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

Electronic Supplementary Information

Magnesium-Regulated Oxygen Vacancies of Nickel Layered Double Hydroxides for Electrocatalytic Water Oxidation

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Materials and characterization methods

All chemical reagents were used as received. Nafion solution (5 *wt*% in mixture of water and 2-propanol) was purchased from Sigma Aldrich. Nickel nitrate hexahydrate ($Ni(NO_3)_2·6H_2O$), magnesium nitrate hexahydrate ($Mg(NO_3)_2·6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3·9H_2O$), manganese (II) nitrate tetrahydrate ($Mn(NO_3)_2·4H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$), calcium nitrate tetrahydrate ($Ca(NO_3)_2·4H_2O$), 2-methylimidazole (Hmim), sodium hydroxide (NaOH), potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), hydrogen peroxide (H_2O_2, 30 *wt*%), hydrazine hydrate ($N_2H_4·H_2O$, >80 *wt*%), sulfuric acid (H_2SO_4, 18.4 M), hydrogen chloride (HCl, 12 M), methanol, RuO_2, and natural graphite were purchased from Sinopharm Chemical Reagent Co., Ltd, China.

Transmission electron microscopy (TEM) was used to characterize microstructures and morphologies of samples on a Tecnai F30 operated at 300 kV. Scanning electron microscopy (SEM) was performed on HITACHI UHR FE-SEM SU8220. X-ray diffraction (XRD) was carried out in a Rigaku D/Max 2400 automatic powder X-ray diffractometer with Cu-*K*α radiation (λ = 1.5418 Å). The thickness of samples was estimated by atomic force microscopy (AFM, Park Systems XE-70) based on non-contact mode. The contents of metal elements were evaluated by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 2000DV). The composition and chemical state of samples was analyzed by X-ray photoelectron spectroscopy (XPS ,Thermo ESCALAB 250Xi) with Al-*K*α radiation ($h\nu$ = 1486.6 eV). Electron spin resonance (ESR) spectra were collected on Bruker A200 at room temperature. Zeta potential was measured on Zetasizer Nano ZS90. Linear-sweep voltammetry (LSV), cyclic voltammetry (CV), and chronoamperometry were measured on a CHI760E electrochemical workstation using a conventional three-electrode cell. Electrochemical impedance spectroscopy (EIS) was investigated on a ZAHNER ENNIUM electrochemical workstation.

Materials synthesis

Synthesis of Ni-LDHs. $Ni(NO_3)_2·6H_2O$ (1.454 g, 5 mmol) and Hmim (0.411 g, 5 mmol) were sequentially added to methanol (15 mL) with vigorously stirring to form a uniform solution in a 20 mL of Teflon-lined stainless steel autoclave. The resulting mixture was heated at 80 ^oC for 4 h. The final pale green product was collected by centrifugation, rinsed thrice by methanol, and dried in vacuum oven at 80 ^oC for 6 h before subjected to characterization.

Synthesis of NiM-LDHs. Ni-LDHs doped with *s*-, *p*-, *d*-, and *ds*-block metals were prepared. In a typical synthetic procedure, $Ni(NO_3)_2·6H_2O$ (1.454 g, 5 mmol), $Mg(NO_3)_2·6H_2O$ (25.6 mg, 0.1 mmol) and Hmim (0.411 g, 5 mmol) were sequentially added to methanol (15 mL) with vigorously stirring to form a uniform solution in a 20 mL of Teflon-lined stainless steel autoclave. The resulting mixture was heated at 80 ^oC for 4 h. The final pale green product was collected by centrifugation, rinsed thrice by methanol, and dried in vacuum oven at 80 ^oC for 6 h before subjected to characterization.

Other NiM-LDHs were prepared by using $Mn(NO_3)_2·4H_2O$, $Zn(NO_3)_2·6H_2O$, and $Al(NO_3)_3·9H_2O$ to substitute for $Mg(NO_3)_2·6H_2O$ under otherwise identical conditions. In the synthetic media, the molar ratio of Ni to M (such as Mg) were allowed to adjust and prepare various NiM-LDHs.

Fabrication of NiMg-LDHs/rGO hybrids. Graphene oxide (GO) was firstly prepared by a modified Hummers method. Briefly, natural graphite (0.5 g) and $NaNO_3$ (0.25 g) were mixed in concentrated H_2SO_4 (20 mL) with stirring while cooling in an ice-water bath, and then $KMnO_4$ (1.5 g) was gradually added. The temperature of the mixture was allowed to warm to room temperature, subsequently was transferred to water bath and heated at 35 ^{o}C for 30 min. After that, deionized water (30 mL) was added, and the suspension was heated at 90 ^{o}C for another 15 min. Another addition of deionized water (80 mL) and H_2O_2 (30 *wt*%, 0.5 mL) were sequentially added to the suspension under stirring for another 1 h. The suspension was filtered and washed with HCl (1 M) and deionized water several times until the pH was ~7. The collected solid was redispersed into deionized water (100 mL) by sonication for 1 h, and centrifuged at 5000 *g* for 15 min. GO sheets in the supernatant were kept for subsequent application.

