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

Supplementary Materials for

In situ TEM visualization of single atom catalysis in solid-state Na-O_2 nanobatteries

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Supplementary Movies

Description of Movie S1. An *in situ* ADF movie showing the formation of spherical discharging products on a SA-Co/rGO cathode in a Na-O_2 nanobattery during discharge in an O_2 ambient with a pressure of 1.0 mbar (corresponding to Fig. 2a-d).

Description of Movie S2. An *in situ* ADF movie showing the morphology evolution of a SA-Co/rGO cathode in a Na-O_2 battery during the discharge/charge process under an O_2 ambient with a pressure of 1.0 mbar (corresponding to Fig. S10a-f).

Description of Movie S3. An *in situ* ADF movie showing the morphology evolution during cycling of a SA-Co/rGO cathode in a Na-O_2 nanobattery under an O_2 ambient with a pressure of 1.0 mbar (corresponding to Fig. 4). Many spherical discharge products formed under a negative bias. When the potential was reversed, the spherical products gradually converted to a shell like scaffold with porous structure. The formation and disappearance of the spherical products were repeatable for three times, indicating the good cyclability.

Supplementary Figures

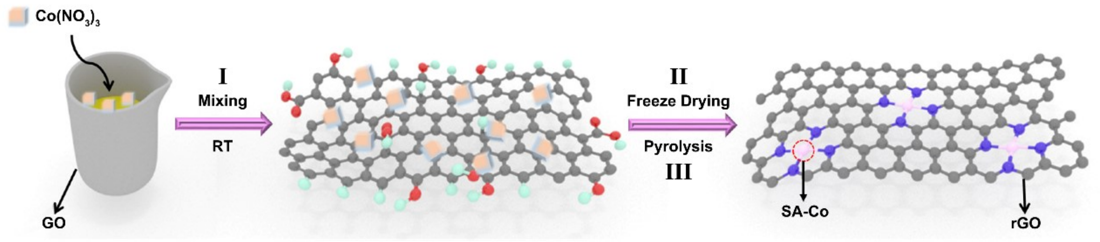

Fig. S1. Schematic illustration showing the synthesis process of SA-Co/rGO.

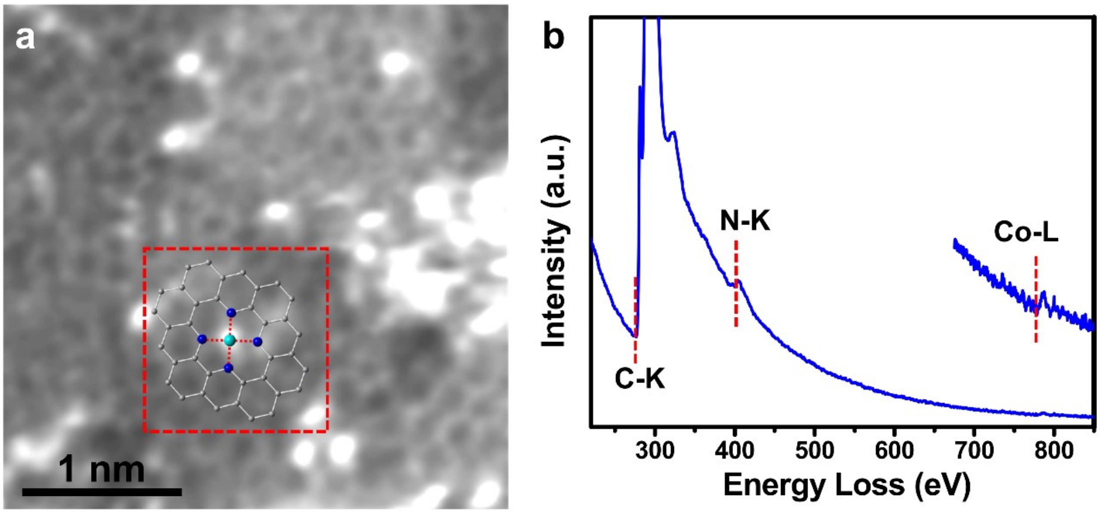

Fig. S2 (a) ADF image of Co + 4N local structure, (b) Corresponding EELS spectrum taken from the region around individual Co atom.

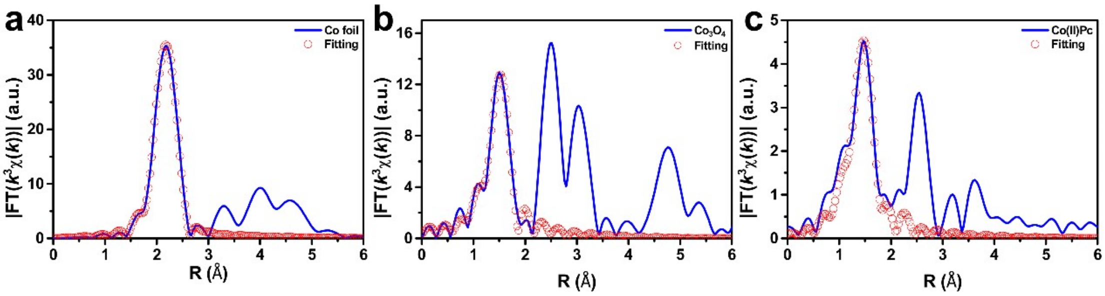

Fig. S3. The EXAFS fitting curves at R space. (a) Co foil, (b) Co_3O_4 and (c) Co(II)Pc. The Fourier transforms are not corrected for phase shift.

