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

Supporting Information

Integration of Single Co Atoms and Ru Nanoclusters Boosts the Cathodic Performance of Nitrogen-Doped 3D Graphene towards Lithium–Oxygen Batteries

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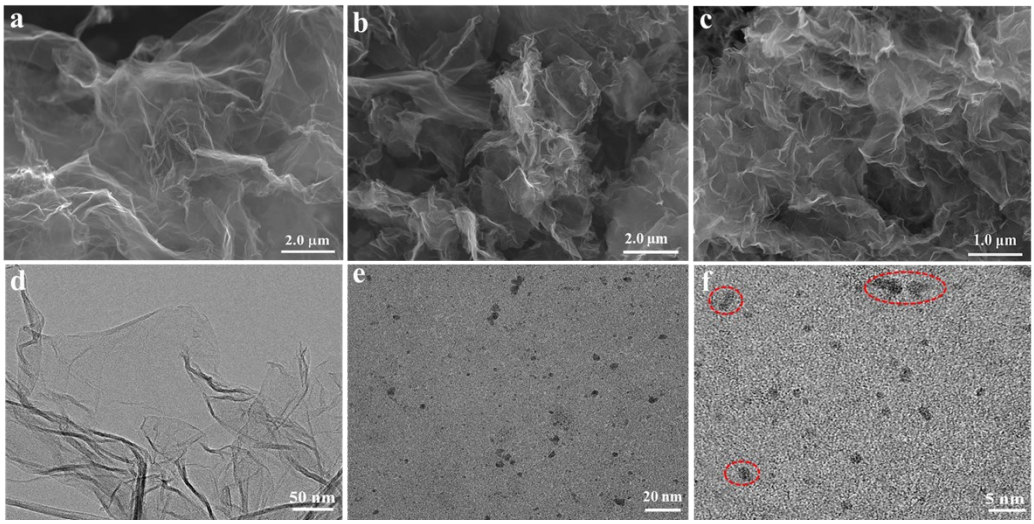

Figure S1. The SEM and TEM images of (a), (d) 3DNG, (b), (e) Co/ 3DNG, (c), (f) Ru_{NC}/3DNG

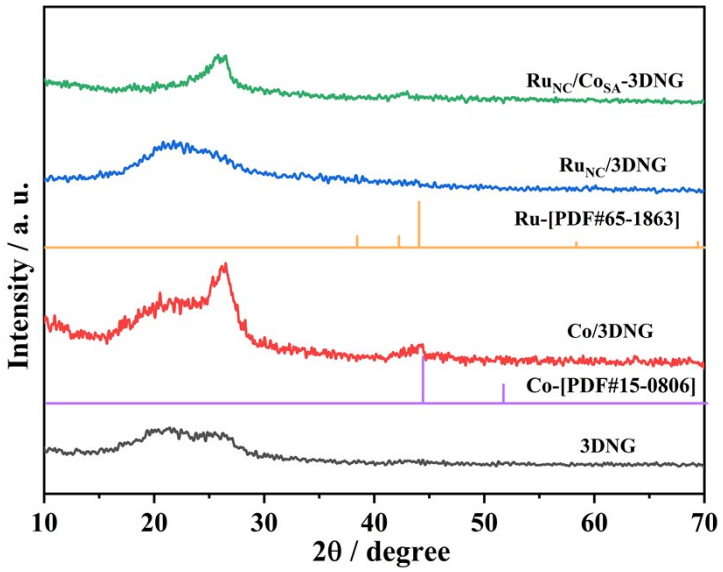

Figure S2. The XRD patterns of the 3DNG, Co/3DNG, Ru_{NC}/3DNG and Ru_{NC}/Co_{SA}-3DNG samples.

