Supporting Information

Solvent mediated hierarchically porous NiCo-LDH decorated with Au nanoparticles for catalytic platforms

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Experimental section

1. Chemicals and reagents

Nickel chloride hexahydrate, Cobalt chloride hexahydrate, Polyethylene oxide (PEO), propylene oxide, Ethylene glycol (EG), Gold (III) chloride trihydrate, sodium borohydride, 4-nitrophenol (4-NP), Potassium hydroxide (KOH) was purchased from Sigma Aldrich, Korea.

2. Synthesis of NiCoLDHs and Au@NiCoLDH-EG

The NiCoLDHs were synthesised in a 3:1 molar ratio (Ni/Co) using 3 mL EG and 4 mL water as solvents. Metal precursors and PEO were dissolved in the EG-water mixture overnight.1.82 mL propylene oxide was added to the above mixture at room temperature and allowed to age at 40 °C for 24 h. The mixture was then hydrothermally treated at 120 °C for 6 h. The obtained precipitate of NiCoLDH was thoroughly washed with water several times and lyophilised to collect the powder. The powdery LDH obtained was denoted as NiCoLDH-EG. For comparison, NiCoLDH-ET was synthesised using the same procedure using ethanol as solvent. The Au nanoparticles were decorated on NiCoLDH-EG by adding 20 mg Au precursor with 0.5 g NiCoLDH-EG in 20 mL EG and 80 mL water, and stirred for 24 h to form Au nanoparticles on NiCoLDH-EG. The sample obtained was washed several times with water and dried in oven at 40 °C, denoted as Au@NiCoLDH-EG.

3. Characterization

The crystalline structure was confirmed using a powder Xray diffractometer (XRD) with a Bruker AXS D2 phaser using Ni-filtered Cu Kα radiation ($\lambda = 1.5406$ Å) at 50 kV at 40 mA. The diffraction patterns were recorded from 2θ from 5-80°, with an interval of 0.02° and a scan speed of 0.5°/min. Crystallite size was calculated using Scherrer's equation (eq.1)

$$\tau = \frac{(0.9\lambda)}{B\cos\theta} \qquad (1)$$

where τ = crystallites size (Å), λ = wavelength of X-ray (1.5405 Å), B = full-width at half-maximum (FWHM), and ϑ = Bragg's angle.

The morphology was analysed by SEM (JSM-7100F, JEOL-USA Inc., Peabody, MA, USA) with an acceleration voltage of 15 kV, after sputtering with platinum for 1 min. The morphology and lattice fringes were analysed using high-resolution TEM (G2 ChemiSTEM Cs Probe, FEI, USA) operated at 200 kV. The zeta potential was obtained from ELS-Z1000 (Otsuka Electronics, Osaka, Japan) after dispersing in DI water at neutral conditions. The electronic state and elemental composition were examined using X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Al Kα source gun type, U.K.). Fourier transform infrared spectra (FT-IR) of the three catalysts were recorded in the attenuated total reflectance (ATR) mode using an FT/IR-4600 spectrometer (JASCO, Tokyo, Japan) over a spectral range of (4000–500) cm^{-1}.Textural parameters obtained from Belsorpmini (BEL Japan, Inc., Osaka, Japan) after pretreatment of the sample at 120 °C for 6 h. The specific surface area, mean pore diameter, and mean pore volume were calculated through the Brunauer–Emmett–Teller (BET) theory. Absorbance was monitored using UV–vis spectra, UV1800 (Shimadzu Corporation).

4. Reduction of 4-nitrophenol

The catalytic activity of three NiCoLDH catalysts was investigated by adding 30 mg $NaBH_4$ in 30 mL aqueous solution of 4-nitrophenol (10^{-4} M). The absorption maxima of nitrophenolate ion at ~400 nm were recorded using UV spectra. After that, 1 mg of the catalyst was added to the above mixture, and UV spectra were recorded in a time-dependent manner in the range of 200-500 nm. The electrocatalytic reduction of 4-NP was carried out using 10 mM 4-NP +1 M KOH in three three-electrode system. The TON was calculated by using the equation TON = moles of substrate converted /moles of active sites, and TOF was calculated using the equation TOF = moles of reacted substrate/ (moles of active sites x reaction time).

5. Electrochemical Characterization

The electrochemical measurements were carried out on an Iviumstat workstation using a three-electrode cell setup with Saturated Calomel Electrode (SCE) as reference, Pt mesh as counter electrode and a carbon cloth as working electrode. A total of 5 mg of the catalyst dispersed in a solution of 0.5 ml ethanol and 20 µL of 5% Nafion, followed by sonicated for 30 mins to prepare catalyst ink. About 50 µL of as prepared catalyst was drop-casted on both sides of 5 mm x 5 mm area of pretreated carbon cloth. The HER linear sweep voltammetry (LSV) measurements were performed at a scan rate of 10 mV s^{-1} in N_2-saturated 1.0 M KOH electrolyte. The potentials were converted to the reversible hydrogen electrode (RHE) scale using Nernst equation: $E_{RHE} = E_{SCE} + 0.241 + (0.059 \times pH)$. Tafel slope (b) values were calculated using the relation: $\eta = a + b \log j$. The electrochemical reduction of nitrophenol was studied using cyclic voltammetry (CV) at a scan rate of 100 mV s^{-1} in an electrolyte containing 0.01 M 4-NP + 1.0 M KOH.

