2</sub> nanowires as

the discharge products inside the batteries. This hierarchical charge and discharge alleviates the sluggish kinetics of ORR and OER in  $Na-O_2$  batteries. This uniquely designed battery with the hierarchical growth of  $NaO_2$  nanostructures nearly reached the theoretical discharge potential; it achieved a very low charge over-potential and long cycle life.

The schematic of high-spin Co<sub>3</sub>O<sub>4</sub> electrocatalyst synthesis is shown in Figure S1a. After the solvothermal synthesis of pure cobalt nanoparticles, the oxidation under an external magnetic field is the main step in gaining the electrocatalyst with highspin nanodendrites. Subsequent quenching provides the suitable situation for unpaired electrons to keep their states. Figure S1b shows the X-ray diffraction (XRD) pattern of  $Co_3O_4$  electrocatalyst with related peaks, which agree with the PDF card no. 00-001-1152. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the catalyst are shown in Figure S1c,d. The general features of agglomerated nanoparticles and the TEM image in Figure S1d show the finger-shaped nanodendrite, which is grown on the surface of these agglomerated particles. The energy dispersive X-ray spectrometry (EDS) mapping of this nanodendrite in Figure S1f-h shows that the oxygen concentration toward the surface of these dendrites is higher than the base particles. These high-concentration regions have the key role in the catalytic performance of these nanoparticles.

The magnetic property of the synthesized catalyst is investigated with magnetic hysteresis loops at 5 and 300 K, respectively. The hysteresis loops of pure cobalt, electrocatalyst, and control samples are shown in panels a-c of Figure S2, respectively. For pure cobalt, the magnetization intensity gradually becomes saturated with an increase of the magnetic field and possesses 129 and 127 emu/g at 5 and 300 K, respectively. The magnetization curves of the electrocatalyst and control sample responses are superimposed, and the paramagnetic regime is linearly field-dependent at a high field range. It is obvious that after the oxidation of pure cobalt the magnetization intensity decreases severely because of the transformation from ferromagnetic cobalt to the Co3O4. In the structure of bulk spinel  $Co_3O_4$ , the magnetic  $Co^{2+}$  and nonmagnetic Co3+ occupy the tetrahedral and octahedral sites, respectively. It is reported that, in the case of nonstoichiometric cobalt oxide (the thin film or nanosize  $Co_3O_4$  spinel), the highspin Co<sup>3+</sup> can stabilize in the spinel octahedral sublattice, and in this way, the samples can show catalytic properties.<sup>23</sup> The comparison of magnetic hysteresis between the purposed electrocatalyst (oxidation with external magnetic field) and control samples (oxidation without an external magnetic field) is shown in Figure 1a. In this figure, because of the surface spins, the symmetric hysteresis with a large saturation magnetization  $(M_s)$  for electrocatalysts, in comparison to the small  $M_{\rm s}$  of the control sample, are proportional to the superparamagnetic and paramagnetic regimes of these two samples. At high temperatures, it is anticipated that more surface spins can be free for fluctuations, and weaker ferromagnetic properties can be then reached.<sup>24</sup> The superparamagnetic behavior relies on the number of uncompensated surface spins, such that the magnetic hysteresis loops of electrocatalyst in Figure 1a prove that the presence of external magnetic fields during the oxidation is effective for gaining more unpaired electrons and higher total magnetic mo-ments.  $^{22,24,25}$  It is reported that Co\_3O\_4 nanoparticles around the oxidation temperature of 773 K have the optimal catalytic performance for ORR because of the hybrid structure.<sup>26</sup> Thus, oxidation at 773 K not only provides enough thermal fluctuation for surface-spin movement in Co3O4 but also is close to the optimized temperature for high catalytic performance. In addition, the use of a permanent magnet with a stability temperature of 823 K to align the surface spins can be safe in this selected temperature. As mentioned previously, the

unpairing of surface spins is possible in high temperatures, and this phenomenon can be facilitated in the presence of external magnetic fields. When the energy required to pair the electrons is higher than the energy to remain as single electrons in the orbital, high-spin splitting takes place. Here, at a temperature of 773 K, the melting-point depression in nanoparticles can facilitate a high-spin position in  $\text{Co}^{3+}$ . The electronic structures of superoxide ions beside the  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  in low-spin and high-spin states are shown in Figure S3.