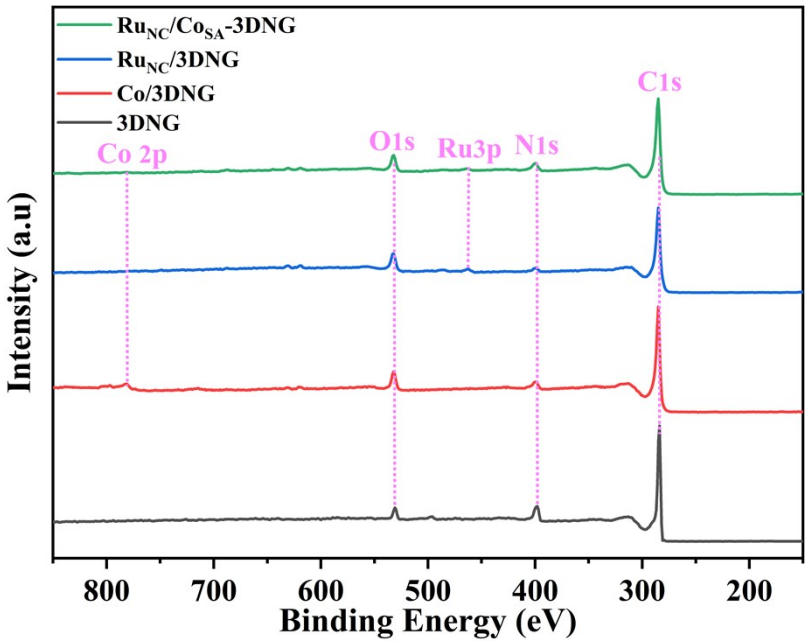

Figure S3. XPS survey spectra of 3DNG, Co/3DNG, Ru$_{NC}$/3DNG and Ru$_{NC}$/Co$_{SA}$-3DNG.

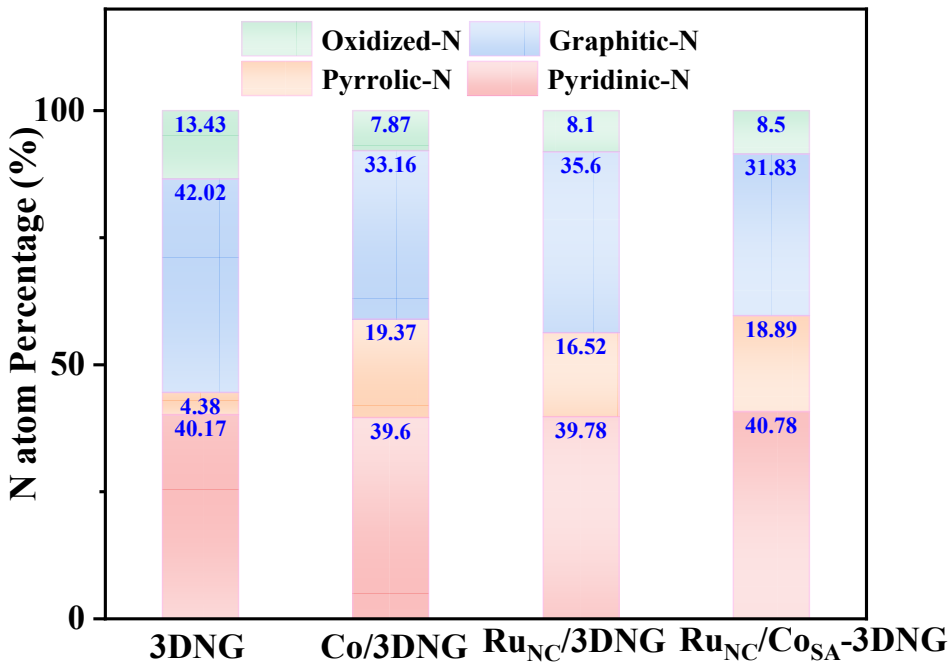

Figure S4. The distribution of the different N species.