To prepare reduced graphene oxide (rGO), $N_2H_4 \cdot H_2O$ (80 μL) was added to an aqueous GO suspension (1 g/L, 100 mL) in a round-bottom flask at room temperature, and the mixture was heated at 100 ^{o}C for 1 h. The precipitates were collected by filtering.

The aqueous suspension of rGO (0.1 g/L, 2 mL) after sonication was added to NiMg-LDHs suspension (10 g/L, 2 mL) dropwise. The mixture was successively stirred for 1 h. The final product was washed with deionized water three times and dried in vacuum oven at 80 ^{o}C for 6 h before subjected to characterization.

Electrochemical measurements

Preparation of electrocatalyst inks: Ni-, NiM-LDHs, and NiM-LDHs/rGO (5 mg) were added to the mixture of water and ethanol with volume ratio of 1:1 (0.975 mL), and Nafion solution (0.025 mL, 5 *wt*%). The suspension was sonicated in an ultrasonic bath for 20 min to form a uniform electrocatalyst inks.

Preparation of work electrodes: Glassy carbon (GC) electrodes (3 mm in diameter) were used as work electrodes, and were polished on a Nylon plate containing alumina and deionized water before utilization. The electrocatalyst ink (5 μL) was drop-casted on the surface of polished GC electrode rinsed with deionized water. The as-prepared work electrodes were naturally dried at room temperature for 1 h. Ag/AgCl (3.5 M KCl) and polished Pt wire were used as the reference electrode and the counter electrode in the conventional three-electron cell, respectively.

Electrocatalytic oxygen evolution reaction (OER): All electrochemical measurements were performed in in 1 M KOH solution. *iR*-compensated LSV curves were collected with a sweep rate of 5 mV s^{-1} between 0.2 to 0.8 V *vs.* Ag/AgCl after 5 successive CV scans between 0.2 V and 0.5 V. CV curves were collected with variable sweep rate from 20 to 100 mV s^{-1} at an increment of 20 mV s^{-1} between 0.2 to 0.3 V *vs.* Ag/AgCl to assess the double-layer capacitance of electrocatalysts. EIS was studied at overpotential of 320 mV in the frequency range from 0.1 Hz to 100 kHz with oscillation potential amplitudes of 5 mV. The durability was studied by successive CV scan for 1000 times at a potential windows of 0.46 to 0.56 V *vs.* Ag/AgCl at a scan rate of 50 mV s^{-1}.

The Tafel plots were calculated from LSV curves origniated from the equation of $\eta = a + b\lg j$.

The potentials *vs.* reversible hydrogen electrode (RHE) were coverted according to the Nernst equation of $E_{RHE} = E_{Ag/AgCl} + 0.0591pH + 0.197$.

The TOF (s^{-1}) were calculated by the equation of TOF = I/(2Fn), where I is current in the LSV curves, F is the Faraday constant, and n is the molar amount of active sites.

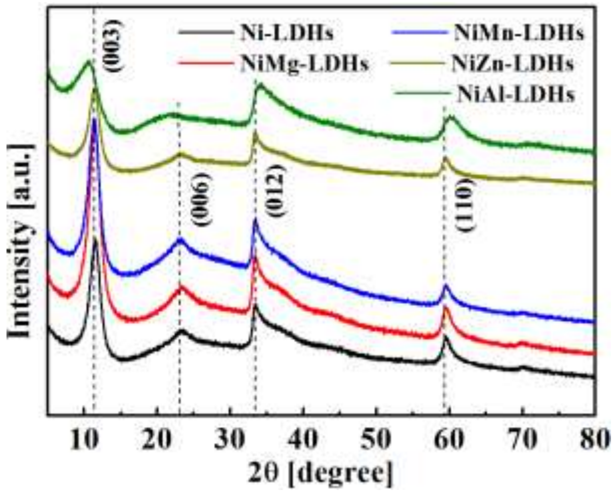

Fig. S1 XRD patterns of Ni- and NiM-LDHs (molar ratio of 50:1 from Ni to M).

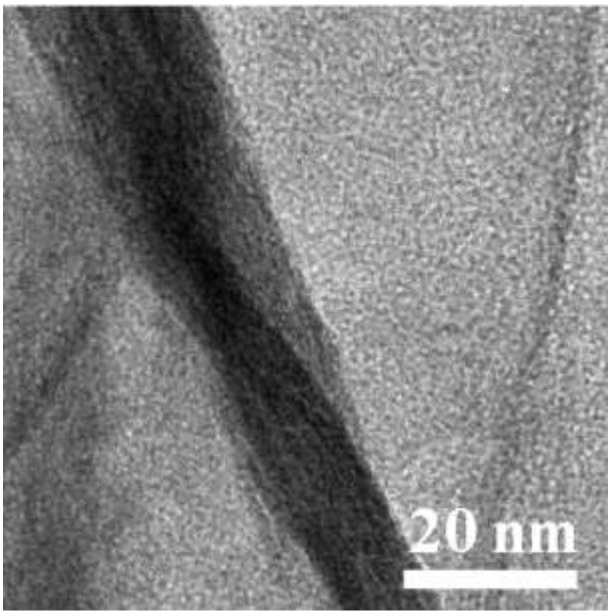

Fig. S2 TEM image of the curled edge of a NiMg-LDH sheet.