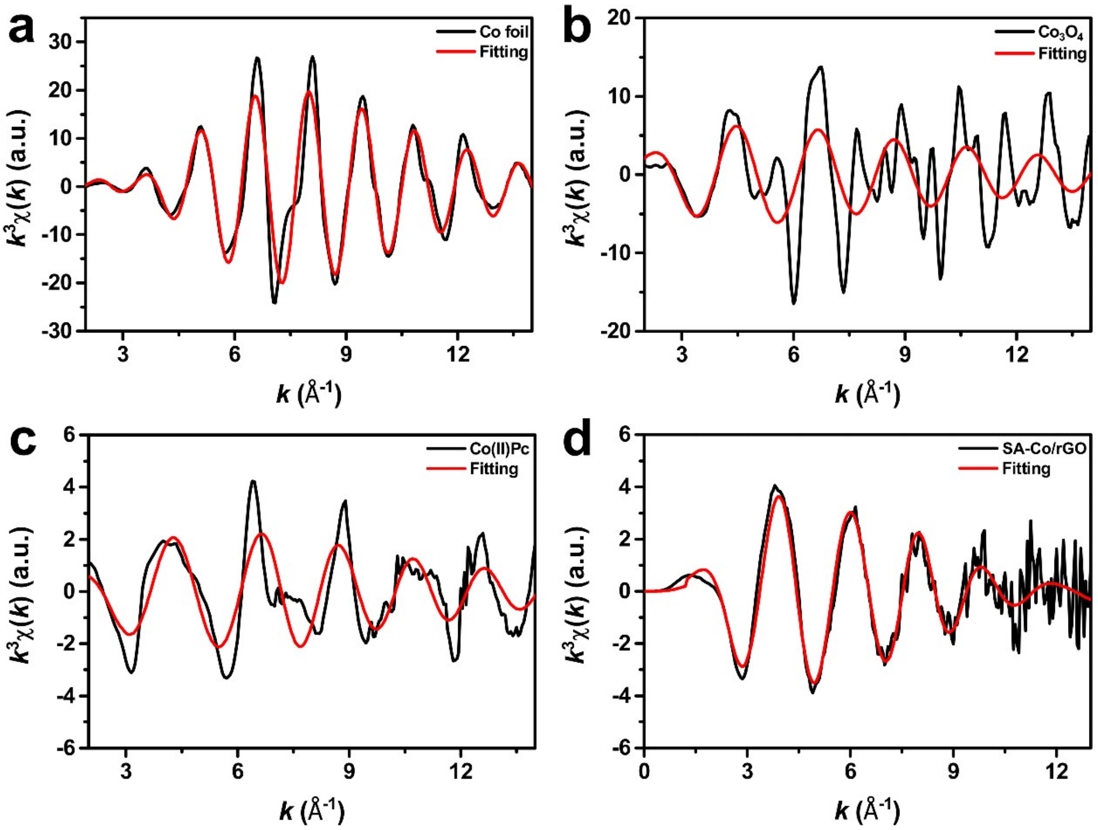

Fig. S4. The EXAFS fitting curves at *k* space. (a) Co foil, (b) Co_3O_4, (c) Co(II)Pc and (d) SA-Co/rGO.