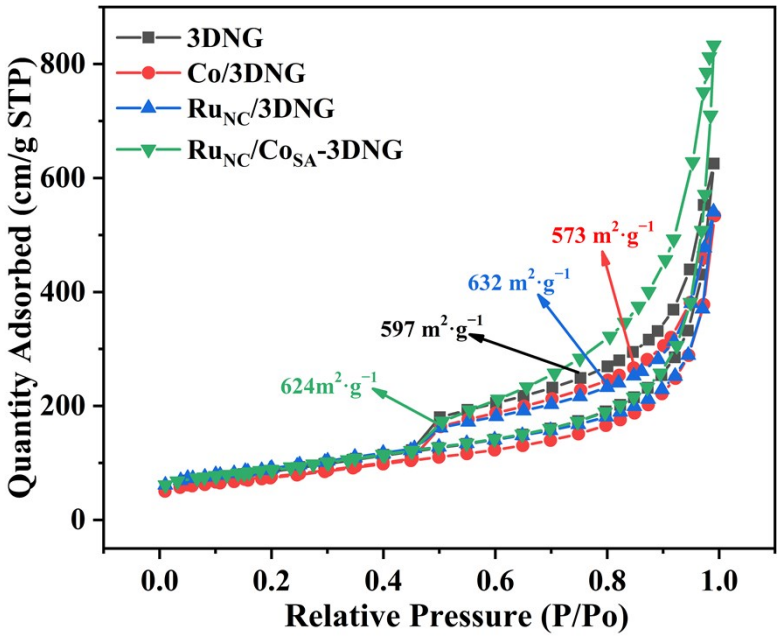

Figure S5. The nitrogen adsorption/desorption isotherms and pore size distribution of 3DNG, Co/3DNG, Ru_{NC}/3DNG and Ru_{NC}/Co_{SA}-3DNG.

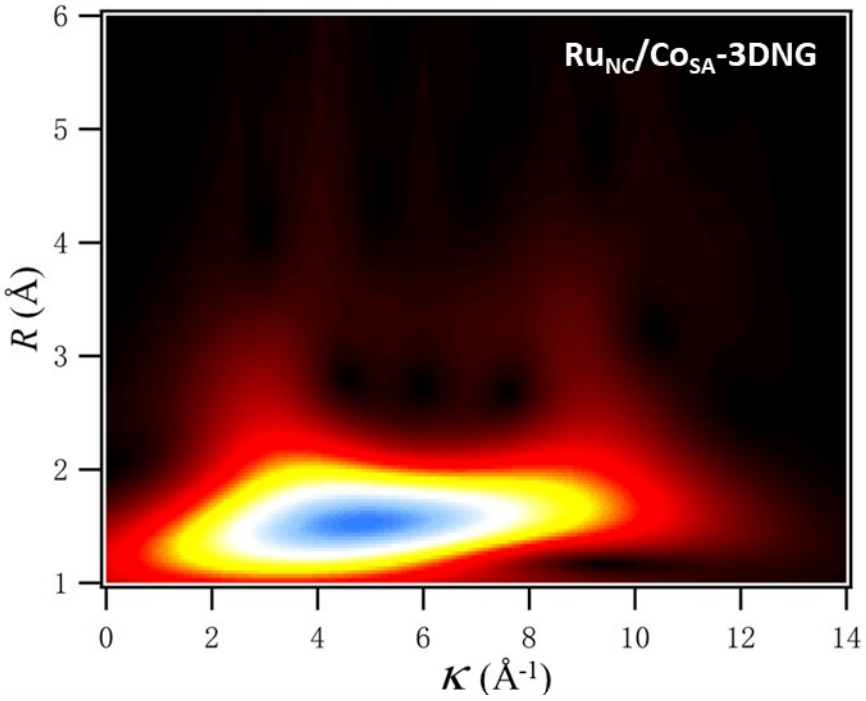

Figure S6. Wavelet transforms for the k^3-weighted Co K-edge EXAFS signals of Ru_{NC}/Co_{SA}-3DNG. The maxima at 4.5 $Å^{-1}$ is associated with the Co-N contributions.