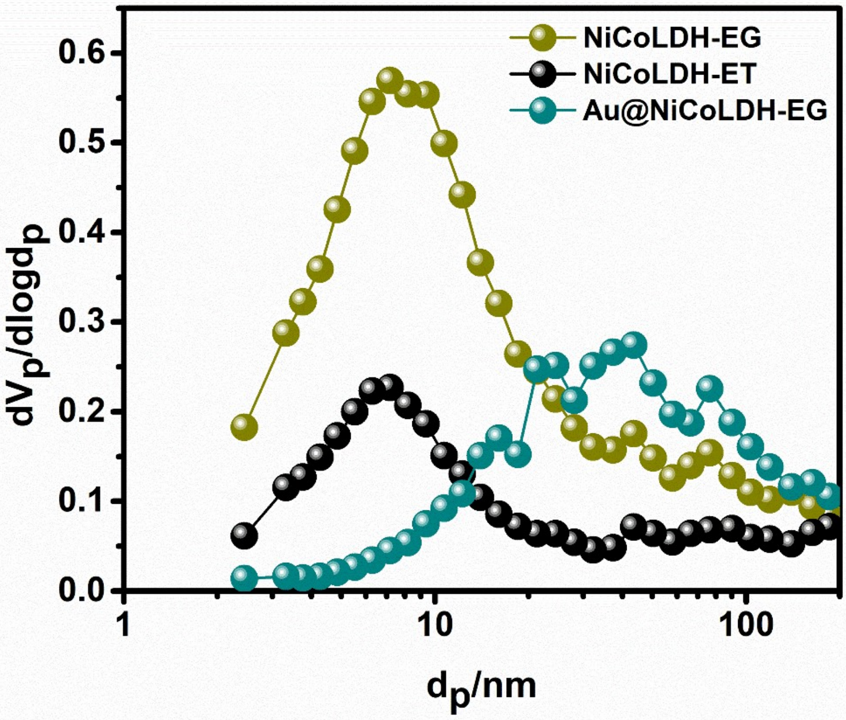
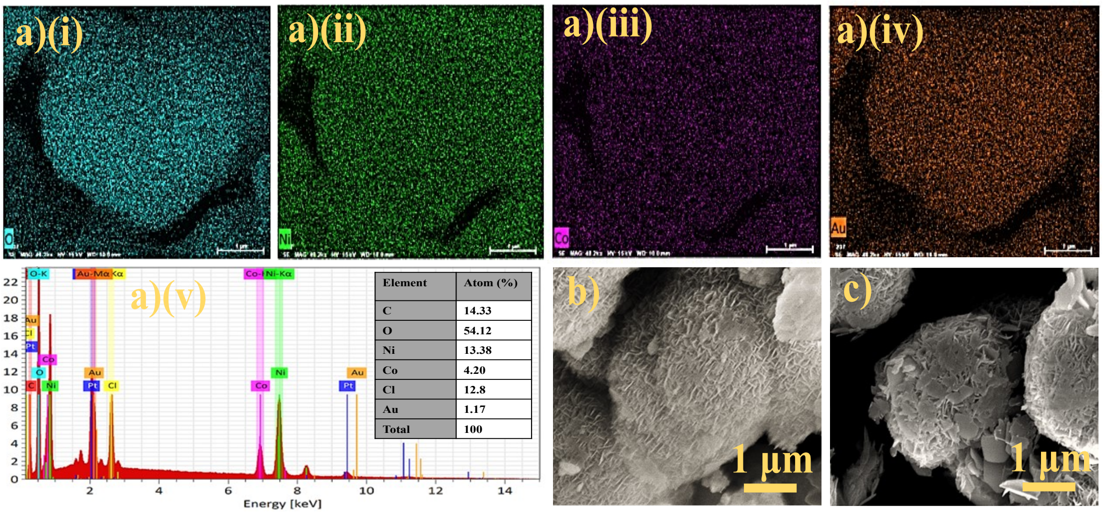


Fig. S1 BJH plots of NiCoLDH-ET, NiCoLDH-EG and Au@NiCoLDH-EG.



Element	Atom (%)
C	14.33
O	54.12
Ni	13.38
Co	4.20
Cl	12.8
Au	1.17
Total	100

Fig. S2 (a(i-iv)) FE-SEM EDS mapping of Au@NiCoLDH-EG, (a(v) EDS spectra, b) FE-SEM of NiCoLDH-EG and c) NiCoLDH-ET.