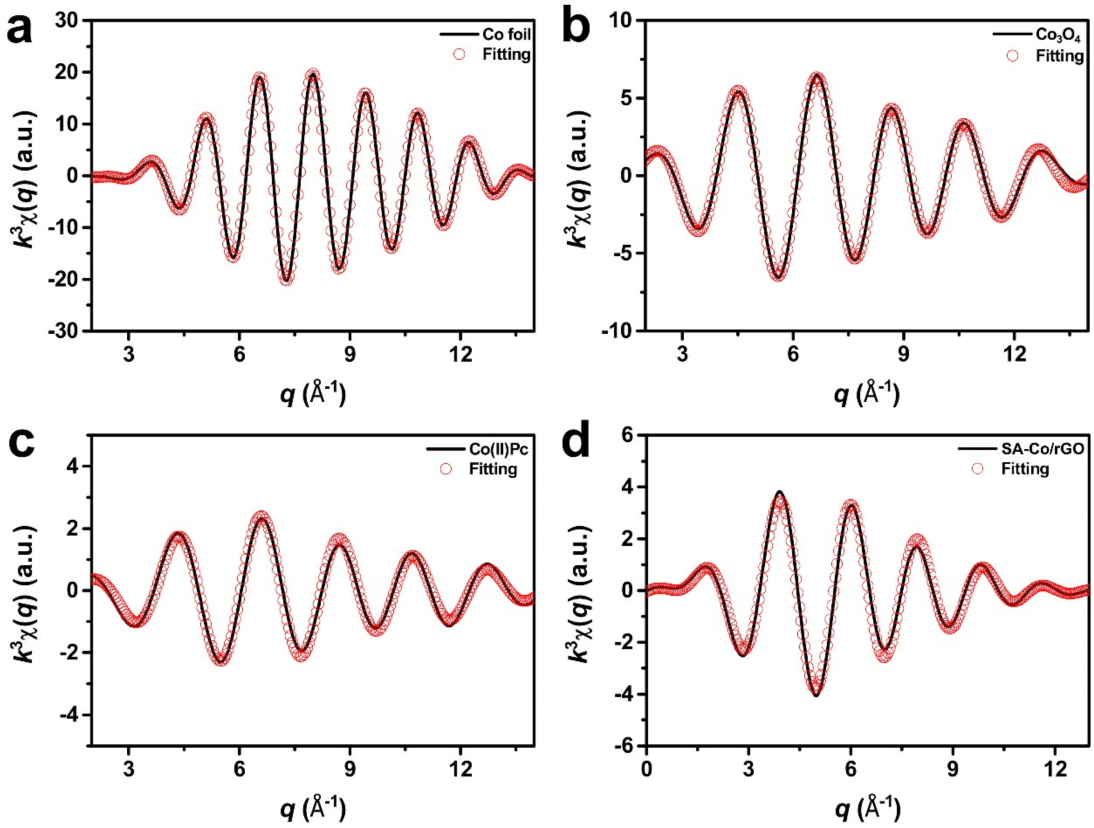

Fig. S5. The EXAFS fitting curves at q space. (a) Co foil, (b) Co_3O_4, (c) Co(II)Pc and (d) SA-Co/rGO.

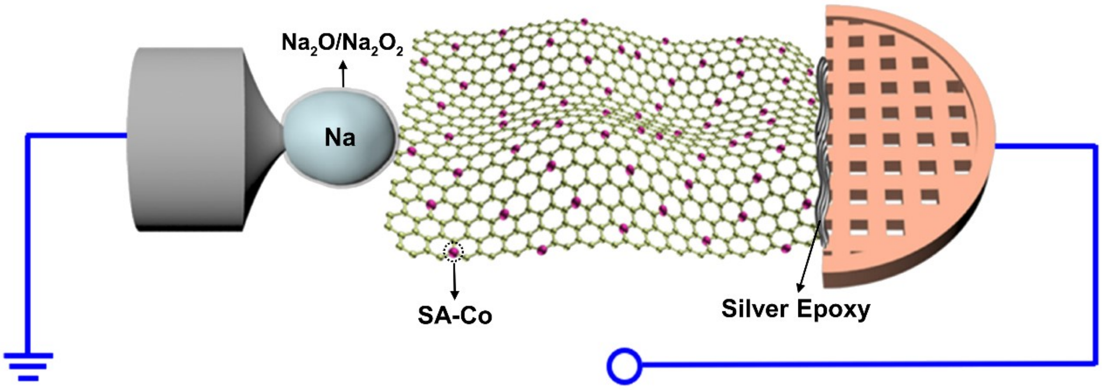

Fig. S6. Schematic of the *in situ* experimental setup of a Na-O_2 nanobattery. The nanobattery consists of a SA-Co/rGO cathode, a Na_2O electrolyte and a Na anode, respectively.

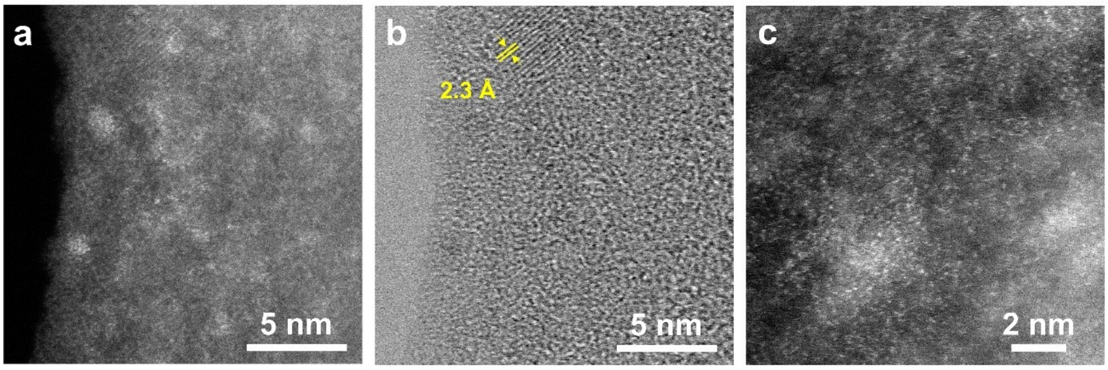

Fig. S7. High magnification STEM images of the discharged SA-Co/rGO air cathode. (a) HAADF and (b) ABF images show the fresh formed Na_2O_2 lattice. (c) HAADF image shows the single Co atoms.