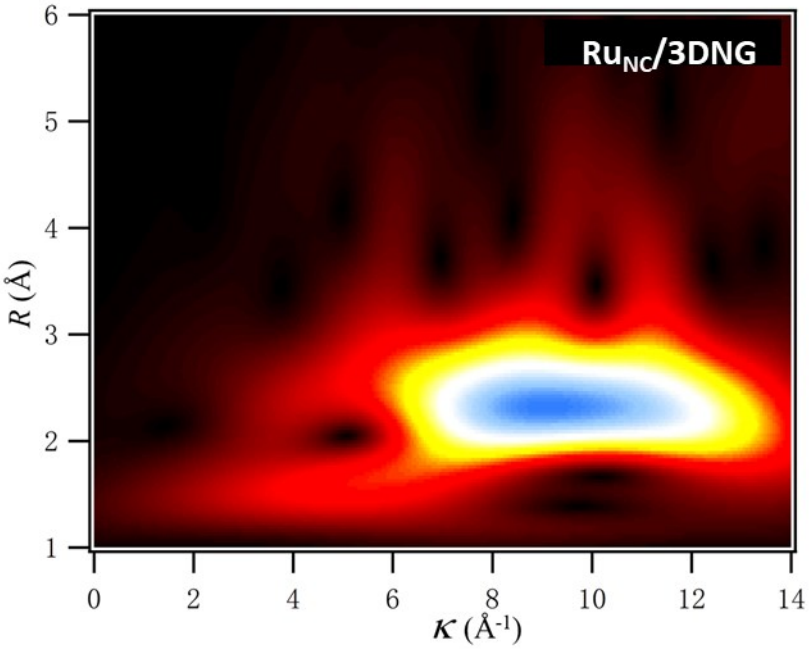

Figure S7. Wavelet transforms for the k^3-weighted Ru K-edge EXAFS signals of Ru$_{NC}$/3DNG. Ru$_{NC}$/3DNG shows a maximum at 9.3 Å^{-1}, which indicates the dominance of metallic Ru nano crystallites.

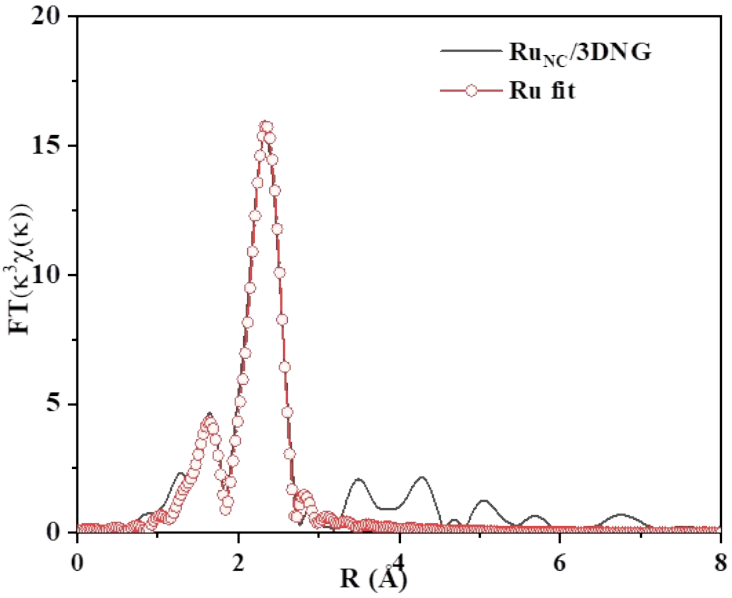

Figure S8. R space Fitting result of Ru K-edge of Ru$_{NC}$/3DNG.

Table S1. EXAFS fitting results of Ru_{NC}/Co_{SA}-3DNG from Figure 3c-f

Sample	Shell	N [a]	R (Å) [b]	σ^2 (Å$^2\cdot10^{-3}$) [c]	ΔE0 (eV) [d]	*R* factor (%)
Ru_{NC}/Co_{SA}-3DNG	Co-N/O	6.0	2.08	9.1	0.3	0.3
	Co-Co	0.5	2.42	10.1	-0.2	
	Ru-N	4.1	2.05	7.8	3.5	1.3
	Ru-Ru	0.7	2.53	7.0	-0.6	
Ru_{NC}/3DNG	Ru-N	1.3	2.02	1.4	-0.5	0.8
	Ru-Ru	6.4	2.67	6.7	-6.2	

