Electronic Supplementary Information (ESI)

Chrysanthemum flower like $NiCo_2O_4$-nitrogen doped graphene oxide composite: An efficient electrocatalyst for Lithium-oxygen and Zinc-air batteries

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EXPERIMENTAL METHODS

Synthesis of active catalyst

The Chrysanthemum flower-like morphology consists of $NiCo_2O_4$ (NCO) incorporated nitrogen doped graphene (N-rGO) composite material was prepared by solvothermal method followed by heat treatment. Graphene oxide (GO) was prepared from graphite flakes using a modified Hummers' method.[1] In a typical synthesis, stoichiometric amounts of nickel acetate, cobalt acetate, ammonium hydroxide, graphene oxide (GO) and ethanol were mixed and refluxed at 80 °C for 10 h, then transferred into an autoclave which was heated at 150 °C for 6 h. The resulting product was separated by centrifugation, washed with deionized water, dried at 70 °C for overnight, and then the product was further calcinated in air at 250 °C for 12 h. Likewise bare NCO nanoparticles prepared without both GO and ammonium hydroxide and N-rGO prepared without metal oxide precursors.[2]

Materials Characterization

The phase purity of the prepared sample was tested by X-ray diffraction (XRD) measurements using a X-ray diffractometer (Rigaku, MiniFlex 600). The Chrysanthemum flower morphology was identified by using a field emission-scanning electron microscope (FE-SEM, Hitachi). To distinguish the NCO and N-rGO of the flower like NCO/N-rGO morphology, a field emission transmission electron microscope (FE-TEM, Hitachi) with elemental mapping was carried out. The nitrogen content in flower like NCO/N-rGO sample was confirmed by elemental analysis (CHNS-VarioMICRICube). The Brunauer–Emmett–Teller (BET) surface area of the flower morphology was tested by a Micromeritics Tristar ASAP 2020 analyzer.

Electrochemical Characterization

The bi-functional (oxygen reduction and evolution) activity of the samples were tested using a three-electrode setup with computer-controlled potentiostat (Biologic) via rotating disk electrode linear sweep voltammetry (LSV) and cyclic voltammetry (CV), in alkaline medium (0.1 M KOH) electrolyte under oxygen saturated condition (before N_2 saturated electrolyte for background correction with the same condition). The catalyst ink was prepared by 2 mg catalyst was ultrasonically dispersed into a solution containing 3 μL of Nafion, 24 μL of deionized water, and 100 μL. 4 μL of catalyst ink was dropped on the glassy carbon disk surface (working electrode) and dried at room temperature. A platinum wire and saturated Calomel electrode served as the counter and reference electrodes, respectively.

Construction and characterization of zinc-air battery

For testing the zinc-air battery a split cell (EQ-STC-MTI-Korea) packed with a Whatman glass microfiber separator saturated with the 6M KOH aqueous solution sandwiched between a polished zinc anode (diameter of 1.54 cm) and a catalyst-coated gas diffusion layer (GDL, the diameter of 1.78 cm). The cathode catalyst ink was prepared by ultrasonic dispersion of 7 mg of as-synthesized flowers like NCO/N-rGO and 3 mg of activated carbon using 1 mL of isopropyl alcohol and 67 μL of 5 wt.% Nafion ionomer for 30 min. Then, the catalyst ink was coated onto the GDL by using a brush coating method, with the total catalyst loading of 1 mg in GDL, and it was dried in a vacuum oven overnight at 80 °C. The discharge−charge cycle was performed in a constant current mode using a battery analyzer (BST8-3) by breathing open air environment in the cathode part at room temperature.