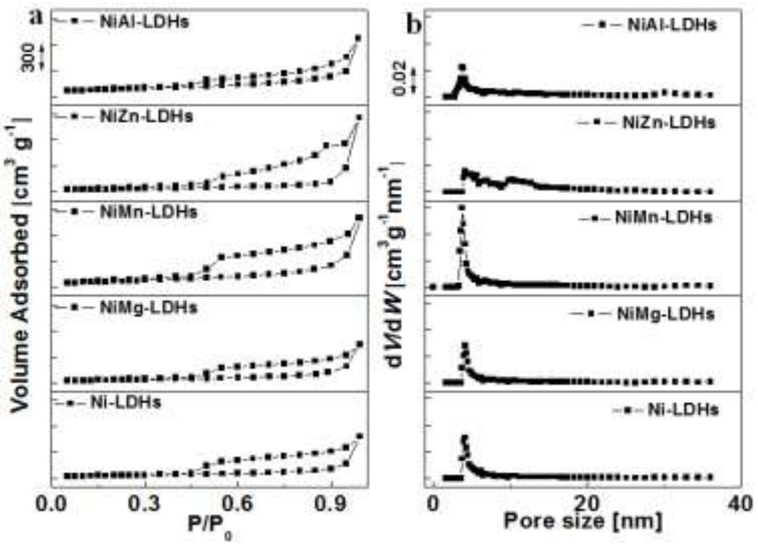

Fig. S3 (a) N_2 adsorption/desorption isotherms at 77 K of all Ni- and NiM-LDHs and (b) corresponding pore size distribution.

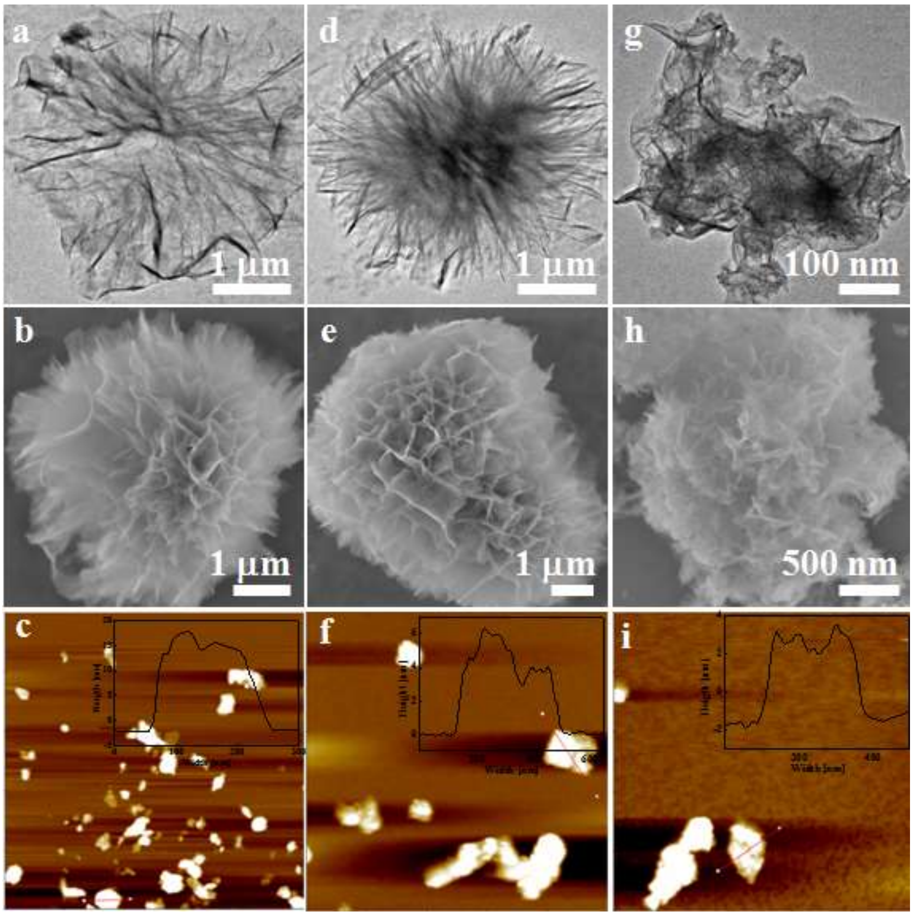

Fig. S4 TEM (top), SEM (middle) and AFM (bottom) images of (a, b, c) NiMn-LDHs, (d, e, f) NiZn-LDHs, and (g, h, i) NiAl-LDHs. Insets is the height cross-sectional profiles of sheets labeled in the AFM images.