[a] *N*: coordination numbers; [b] *R*: bond distance; [c] σ^2: Debye-Waller factors; [d] ΔE_0: the inner potential correction. *R* factor: goodness of fit. *S*02 were set as 0.89/0.90 for Co-O/Co-Co , which were obtained from the experimental EXAFS fit of reference CoO/Co foil by fixing CN as the known crystallographic value and was fixed to all the samples. S02 were set as 0.85/0.90 for Ru-N/O, Ru-Ru, which were obtained from the experimental EXAFS fit of reference RuO_2/Ru powder by fixing CN as the known crystallographic value and was fixed to all the samples.

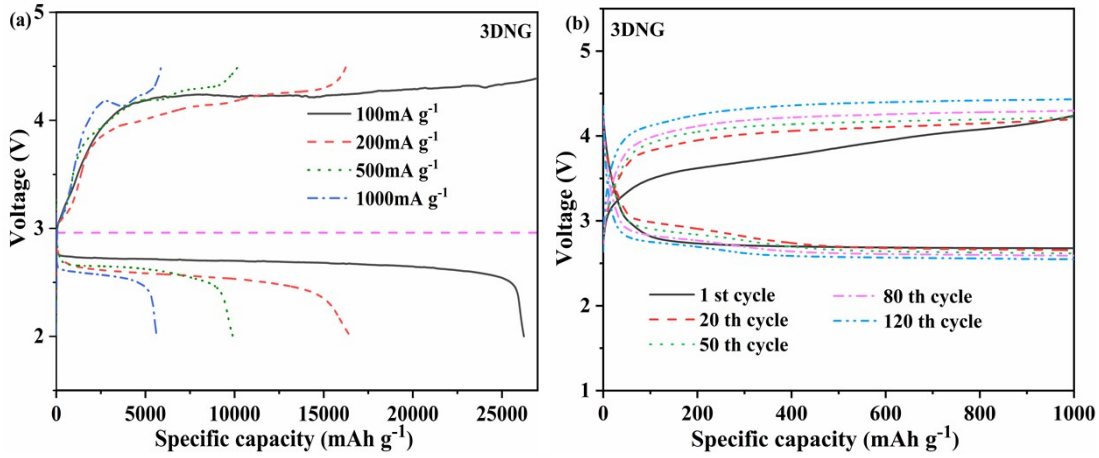

Figure S9. The rate performance of 3DNG cathode (2.0-4.5 V), and corresponding discharge–charge voltage profiles different cycles under specific capacity limit of 1000 mAh g^{-1} at a rate of 200 mA g^{-1}.

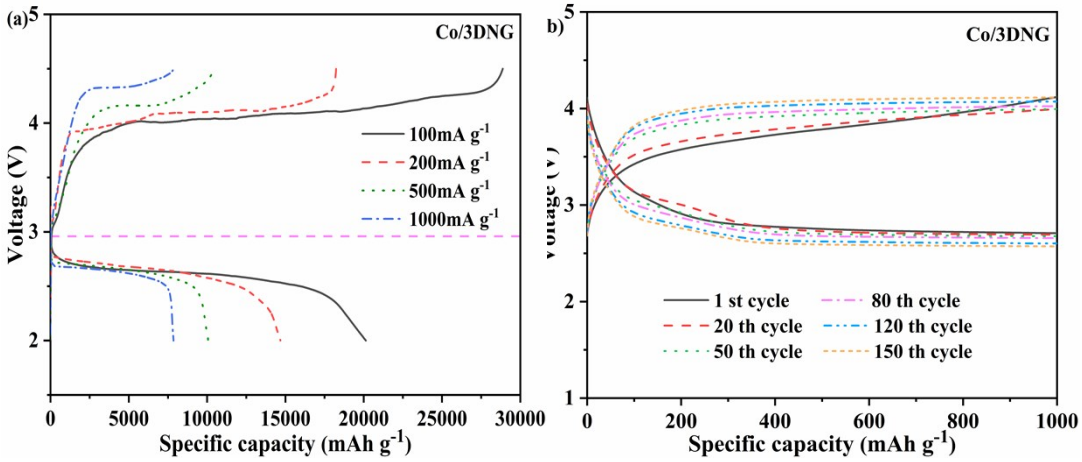

Figure S10. The rate performance of Co/3DNG cathode (2.0-4.5V), and corresponding discharge–charge voltage profiles different cycles under specific capacity limit of 1000 mAh g^{-1} at a rate of 200 mA g^{-1}.