In fact, inducing the external magnetic field on the pure cobalt nanoparticles at high temperatures provides the alignment of domains and unpairing of spins parallel ( $m_s = -1/2$ ) or anti-parallel ( $m_s = +1/2$ ) to the external field with specific energy. This phenomenon is following the Zeeman effect, which can determine the specific energy of this alignment in paramagnetic materials.<sup>27</sup>

Electron paramagnetic resonance (EPR) spectroscopy is known as the most reliable way to determine the presence of unpaired electron spins. The EPR spectra of high-spin electrocatalysts and control samples (Figure 1b) were measured at room temperature. The difference between the spectra of the two samples is very obvious. When the external magnetic field is induced during the oxidation at 773 K, the intense and symmetric peak with a g value of 2.2592 appears clearly. In this way, the resonance of synthesized high-spin electrocatalyst (g =2.2592) is very sharp and visible in comparison to the control sample (g = 2.5689). The control sample, in fact, involved a broad asymmetric resonance. The Co<sup>2+</sup> cations occupy the tetrahedral sites in spinel lattice, which provides a single EPR peak with a Lorentzian signal shape. The g factor for this resonance is reported around 2.25. Here, the EPR spectra of high-spin catalyst (red line) matches with the characterization of high-spin Co<sup>2+</sup> and Co<sup>3+</sup> as described. This intense symmetric shape peak of selected catalyst in comparison to the broad and asymmetric line in the control samples proves the vital role of an external magnetic field in providing the highspin state for catalyst. It should be noted that the samples are quenched in the air after oxidation and that the  $Co^{2+}$  EPR signals appear in this way. In fact, the end quenching step is a wise way to retain the unpaired electrons of high-spin Co<sup>2+</sup> and Co<sup>3+</sup> in their positions.<sup>23,27,28</sup>

Panels c and d of Figure 1 show the completely different zero-field cooled (ZFC) and field-cooled (FC) magnetic behaviors of the electrocatalyst and control samples, respectively. The peaks appearing at about 33 K can be attributed to the ordering temperature of  $Co_3O_4$ . Above the ordering temperature,  $Co_3O_4$  will display paramagnetic properties. The positive slope of magnetization with an increase of the temperature in Figure 1c and the higher magnetic moment, in contrast with that shown in Figure 1d, indicate the presence of more unpaired electrons at surface. In this way, the efficacy of the external magnetic field during oxidation to gain the high-spin  $Co^{2+}$  and  $Co^{3+}$  with more single electrons can be verified.

To investigate the binding energy of catalyst particles, X-ray photoelectron spectroscopy (XPS) is employed. The XPS spectra of cobalt for the synthesized catalyst are shown in Figure 1e. They show that, with induction of the external magnetic field during oxidation, the main peaks are shifted to lower values. With the induction of the external magnetic field, the binding energy for Co 2p1/2 and Co 2p3/2 decrease from 794.88 and 779.78 eV to 794.48 and 779.48 eV, respectively. In addition, the comparison of two spectra shows that, in the case of external magnetic fields, the satellite peaks are diminished.





**Figure 2.** Charge–discharge curves of  $Na-O_2$  batteries for (a) the first 100 cycles, (b) the 120th to 200th cycles, and (c) the 220th to 400th cycles with a fixed specific capacity of 1000 mA h g<sup>-1</sup> at a current density of 100 mA g<sup>-1</sup>. (d) The 1st to 160th cycles with a fixed specific capacity of 1000 mA h g<sup>-1</sup> at a current density of  $Na-O_2$  battery for three cycles at a scan rate of 5 mV s<sup>-1</sup>. (f) EIS spectra of  $Na-O_2$  batteries for pristine samples after the 1st and 10th discharge and recharge.