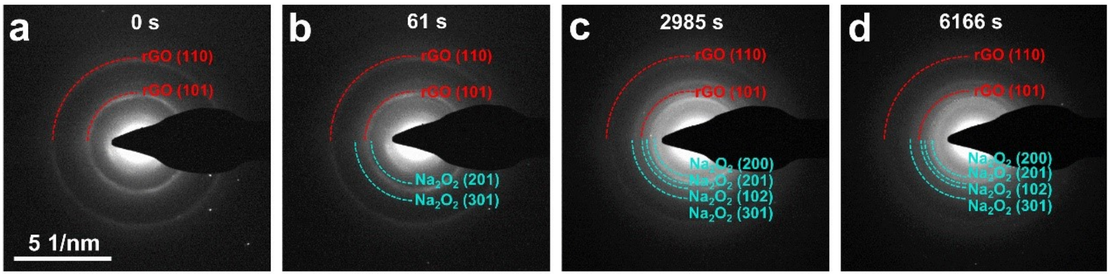

Fig. S8. Time lapse EDP evolution of the SA-Co/rGO cathode in a Na-O_2 nanobattery during discharge process in an O_2 environment. Before the discharge process, the EDP showed sharp diffraction rings which are indexed as rGO (a). With the propagation of the reaction front, minor Na_2O_2 diffraction rings were formed on the pristine SA-Co/rGO (b). After fully discharged, strong Na_2O_2 diffraction rings superimposed on SA-Co/rGO diffraction rings (c-d).

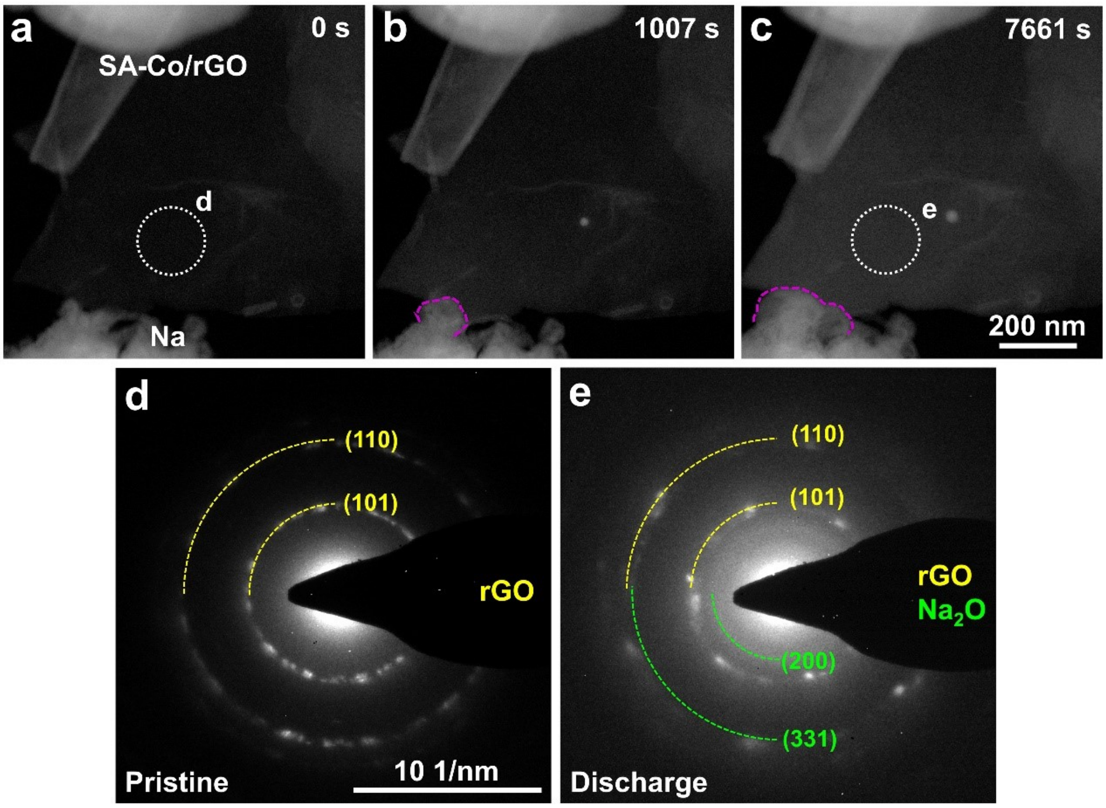

Fig. S9 *In situ* TEM observation and characterization of a nanobattery in high vacuum condition. (a-c) Time-lapse structure evolution of the SA-Co/rGO cathode during discharging process. (d-e) EDPs of the pristine samples and discharge products on the SA-Co/rGO cathode. White circles mark the locations where EDPs were acquired.