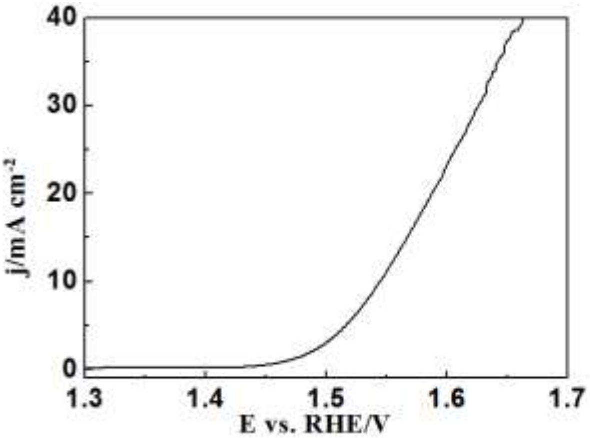

Fig. S5 *iR*-compensated polarization curve of RuO_2 towards OER in 1.0 M KOH.

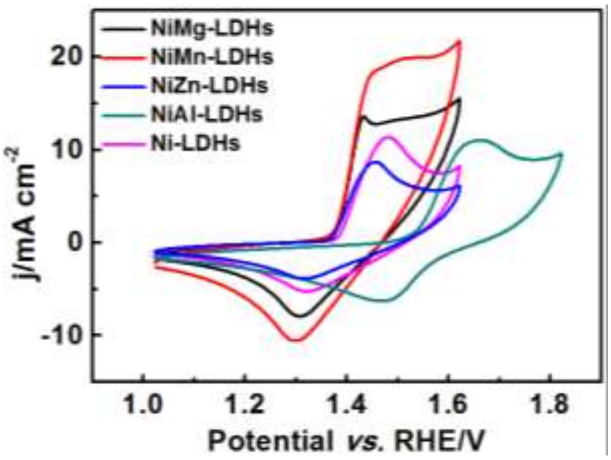

Fig. S6 Cyclic voltammetry (CV) curves of various LDHs in 1.0 M KOH at a scan rate of 100 mV s^{-1}.

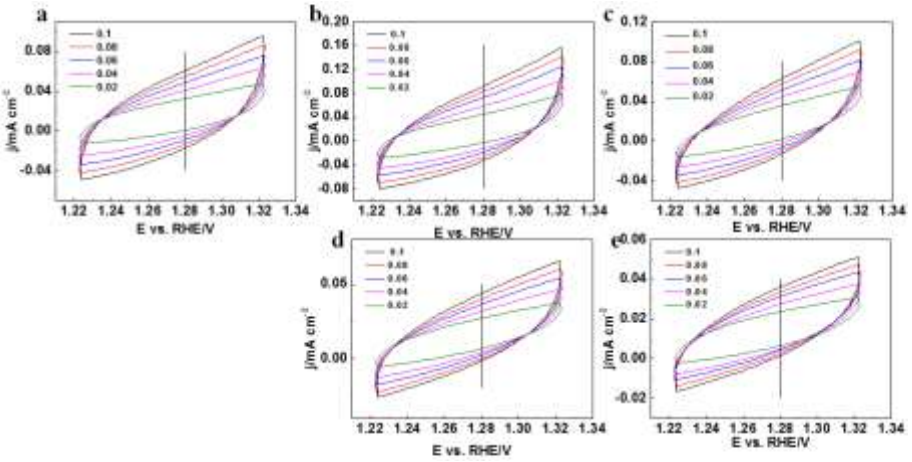

Fig. S7 CV curves measured with different scan rates of 20, 40, 60, 80, and 100 mV/s: (a) Ni-LDHs, (b) NiMg-LDHs, (c) NiMn-LDHs, (d) NiZn-LDHs and (e) NiAl-LDHs.

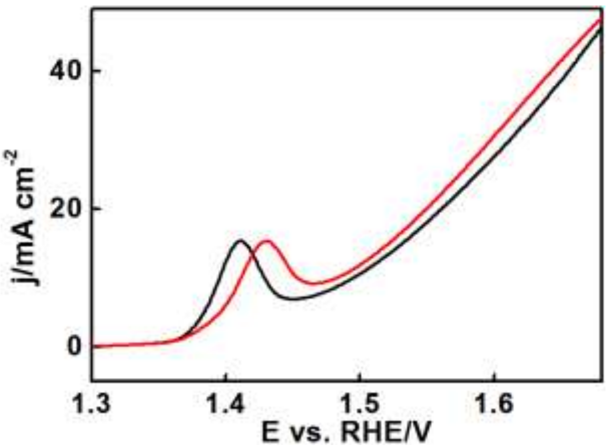

Fig. S8 The comparison of *iR*-compensated LSV curves of NiMg-LDHs before (red) and after (black) successive 1000 times CV scans.