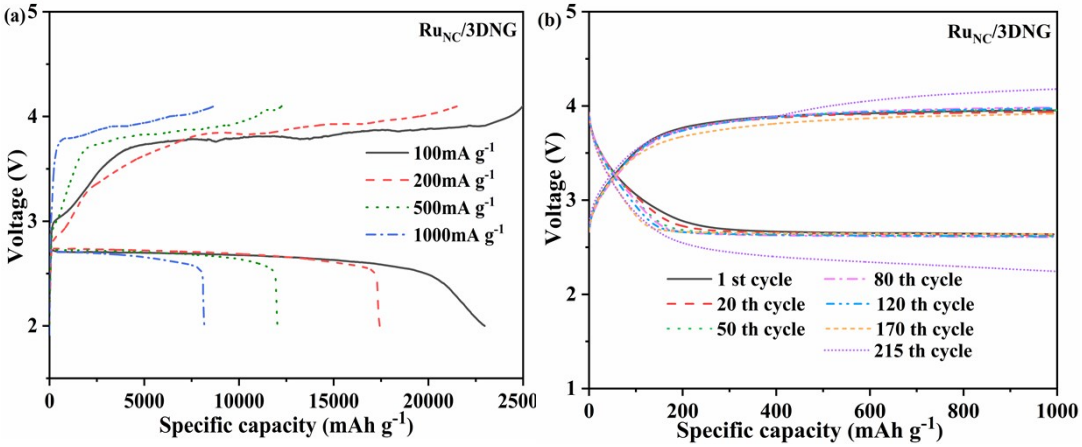

Figure S11. The rate performance of Ru_{NC}/3DNG cathode (2.0-4.1V), and corresponding discharge–charge voltage profiles different cycles under specific capacity limit of 1000 mAh g^{-1} at a rate of 200 mA g^{-1}.