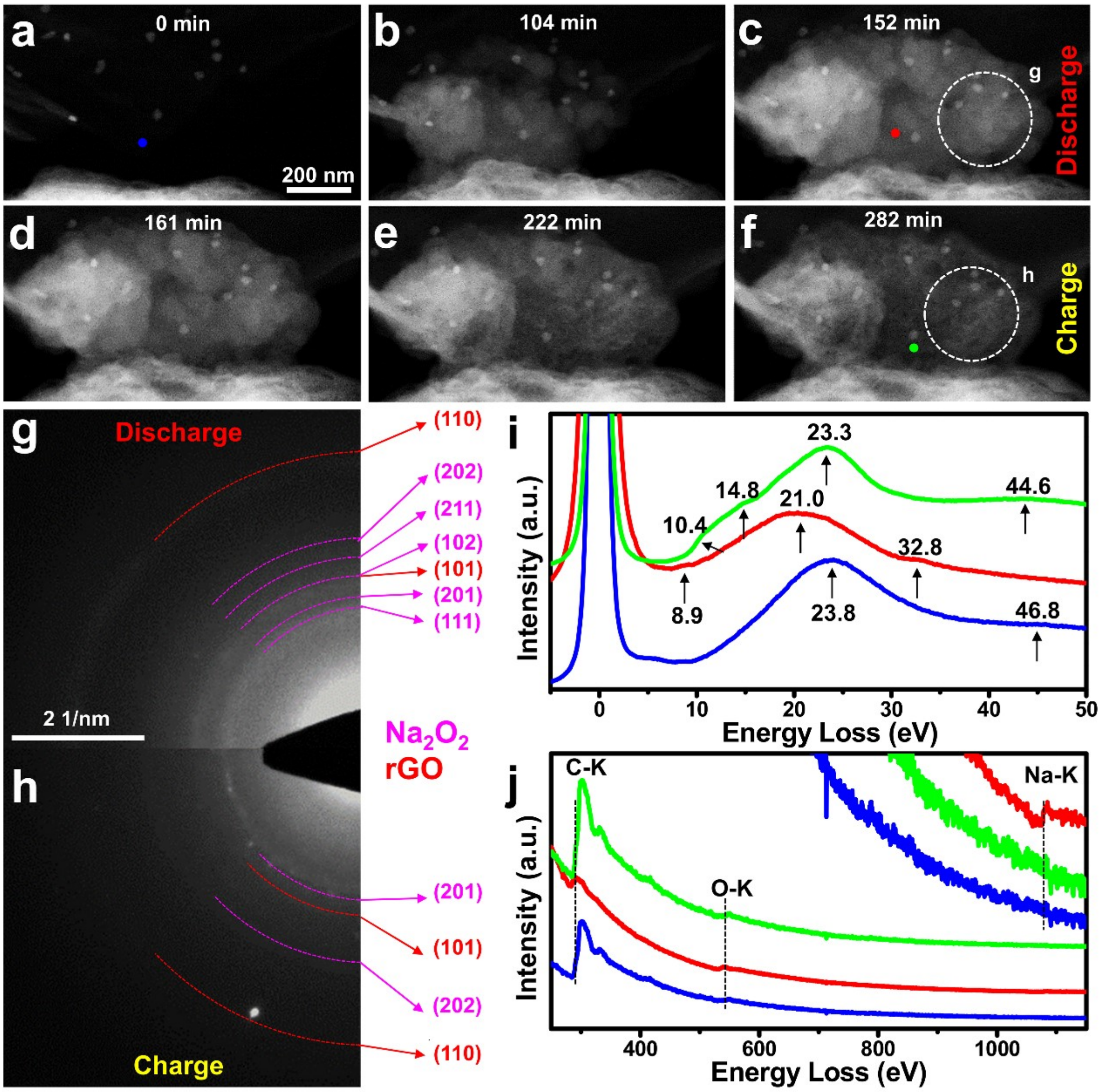

Fig. S10. *In situ* TEM observation and characterization of Na-O_2 nanobattery with SA-Co/rGO cathode during the first discharge-charge cycle. (a-f) Time-lapse structure evolution of the SA-Co/rGO cathode in a Na-O_2 nanobattery during the discharge/charge process. (g-h) EDP and (i-j) EELS of the SA-Co/rGO after the discharging and charging processes, respectively.