Construction and characterization of lithium-oxygen battery

For testing the lithium-oxygen battery a CR2032 coin cells punched bottom case (316 SS-MTI-Korea) packed with a Whatman-GF/A glass microfiber separator saturated with the lithium bis(trifl uoromethane) sulfonimide (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME) solvent sandwiched between a polished lithium disc anode (MTI Korea) and a catalyst-coated gas diffusion layer (GDL, area 2.54 cm^2). The cathode catalyst slurry was prepared by mixing N-methyl-2-pyrrolidone (NMP) with prepared as-synthesized flower like NCO/N-rGO, electronic conducting super p carbon black (Daejung, Korea) and poly-vinylidene fluoride (PVdF) binder in the weight ratio of 70:20:10 respectively. Then, the catalyst slurry was deposited over GDL by using a doctor blade technique, and it was dried in a vacuum oven overnight at 55 °C to obtain a composite cathode with an electrode mass of about 1 $mg.cm^{-2}$ loaded on Gas diffusion layer. The lithium-oxygen cell was then assembled in an Ar-filled dry glove box using a 2032 coin cell with openings at the cathodic part for allowing oxygen. The cells were galvanostatically cycled by a battery analyzer at room temperature between 4.5-2.0 V vs. Li^+/Li at a current density of 200 $mA.g^{-1}$ by breathing pure oxygen at the rate of 1-atmosphere pressure. For charging and discharging the cut-off voltage was fixed with 2.0 V for discharging and 4.5 V charging vs. Li.

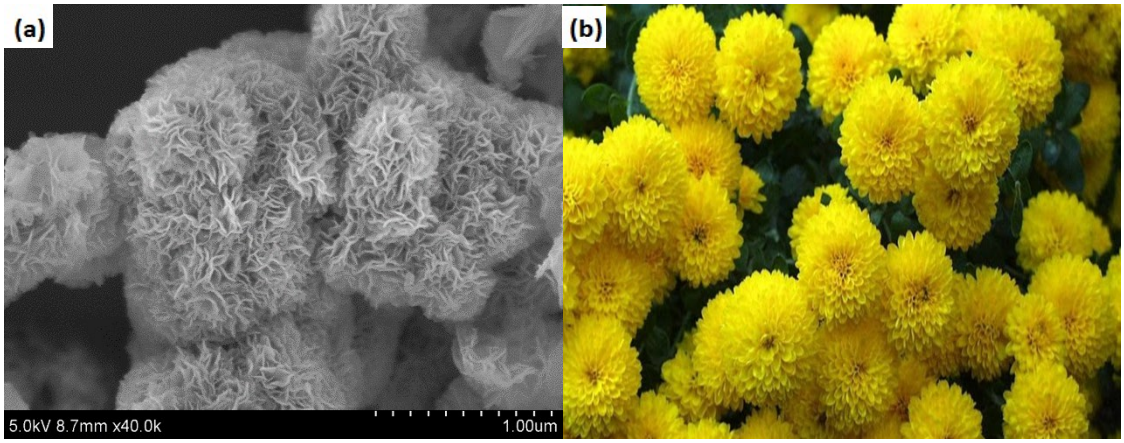

Fig. S1. (a) FE-SEM image of as-synthesized flower like NCO/N-rGO; (b) Photo image of Chrysanthemum flower.