Although the spinel  $Co_3O_4$  has been investigated for years, there are many uncertainties about it. The possibility of nonstoichiometric cobalt oxide in the thin-film oxidation of cobalt and the anomaly of  $Co_3O_4$  around 1000 K due to the spin unpairing of  $Co^{3+}$  are reported.<sup>20</sup> Here, the oxidation of nanoparticles of pure cobalt around a temperature of 773 K in the presence of an external magnetic field shows another anomaly in XPS spectra. It seems that the simultaneous high temperature and external magnetic field conditions not only provide a suitable environment for the alignment of unpaired spins in  $\text{Co}^{2+}$  but also cause the spin unpairing and alignment in  $\text{Co}^{3+}$ . It should be noted that surface spins have higher magnetocrystal anisotropy because of reduced symmetry, so the surface spins have more mobility and freedom to influence the



Figure 3. (a, b) SEM images of NaO<sub>2</sub> nanowires (discharge product of Na–O<sub>2</sub> batteries) beside the high-spin  $Co_3O_4$  electrocatalyst. (c–e) Element mapping of selected NaO<sub>2</sub> nanowire and related maps of sodium and oxygen. (f, g) TEM images of a NaO<sub>2</sub> nanowire web beside the high-spin  $Co_3O_4$  electrocatalyst particles in different magnifications.

external magnetic field in high temperatures.<sup>27</sup> Because the XPS results mainly give the surface information on a material, the decrease in the binding energy and the lack of satellite peaks in the case of oxidation with external magnetic fields is a sign indicating the presence of nonstoichiometric cobalt oxide on the surface of the electrocatalyst.

Figure 1f shows the XPS spectra of oxygen for high-spin catalyst and control samples. Similar to the spectrum of cobalt, the peak for oxygen (O 1s) in oxidation with an external magnetic field is decreased from 529.88 to 529.68 eV. As mentioned previously, the nonstoichiometric cobalt oxide on the surface of  $Co_3O_4$  nanoparticles can follow the formula of

 $Co_{3-x}O_4$  with a higher contribution of oxygen. The special synthesis process of catalyst has increased the number of highspin  $Co^{3+}$  as well as unpaired electrons, which increases the nonstoichiometric on the surface of the catalyst nanoparticles. This increase in the nonstoichiometric properties of the surface brings the lower binding energy for O 1s, as previously seen. The presence of the cationic and bulk defects in non-stoichiometric states results in the excess quantity of oxygen on the surface of nanoparticles, as shown in the previous EDS mapping of the catalyst. As shown in the XPS spectra of Figure 1f, this excess oxygen provides higher coordination and lower binding energy.<sup>28</sup> In fact, the high catalytic performance of this



**Figure 4.** (a) XRD pattern after 20 and 40 h of discharging with a subsequent 20 and 40 h of recharging for a  $Na-O_2$  battery. The Miller indices on the peaks correspond to  $NaO_2$  according to PDF card no. 00-006-0500. The asterisks correspond to the  $Co_3O_4$  electrocatalyst according to PDF card no. 00-001-1152. (b) Raman spectra of cathode materials after the discharging of the  $Na-O_2$  battery. (c) EDS spectra of  $NaO_2$  nanowire as a discharge product of  $Na-O_2$  batteries.

catalyst is related to the ability to adsorb  $O^-$  with this nonstoichiometric cobalt oxide on the surface of nanoparticles. In total, the high-spin state of  $Co^{2+}$  and  $Co^{3+}$  relies on more unpaired electrons and the energy level in these cations. In this way, the comparison of magnetic hysteresis showed a possibility for more unpaired electrons in a high-spin state for electrocatalyst, and then the EPR, ZFC and FC, and XPS results confirmed this possibility, as was discussed.

For electrochemical testing, the  $Na-O_2$  battery was assembled with this high-spin electrocatalyst. For more details, see the Supporting Information. Charge and discharge curves for  $Na-O_2$  battery (400 cycles) at a current density of 100 mA  $g^{-1}$  are shown in Figure 2a–c. It is clear that, in the first 100 cycles, the charge and discharge curves with a fixed specific capacity of 1000 mA h  $g^{-1}$  have unique performances with the lowest possible over-potential. The discharge potential during these cycles is around 2.26 V, which is very close to the  $E_0$  potential of NaO<sub>2</sub> formation.