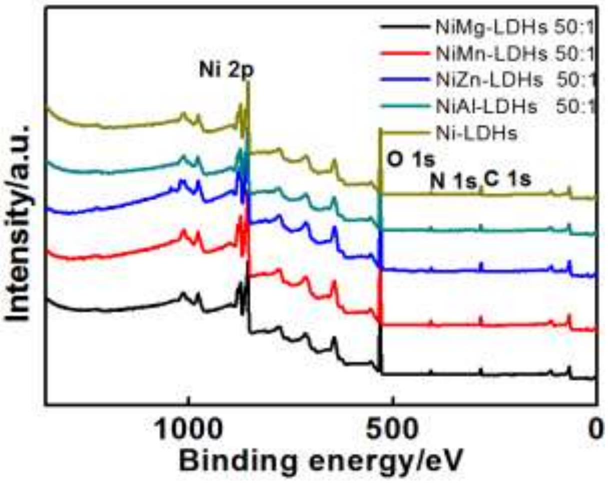

Fig. S9 Survey XPS spectra of all samples.

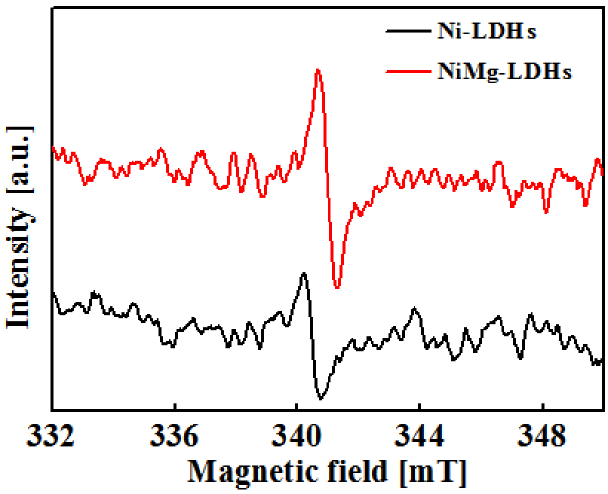

Fig. S10 ESR spectra of Ni- and NiMg-LDHs.

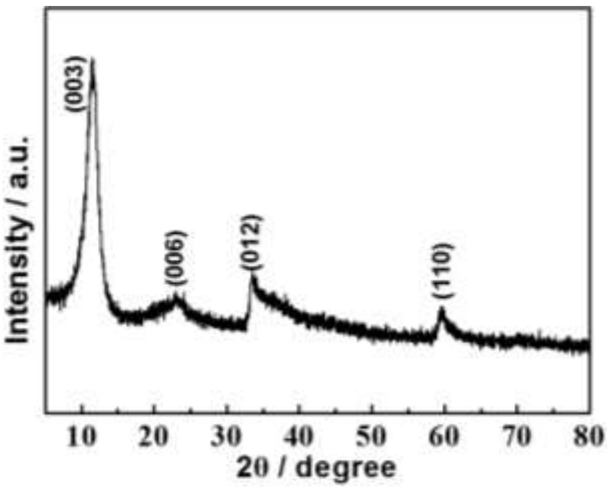

Fig. S11 XRD pattern of the sample prepared from Ni(NO_3)$_2$, Ca(NO_3)$_2$ and Hmim in methanol.

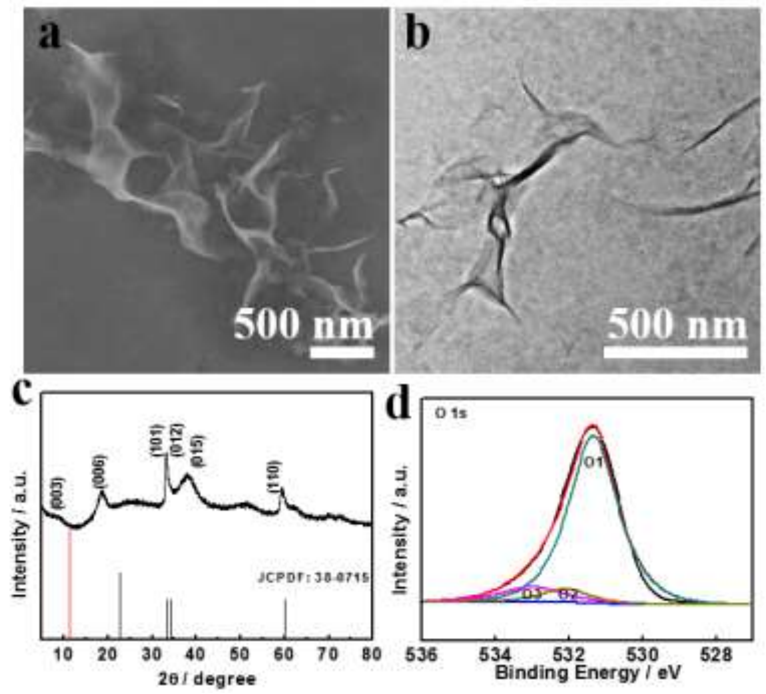

Fig. S12 The sample of NiMg-LDHs prepared by a solvo/hydrothermal synthetic route: (a) SEM and (b) TEM images, (c) XRD pattern, and (d) XPS spectrum of O 1s.