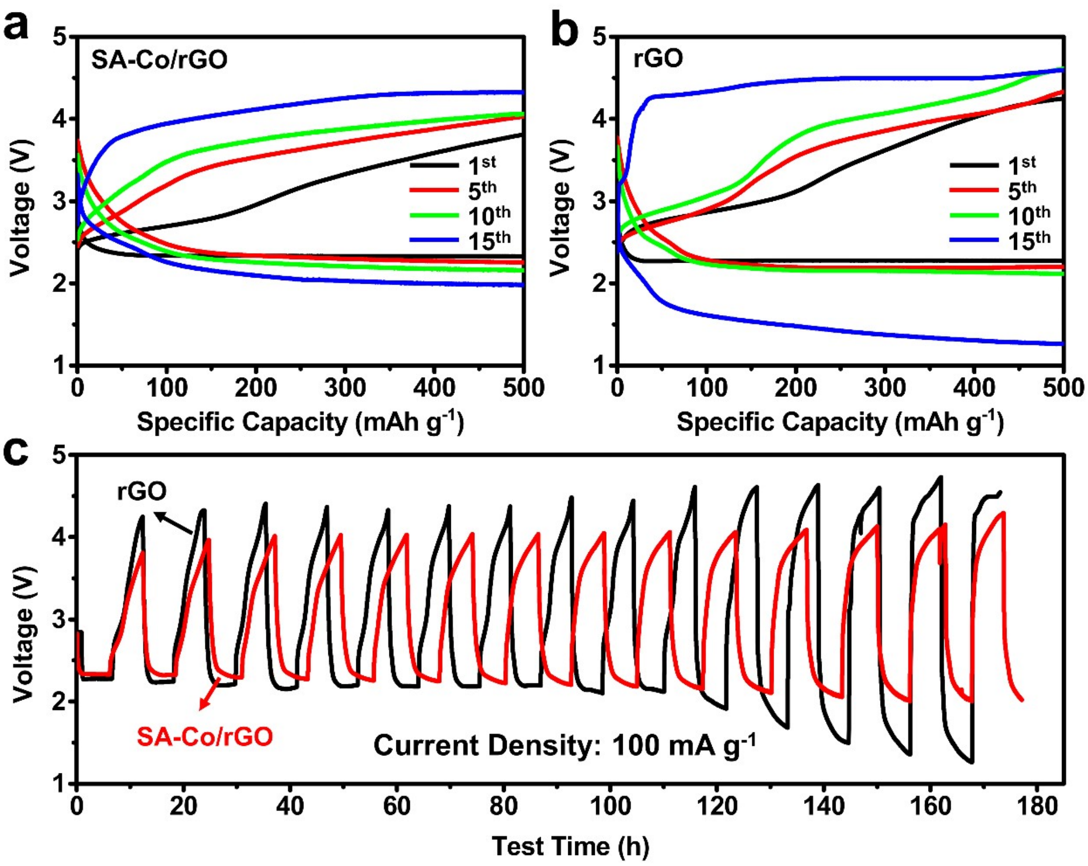

Fig. S11. Performance of coin cell Na-O_2 batteries. (a-b) Charge-discharge curves of a coin cell Na-O_2 batteries with SA-Co/rGO cathode and pure graphene cathode, respectively. (c) Cycling stability and terminal discharge/charge voltages of the coin cell Na-O_2 batteries with SA-Co/rGO cathode and pure graphene cathode at a rate of 100 mA g^{-1} with a limited specific capacity of 500 mAh g^{-1}.