The charge voltage in these 100 cycles is about 2.32 V, which shows an extremely low over-potential of ~60 mV. This small over-potential, in comparison with previous reports (200 mV), shows the considerable progress in Na–O<sub>2</sub> batteries (see Table S1).<sup>14</sup> As discussed previously, if the situation for hierarchical nanowire growth can be provided, then near-ideal charging and

discharging are anticipated. Here, the results of charge and discharge curves in these 100 cycles have confirmed this. Figure 2b shows that, after 160 cycles, the charge over-potential increases smoothly. Although the performance of these batteries in comparison with reported Na-O<sub>2</sub> batteries is still much better, in comparison with the first 100 cycles, the charge over-potential is increased. The difference in charging potential according to the composition of the discharged product is reported before. Ydegari et al. have considered three specific regions with different ranges of charging voltages for Na-O2 batteries.<sup>29</sup> Here, the change of charging potential from panels a to c in Figure 2, among 400 cycles, is in agreement with partial change of the composition of the discharged product. The formation of paramagnetic superoxide ions ( $O_2 + e^- \rightarrow$  $O_2^-$ ) as an exothermal reaction needs only 0.87 eV, while forming the peroxide ion  $(O_2^- + e^- \rightarrow O_2^{2-})$  consumes an additional 2.1 eV. It seems that, after about 200 cycles, the kinetic situation is changed, and some sodium peroxides are formed beside the  $NaO_2^{30}$  Proportional to this formation in discharge, the charge potential increases from 2.32 to  $\sim$ 3.0 V. The charge and discharge curves for Na-O2 batteries at a current density of 200 mA  $g^{-1}$  and a fixed specific capacity of 1000 mA h  $g^{-1}$  are shown in Figure 2d. Among these 160 cycles, except for the first cycle, all of the other charge curves are close together. It seems that the current density of 200 mA  $g^{-1}$  provides the more-stable conditions for OER; however, the charge over-potential is slightly higher in comparison to the current density of 100 mA  $g^{-1}$ . Cyclic voltametric (CV) curves of  $Na-O_2$  battery are shown in Figure 2e for three subsequent cycles. Reversibility in three cycles is shown in the overlapping of curves. ORR and OER in Na-O2 batteries correspond to the peaks of the CV curve in forward-reverse scans. Electrochemical impedance spectroscopy (EIS) was employed to declare the resistance during charge and discharge. The results of these measurements are shown in Figure 2f. The EIS results are surprising at first because the charge-transfer impedance  $(R_{ct})$  after discharge is lower than the  $R_{ct}$  of pristine samples. It seems that the growth of discharged products in nanowire shapes generate the facile pathway for charge transfer among the cathode materials. It is shown in the SEM images of cathodes after discharge that an internal web of NaO<sub>2</sub> nanowires can facilitate the charge transfer. However, the EIS curves after discharge and recharge are reversible. This reversibility suggests the role of hierarchical charge and discharge for high-performance cycling. The charge and discharge curves of the control sample, synthesized with normal Co<sub>3</sub>O<sub>4</sub> electrocatalyst, are shown in Figure S4a. The sudden death and high charge over-potential of the batteries is clear in these curves. The SEM images and proportional element mapping of the discharged products are shown in Figure S4b-d. The morphology of discharge products in the control sample are in particles and cubic shapes, which is similar to the other reports.

The SEM images in Figure 3a,b show the nanowire growth of the discharged product of Na–O<sub>2</sub> batteries with high-spin electrocatalysts. Interestingly, it is shown the nanowires nucleate on the surface layer of catalyst particles and grow through the space between them. The element mapping of NaO<sub>2</sub> nanowire is shown in Figure 3c–e. It seems that the sodium peroxide first covers the surface of catalyst generally, and then the NaO<sub>2</sub> nanowires grow from this layer, as shown in the SEM images in Figure S5. The NaO<sub>2</sub> nanowires as the discharge products of Na–O<sub>2</sub> batteries are shown clearly in the TEM images of Figure 3f,g. A diameter of 10-20 nm can be estimated for the NaO<sub>2</sub> nanowires in these figures.