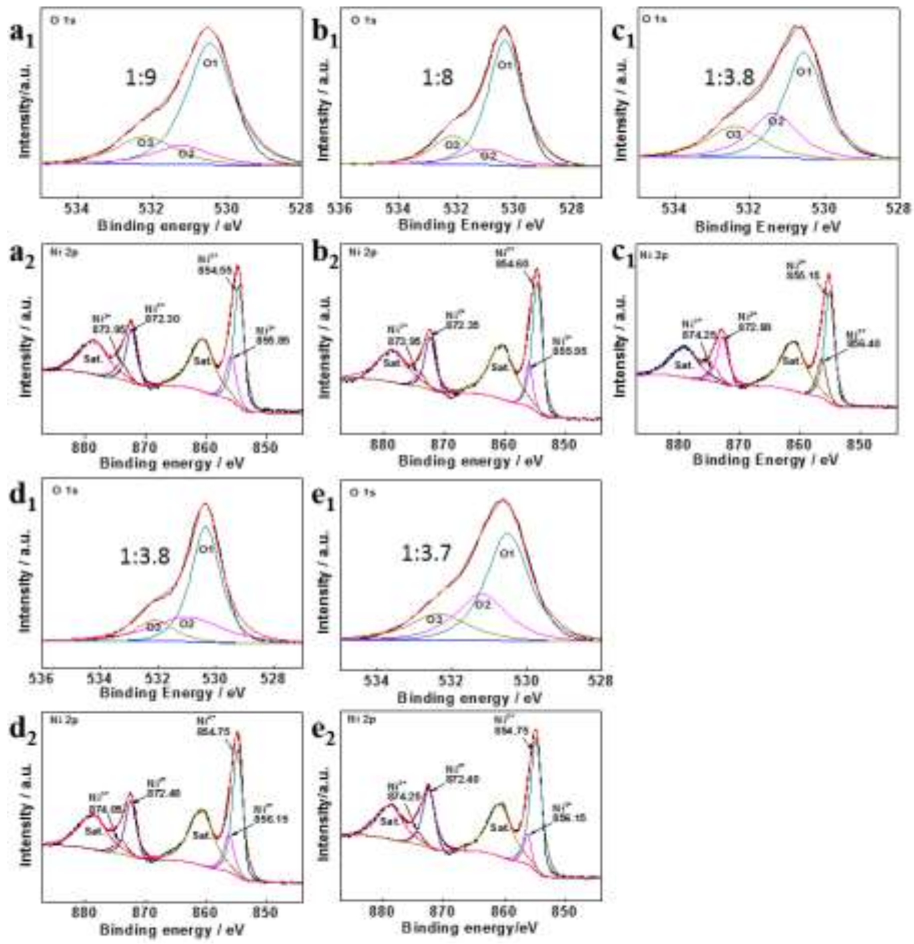

Fig. S13 High resolution XPS spectra of O 1s and Ni 2p core levels of NiMg-LDHs prepared at different molar ratio from Ni to Mg: (a_1 and a_2) 100:1, (b_1 and b_2) 80:1, (c_1 and c_2) 50:1, (d_1 and d_2) 30:1, and (e_1 and e_2) 5:1.

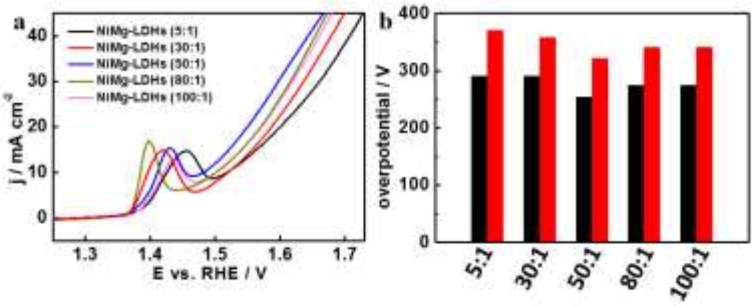

Fig. S14 (a) *i*R-compensated LSV curves measured in 1 M KOH and (b) η_{10} and η_{20} of NiMg-LDHs prepared with different molar ratio from Ni to Mg.

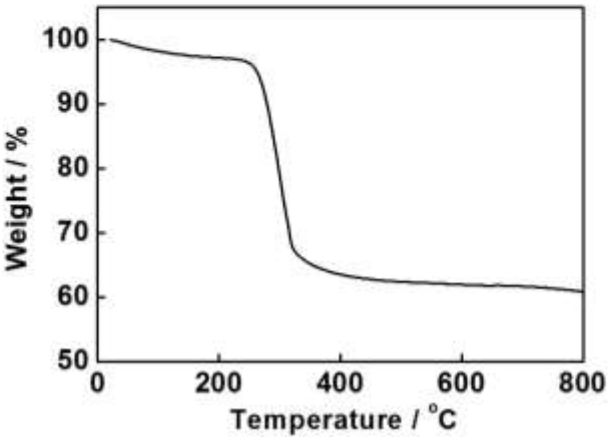

Fig. S15 Thermogravimetric curve of NiMg-LDHs-(50:1).