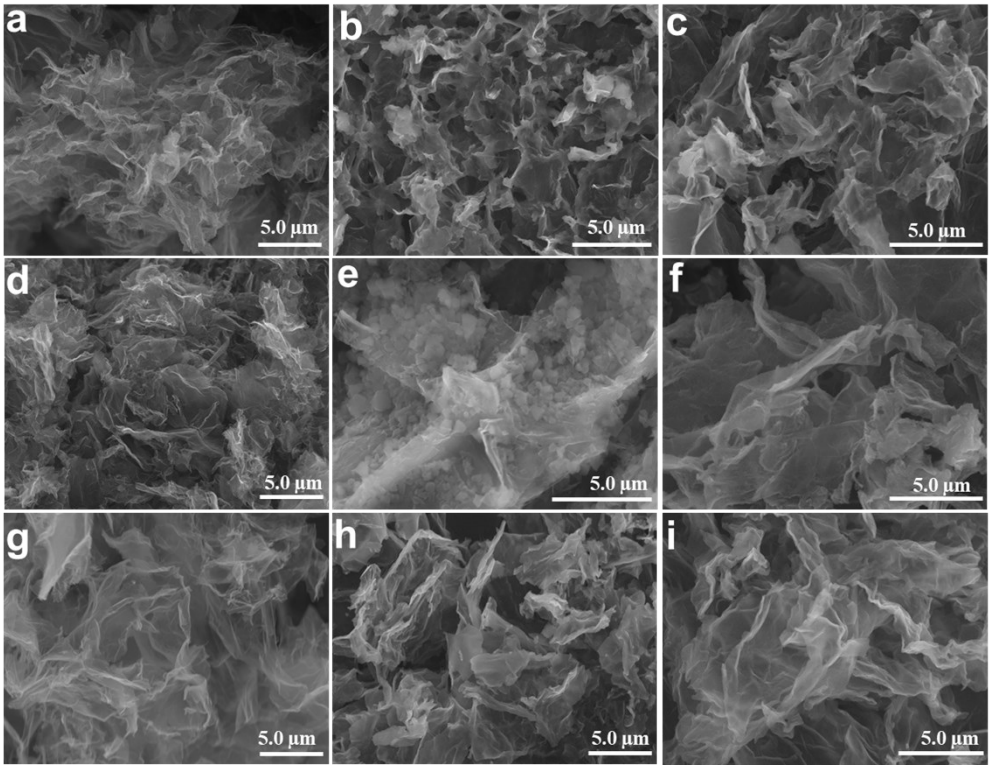

Figure S12. SEM images of pristine, discharged (2.0 V) and subsequent recharged (to 4.3V) cathodes of 3DNG (a, b, c), Co/3DNG (d, e, f), Ru_{NC}/3DNG (g, h, I)

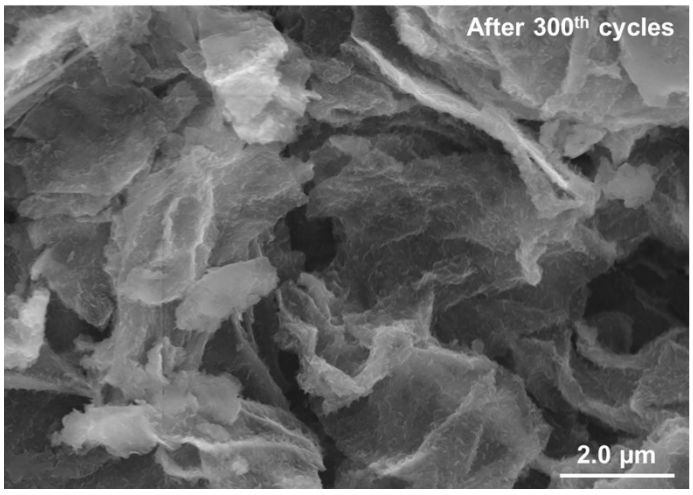

Figure S13. SEM images of Ru_{NC}/Co_{SA}-3DNG cathode after 300^{th} cycles of discharge and charge process