The growth of the discharged products in nanowire morphology not only provides suitable conditions for better electronic conduction but also means that the mechanical and chemical stability of these nanowires will be better than that of microscale cubic morphology. This stability retains contact with  $NaO_2$  nanowires and the current collector until charging is complete.<sup>10</sup>

Figure 4a shows the XRD patterns, which are obtained from the air electrode of Na-O2 batteries after 20 and 40 h of discharging with a subsequent 20 and 40 h of recharging. The XRD pattern of pristine samples at open-circuit voltage (OCV) includes the peaks of Co<sub>3</sub>O<sub>4</sub> catalyst according to the PDF card no. 00-001-1152. After 20 h of discharging with a current density of 100 mA  $g^{-1}$ , the broad peaks of NaO<sub>2</sub> are initiated at  $26.3^{\circ}$  and  $33.4^{\circ}$  corresponding to the (110) and (101) planes according to the PDF card no. 00-006-0500. After 40 h of discharging, the mentioned peaks intensify, and peaks at 42.4° and  $63.6^{\circ}$  appear too. These new peaks correspond to the (200) and (022) planes. It is clear that with subsequent recharging, after 20 h, the related peaks of NaO<sub>2</sub> decline, and finally, after 40 h, only the related peaks of  $Co_3O_4$  remain. In this way, the sodium superoxide (as the discharged product of this  $Na-O_2$  battery) is recognized. The appearance of peaks for the (200) planes of  $NaO_{2}$ , even beside the strong peak of  $Co_3O_4$ , is the result of the predominant 1D growth of NaO<sub>2</sub> nanowires along the orientation of the normal vector of these stable and low-index planes.<sup>12</sup> In addition, the reversible charge and discharge of this battery was confirmed by the disappearance of NaO<sub>2</sub> peaks after recharging. The composition of the discharged products was characterized by Raman spectroscopy (Figure 4b) as well. In this spectrum, the strong peak at a frequency of 1156 cm<sup>-1</sup> for discharged product is in agreement with the reported frequency of NaO2, which is mainly gained from the vibration frequency of  $O_2^-$  anions.<sup>7,</sup> Besides the strong peak of  $NaO_2$  (the main discharge product), the rare amount of Na2CO3 and Na2O2 can be detected according to their small peaks in the Raman spectra. The small shifting in the peaks of  $Co_3O_4$  may be related to the distortion of some planes, which is caused by spin-spin interactions. Sample preparation for the XRD and Raman characterization of discharged products is mentioned in the Supporting Information. The EDS spectra of NaO<sub>2</sub> nanowires (Figure 4c) were collected to determine the composition of NaO<sub>2</sub> nanowire as a discharge product of Na-O2 batteries. Because the size of the nanowire is around 20 nm in diameter, the collected peaks of oxygen and sodium, in comparison to the peak of carbon in the background, is very weak. The XPS spectra of the cathode after discharge are shown in Figure S6. It is shown that the peaks for Na 1s are around 1071.8 and 1071.6 eV. To our knowledge, a clear assignment for the XPS spectra of sodium peroxide or sodium superoxide is not available, but the binding energy in this work is close to the previous reports (~1071.2 eV) for NaO<sub>2</sub> as a discharge product of Na-O<sub>2</sub> batteries.<sup>11</sup>

The possible mechanism for the growth of NaO<sub>2</sub> nanowires inside the batteries might be due to the enhanced magnetic properties of high-spin Co<sub>3</sub>O<sub>4</sub> catalysts compared to the control sample (Figure S7). Briefly, sodium superoxide is considered paramagnetic because of unpaired electrons in O<sub>2</sub><sup>-</sup>, and its magnetic susceptibility is around 1820 at 293 K. However, the high-spin electrocatalyst includes high-spin Co<sup>2+</sup> and  $\text{Co}^{3+}$ . During the charge and discharge of Na–O<sub>2</sub> batteries, the O<sub>2</sub><sup>-</sup> orientation disorder of NaO<sub>2</sub> can freely rotate to get an Fm3m structure.<sup>12</sup> Free radicals are usually considered shortlived because of their reactivity, but molecular oxygen can be categorized in long-lived radicals.<sup>32</sup> The compounds with uncompensated electrons are sensitive to their microenvironment. The NaO<sub>2</sub> has its own magnetic moment. The synthesized Co<sub>3</sub>O<sub>4</sub> under an external magnetic field has gained more unpaired electrons with the same alignment. The mechanism includes three phenomena that have synergistic behavior. First, the surface of the high-spin catalyst is covered by NaO<sub>2</sub>, and because of spin–spin interactions between the high-spin regions of the catalyst and NaO<sub>2</sub>, the NaO<sub>2</sub> in the interface of this region behaves as a seed. The spin–spin constant follows the cosine formula