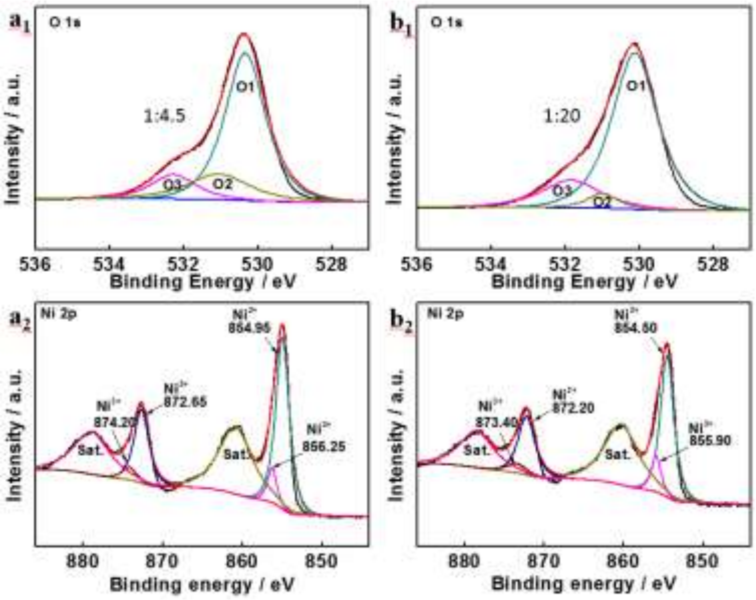

Fig. S16 High-resolution XPS spectra of O 1s and Ni 2p core levels of NiMg-LDHs-(50:1) after thermal treatment under (a_1 and a_2) N_2 and (b_1 and b_2) O_2 atmospheres, respectively.

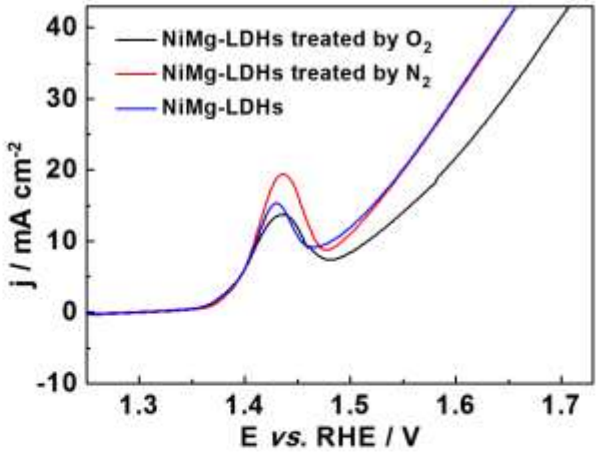

Fig. S17 *iR*-compensated LSV curves of NiMg-LDHs-(50:1) with and without thermal treatment under N_2 and O_2 atmospheres towards OER in 1.0 M KOH.

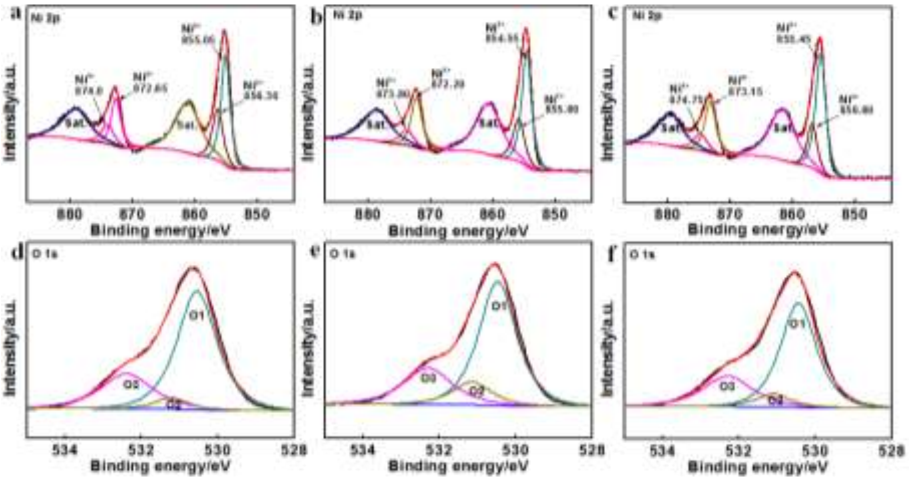

Fig. S18 High-resolution XPS spectra of Ni 2p and O 1s of (a, d) NiMn-LDHs, (b, e) NiZn-LDHs and (c, f) NiAl-LDHs.