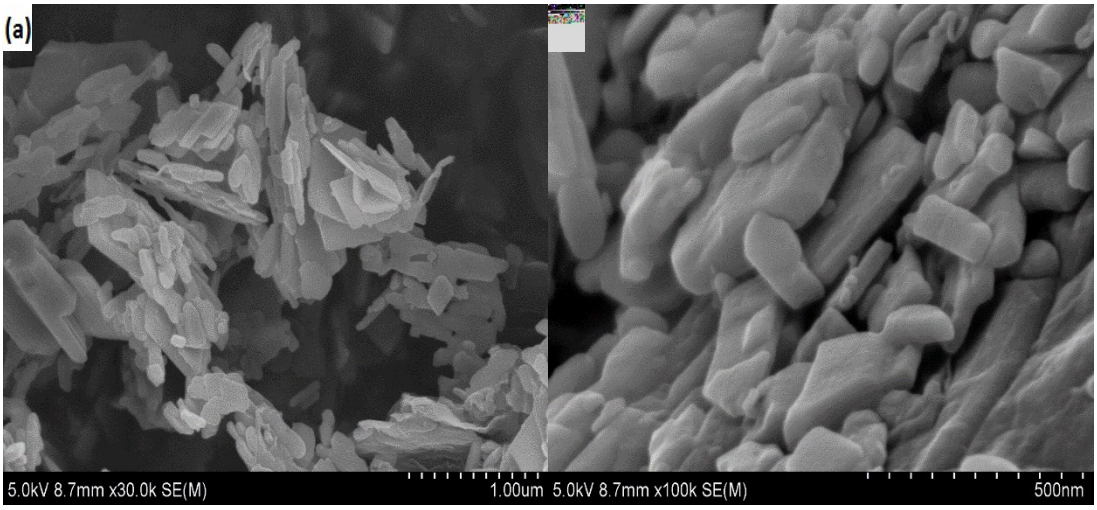

Fig. S2. FE-SEM images of as-synthesized bare NCO

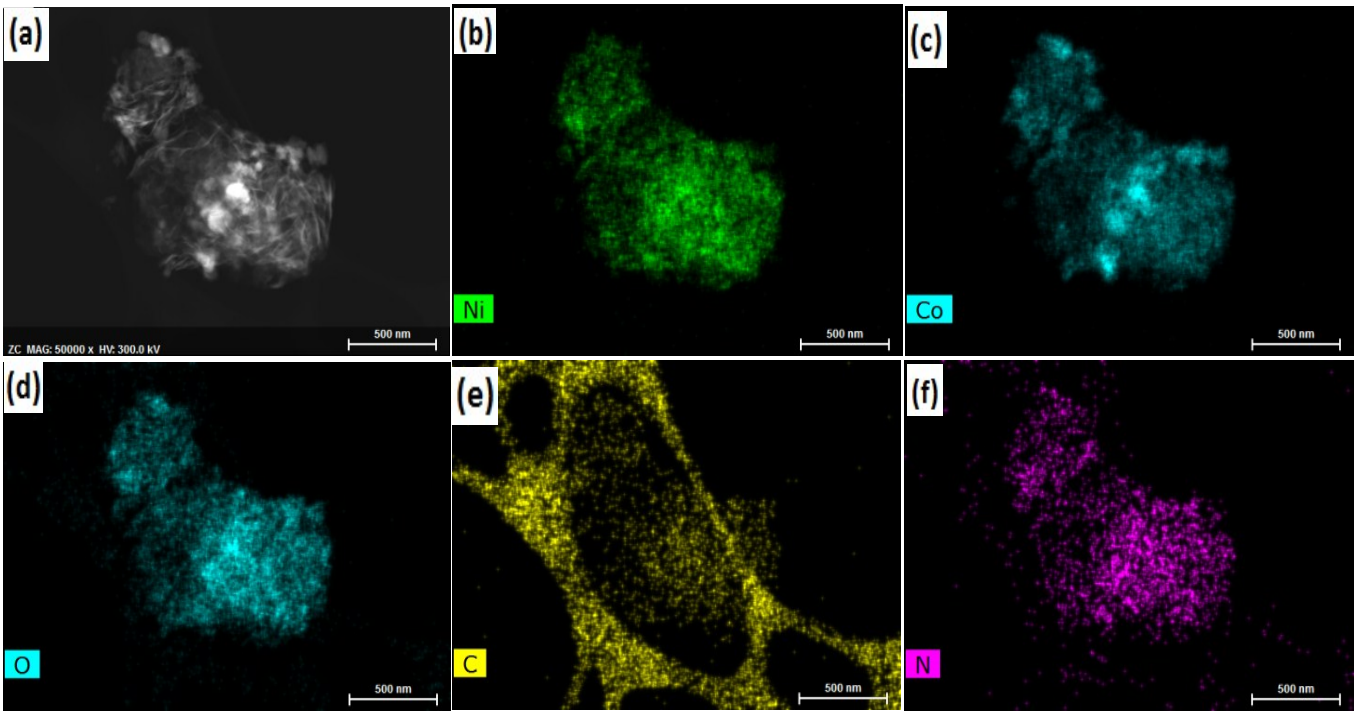

Fig. S3. (a) STEM image of flower like NCO/N-rGO, and the corresponding elemental maps of (b) Ni-K edge, (c) Co-K edge, (d) O-K edge, (e) C-K edge, and (f) N-K edge.