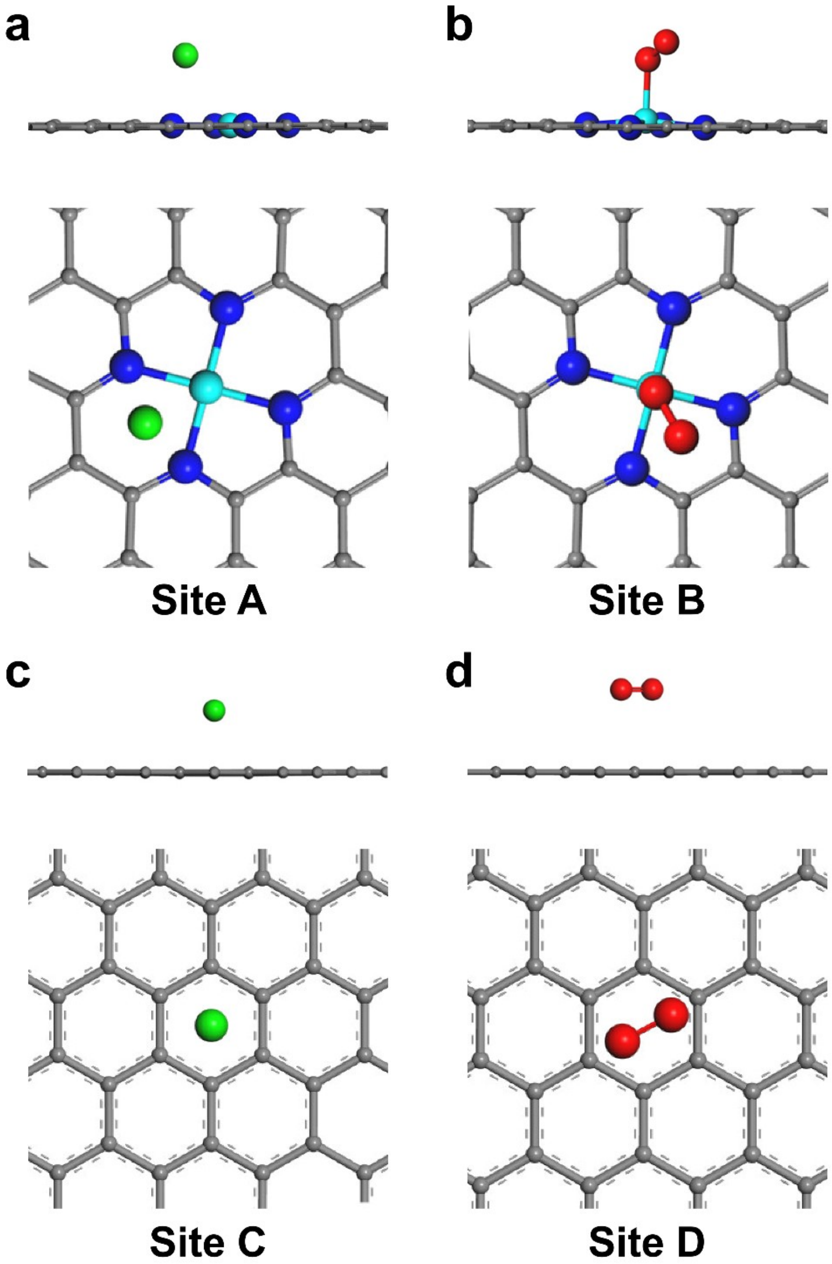

Fig. S12. Optimized structures after DFT calculations. (a) Na atom adsorption configurations on monolayered SA-Co/rGO with side and top views of Site A, which is the hollow site above the center of a C-N-Co ring; (b) O_2 adsorption configurations on monolayered SA-Co/rGO, side and top views of site B, in which the O_2 lay on the top site above the single Co atom with one O atom bonded with Co; (c) Na atom adsorption configurations on monolayered graphene with side and top views of Site C, which is the hollow site above the center of a C6 ring; (d) O_2 adsorption configurations on monolayered graphene with side and top views of site D, in which O_2 lay across two opposing carbon atoms and oriented parallel to the graphene plane.