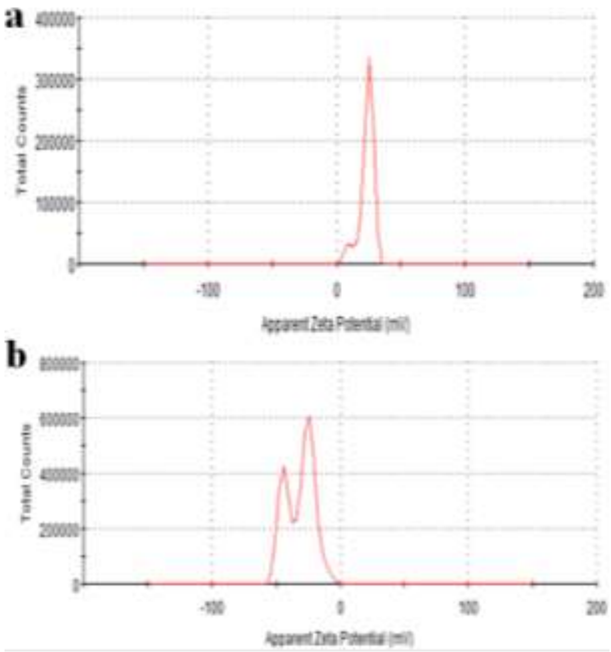

Fig. S19 Zeta potential of (a) NiMg-LDHs and (b) rGO.

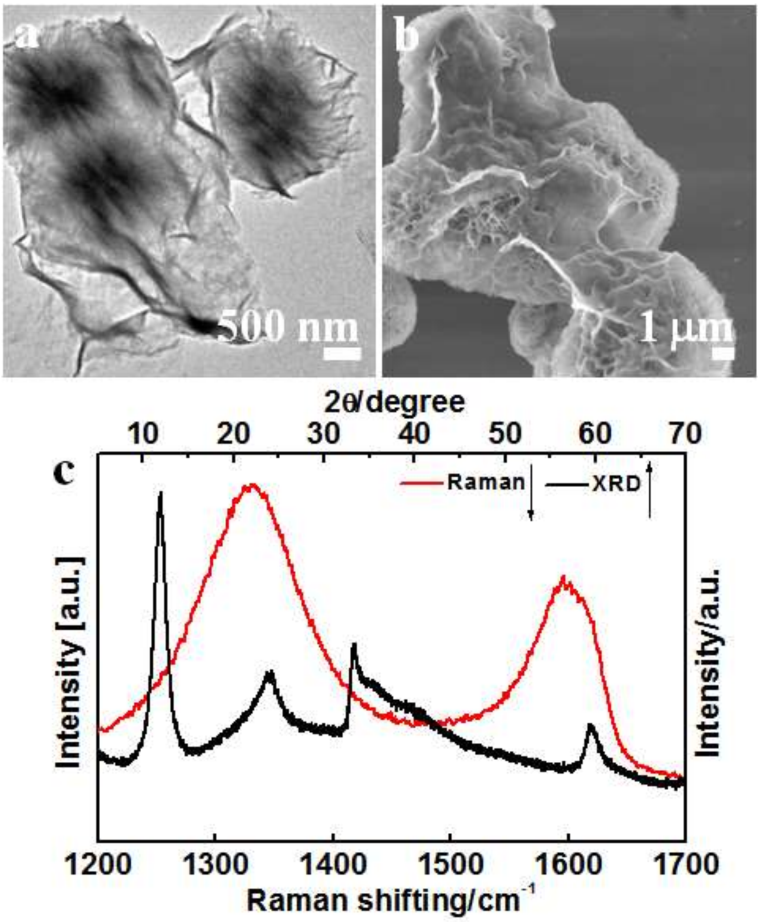

Fig. S20 (a) TEM and (b) SEM images and (c) XRD pattern and Raman spectrum of NiMg-LDHs/rGO hybrids.

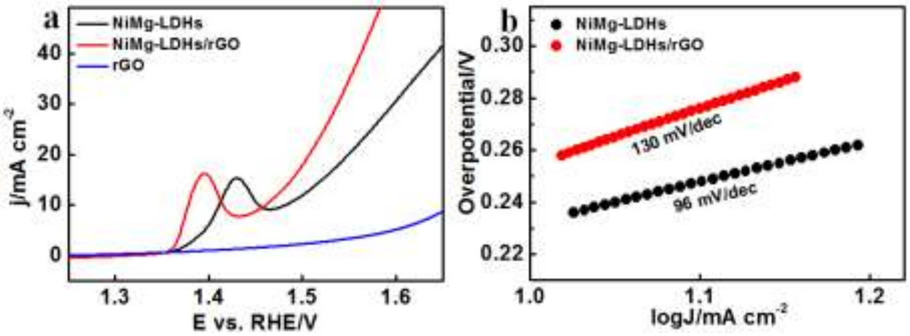

Fig. S21 Electrocatalytic performance of NiMg-LDHs/rGO hybrids towards OER in 1.0 M KOH solution. (a) LSV curves with *iR*-compensation and (d) Tafel slopes