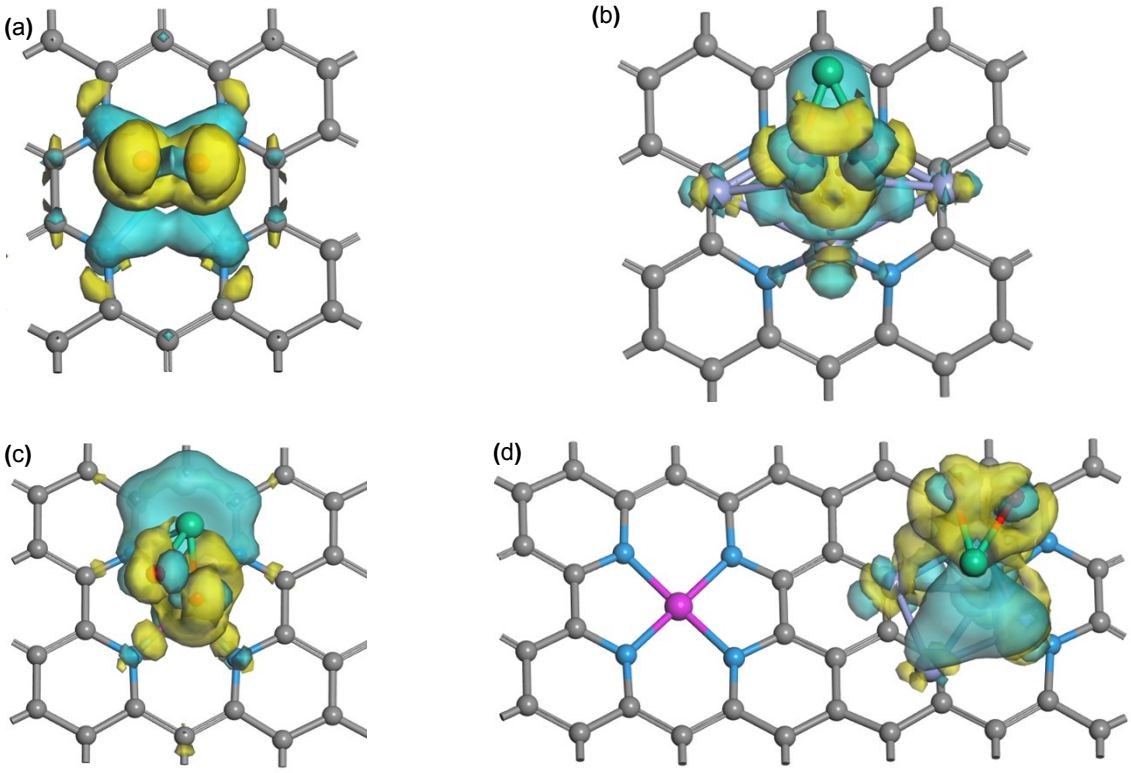

Figure S14. 3D plots of the charge density difference of the LiO_2 molecule adsorption on (a) 3DNG, (b) Ru_{NC}/3DNG, (c) single Co atoms and (d) Ru clusters of Ru_{NC}/Co_{SA}-3DNG. The yellow and green isosurfaces represent the electron gain and lose, respectively. The corresponding isosurface value is 0.002 e/Bohr^3.

Table S2. Comparison of specific capacity for various Ru/graphene-based cathodes.

Cathode	Mass loading (wt.%))	Current density (mA/g)	Discharge Capacity (mAh/g)	overpotential	references
Ru@ Porous graphene	20.34	200	17700	0.35 V	[1]
Ru-graphene aerogels	18	0.1mA/cm^2	12000	1.25 V	[2]
Ru@ VGNS@ Ni foam	43	200	23864	0.86 V	[3]
Ru-FeCoN/rGO	20	200	23905	~1.0 V	[4]
Ru@MPG	30	200	6433	~1.0 V	[5]
Ru/N-CNFs@TiO_2	20.3	0.15 mA/cm^2	2.0 mAh/m^2	~0.94 V	[6]
Ru/3D-NrGO	9.37	200	18727	0.88 V	[7]
Ru QD/NHG	--	300	2700	1.04 V	[8]
$Ru_{0.3}$ SAs-NC	2.48	0.02mA/m^2	13424	1.37 V	[9]

Ru@MWCNTP	9.0	500	~27000	1.04 V	[10]
Ru_{NC}/Co_{SA}-3DNG	**8.82**	**100**	**25632**	**0.84 V**	**This work**

Table S3. Comparison of cycling stability for various Ru/graphene-based cathodes.

Cathode materials	Current density (mA/g)	Discharge Capacity (mAh/g)	Cycling numbers	overpotential	references
Ru@ Porous graphene	200	1000	200	~0.94 V	[1]
Ru-graphene aerogels	0.1mA/cm^2	500	50	~1.04 V	[2]
Ru@ VGNS@ Ni foam	200	1000	200	~0.23 V	[3]
Ru-FeCoN/rGO	200	600	300	~1.04 V	[4]
Ru@MPG	100	500	55	~1.24 V	[5]
Ru/N-CNFs@TiO_2	500	1000	132	~1.24 V	[6]
Ru/3D-NrGO	200	1000	200	~1.04 V	[7]
Ru QD/NHG	300	500	20	~0.85 V	[8]
$Ru_{0.3}$ SAs-NC	0.02mA/m^2	1000	60	~1.29 V	[9]
Ru@MWCNTP	500	5000	50	~1.31 V	[10]
Ru_{NC}/Co_{SA}-3DNG	**200**	**1000**	**300**	**~1.02 V**	**This work**

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