$$\left(\frac{\mu_0}{4\pi} \times \frac{\gamma_C \gamma_N \hbar}{r_{C-N}^3} \times \frac{1}{2} [3\cos^2 \theta_{C,N} - 1]\right)$$

and obtains maximum values at 0 and 180 degrees, which makes a linear orientation for nanowire growth (for more details, see the Supporting Information). In the second step, the new NaO<sub>2</sub> can precipitate directly on the surface of former NaO<sub>2</sub> seeds because of the direct reduction of oxygen on this interface. As mentioned in the EIS test, the conductivity after discharge is higher than the pristine and charge states. It means that the formation of NaO2 in nanowire shapes provides enough conductivity for the direct reduction of oxygen on the surface of the discharge product. This phenomenon continues to form a long nanowire, and among them, the magnetogyration (as the third function) behaves as a chain to join these molecules in a nanowire shape. $^{33-35}$  In other words, the interim chain of Co-O-Na during the formation of the NaO<sub>2</sub> can delocalize its position in preferred linear directions. Because the (100) surface is the lowest-index surface of disordered pyrite NaO<sub>2</sub>, its growth in the performed linear direction of spin interactions can be further facilitated along these planes. In this way,  $O_2$  can directly be reduced on the NaO<sub>2</sub> surfaces. However, the aligned spins of electrocatalysts can spin up or down during the synthesis. It should be noted that the spin-up alignment in the electrocatalyst is more effective because the spin-down state of  $NaO_2$  has a half-metallic character with higher conductivity.<sup>12,36,37</sup>  $NaO_2$  exhibits unique magnetic properties similar to those of the transition metal oxides because of the p-electron origin. The rich magnetic properties of NaO<sub>2</sub> provide a strong chain of NaO<sub>2</sub> by magnetogyration in the nanowire shape.<sup>1,38,3</sup>

In summary, we demonstrate that the growth of NaO2 nanowires induced by high-spin electrocatalysts inside Na-O2 batteries significantly boosts the performance. The influence of external magnetic fields at high temperatures to gain the highspin regions on electrocatalysts was confirmed by magnetic measurements and EPR and XPS investigations. Na-O2 batteries could run more than 400 cycles with a fixed capacity of 1000 mA h  $g^{-1}$  at current densities of 100 and 200 mA  $g^{-1}$ . The batteries exhibit a very low over-potential of only  $\sim 60 \text{ mV}$ during charging and a near-zero over-potential for discharge, which is unique to the best of our knowledge. The analytical calculation of the spin-spin interaction between the high-spin electrocatalyst and NaO<sub>2</sub> provides suitable conditions for some NaO<sub>2</sub> to behave as a seed for nanowire growth. The synergistic behavior of this interaction with direct oxygen reduction on the surface of the discharge product and magnetogyration between

the NaO<sub>2</sub> continues the nanowire's web formation. The nanowire growth of NaO<sub>2</sub> as discharge product was recognized by SEM, TEM, and EDS results. The Raman spectra, XRD patterns, and EDS spectra of the discharged product proved the sodium superoxide as a main discharge product for this Na–O<sub>2</sub> battery. The web of NaO<sub>2</sub> nanowires in SEM and TEM images of the cathode after discharging is a reminder that this hierarchical method can be employed as a new way to synthesize the nanowires.

## ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.8b01315.

Additional details on the experimental methods. Figures showing the schematic synthesis process; XRD, SEM, TEM, EDS, XPS, and EDX results; magnetic measurements; electronic structures; charge and discharge curves; a schematic illustration of nanowire growth; spin-spin interactions; and positioning of catalyst and discharge products. A table showing a comparison of characteristics. (PDF)

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#### **Author Contributions**

S.M.B.Kh., L.Q.M., and L.X. conceived of the idea. S.M.B.Kh. and J.L. performed the electrochemical tests. S.M.B.Kh. and G.Z. performed the XRD and Raman characterization. S.M.B.Kh., G.Z., and L.S.W. measured the magnetic properties. S.M.B.Kh. and S.T. characterized the SEM, TEM, and XPS. S.M.B.Kh., X.L., and Y.Z. contributed in the analytical calculations and mechanism definition. All coauthors discussed and commented on the results.

#### Notes

The authors declare no competing financial interest.

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## **Nano Letters**

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