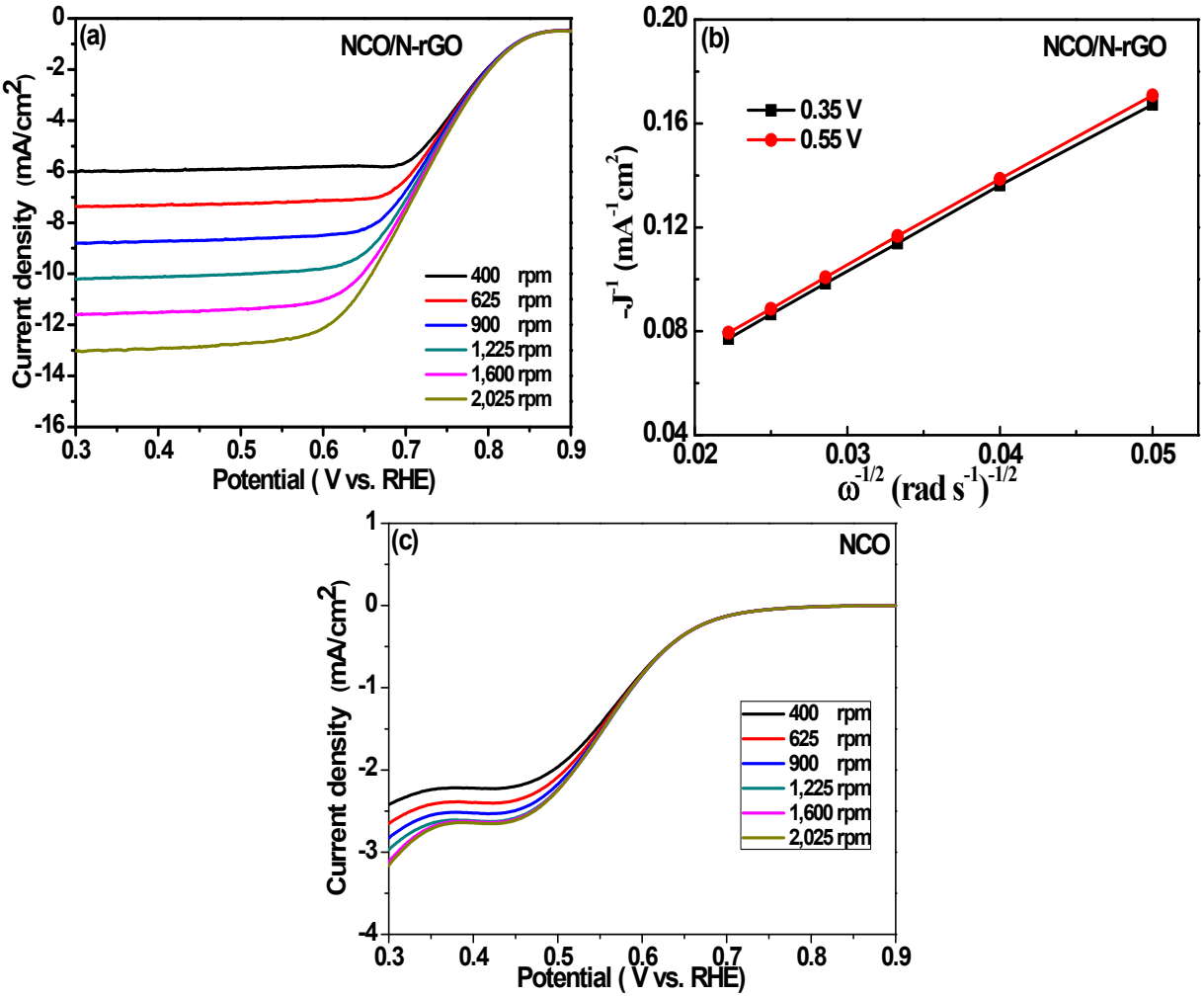

Fig. S4. (a) Oxygen reduction RDE polarization curves for flower like NCO/N-rGO; (b) and corresponding Koutecky–Levich plots at different potentials (0.35 and 0.55 V); (c) Oxygen reduction RDE polarization curves for bare NCO; Experiments were carried out at different rotation speeds (400–2025 rpm) in 0.1 M KOH at a scan rate of 5 mV s^{-1}.