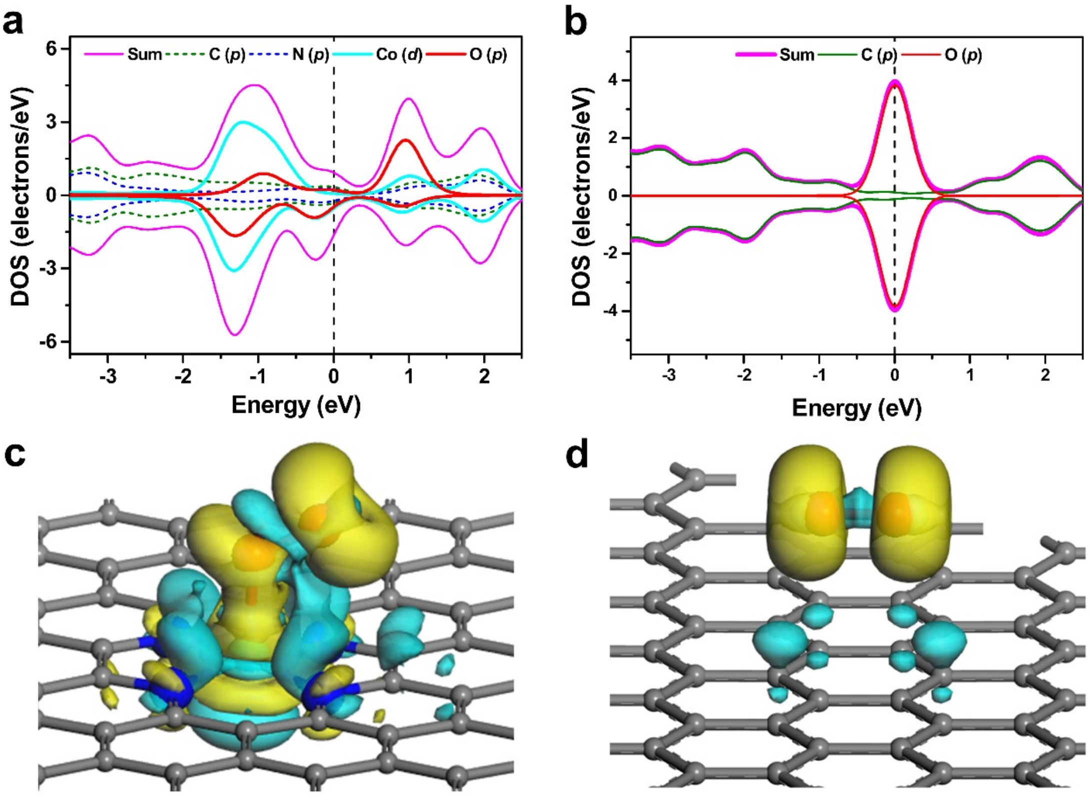

Fig. S13. The density of states (DOS) and partial density of states (PDOS): (a) O_2 molecule adsorbed on monolayered SA-Co/rGO surface; (b) O_2 molecule adsorbed on monolayered graphene surface; Isosurface of the difference electron density $\Delta\rho$ for O_2 adsorbed on: (c) monolayered SA-Co/rGO surface; (d) monolayered graphene surface. (yellow for $\Delta\rho > 0$ and blue for $\Delta\rho < 0$)

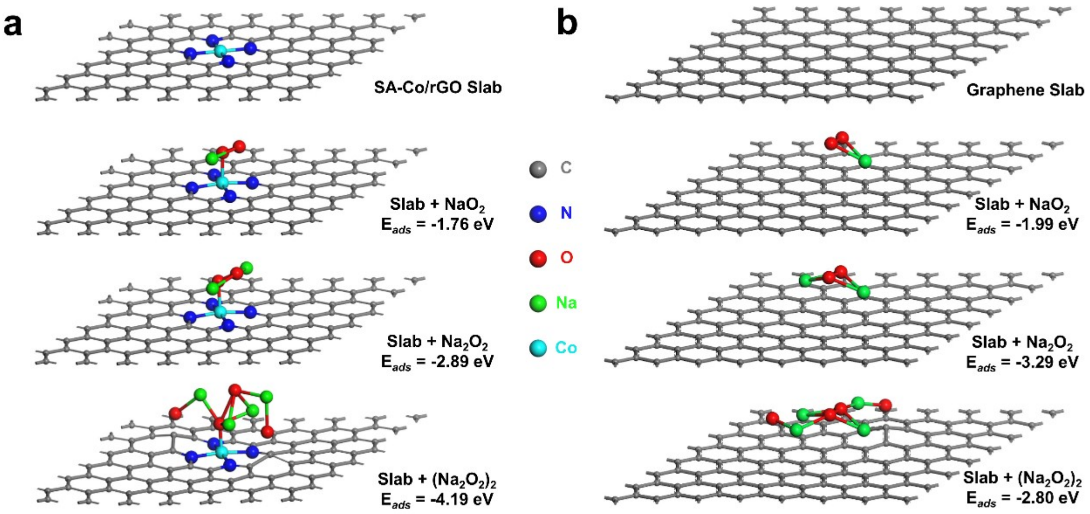

Fig. S14. Side view of the optimized structures corresponding to the diagrams for the discharge-charge reactions. (a) monolayered SA-Co/rGO; (b) monolayered graphene.

Supplementary Tables

Table S1. Structural parameters extracted from the Co K-edge EXAFS fitting

Sample	Scattering pair	CN	R (Å)	σ^2 (10^{-3}Å)	ΔE_0 (eV)	R factor
Co foil	Co-Co	12*	2.493	6.38	7.051	0.001
Co_3O_4	Co-O	5*	1.913	3.43	3.122	0.018
Co(II)Pc	Co-N	4*	1.904	4.48	-6.903	0.007
SA-Co/rGO	Co-N	4.6	2.014	4.41	-3.592	0.016
	Co-O	1.4	2.143	1.82	5.607	

S_0^2 is the amplitude reduction factor; CN is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms); σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatter distances); ΔE_0 is edge energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting. S_0^2 for Co-Co, Co-O and Co-N was set as 0.77, 0.74 and 0.84, respectively, which were obtained from the experimental EXAFS fit of Co foil, Co_3O_4 and Co(II)Pc references by fixing CN as the known crystallographic value and were fixed to all the samples. * This value was fixed during EXAFS fitting, based on the known structure. Error bounds that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as N ± 20%; R ± 1%; σ^2 ± 20%; ΔE_0 ± 20%.

Co foil (FT range: 3.0-13.0 Å^{-1}; fitting range: 1.5-3.0 Å), Co_3O_4 and Co(II)Pc (FT range: 3.0-13.0 Å^{-1}; fitting range: 0.8-2.0 Å), SA-Co/rGO (FT range: 2.0-13.0 Å^{-1}; fitting range: 0.8-2.0 Å)

Table S2. Adsorption energy of Na atom and O_2 molecular at preferred adsorption sites in monolayered SA-Co/rGO and graphene.

Absorption Site	Absorbate	Substrate	Absorption Energy (eV)
Site A	Na atom	SA-Co/rGO	-0.87
Site B	O_2 molecular		-1.27
Site C	Na atom	Graphene	-1.50
Site D	O_2 molecular		-0.02