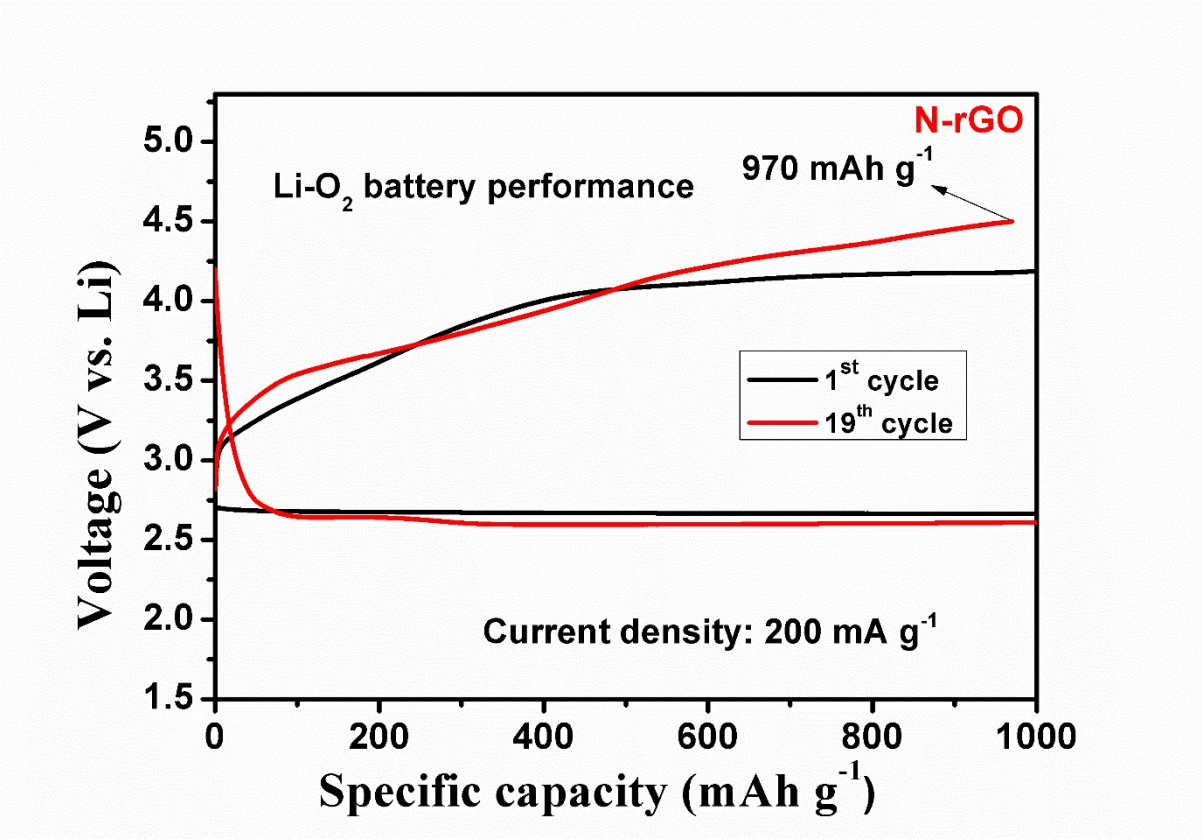

Fig.S5. Galvanostatic cycles of N-rGO with a controlled capacity of 1000 mAh g^{-1} at a current density of 200 mA g^{-1} to a cut-off voltage of 2.0 V (discharge) and 4.5 V (charge) vs. Li.

Table S1. Summary of charge and discharge (C-D) potential gap of flower like NCO/N-rGO cathode catalyst for zinc-air battery at different current densities calculated from Galvanodynamic discharge and charge curve.

Current density ($A\ g^{-1}$)	C-D voltage gap (V vs. Zn)
1	0.26
10	0.70
20	1.03
30	1.30
40	1.56
50	1.68
60	1.83
70	2.00

Table S2. Summary of charge and discharge potential gap of flower like NCO/N-rGO cathode catalyst for zinc-air and lithium-oxygen battery over 50 cycles calculated from Galvanostatic discharge and charge curve.

Metal-air Battery	1st cycle			50th cycle		
	Discharge potential	Charge potential	C-D potential gap	Discharge potential	Charge potential	C-D potential gap
Zinc-air (V vs. Zn)	1.13	1.83	0.70	1.07	1.84	0.77
Lithium-oxygen (V vs. Li)	2.63	4.39	1.76	2.55	4.45	1.90

References

(1) Hummers, W. S, Offeman, R. E. J. Am. Chem. Soc. 1958, 80, 1339−1339.

(2) M. Prabu, P. Ramakrishnan and S. Shanmugam, Electrochem. Commun. 2014, 41, 59–63.