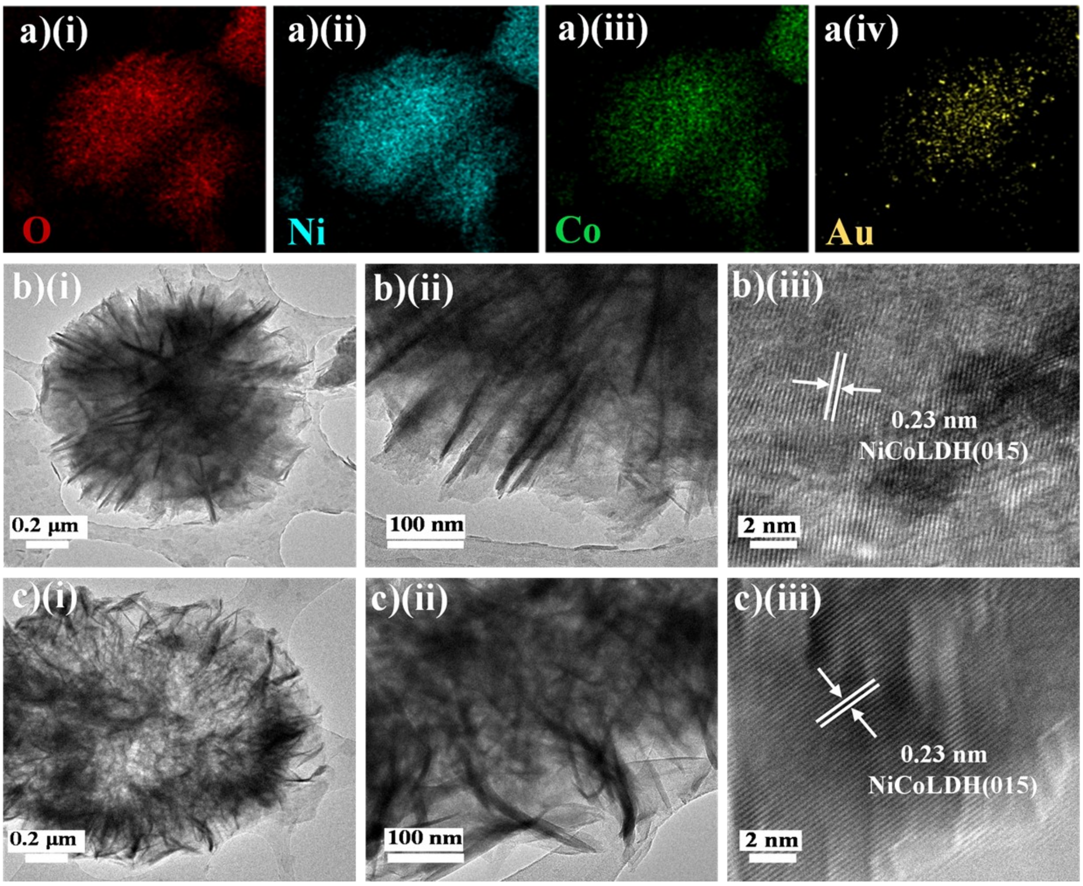


Fig. S3 (a(i- iv) HR-TEM EDS mapping of Au@NiCoLDH-EG, (b)(i-iii) HR-TEM images of NiCoLDH-EG, and (c)(i-iii) NiCoLDH-ET.

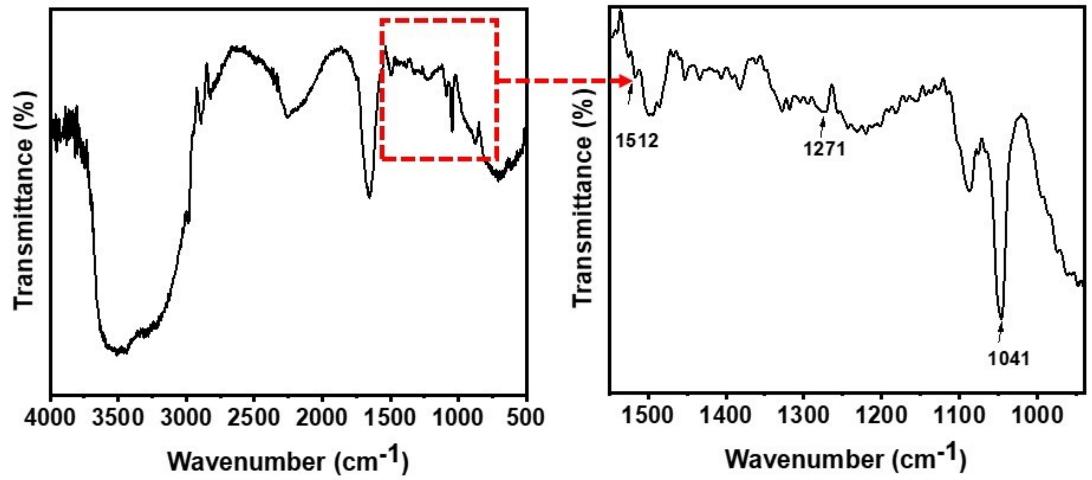


Fig. S4 FT-IR spectra of 4-AP (product after reduction of 4-NP)

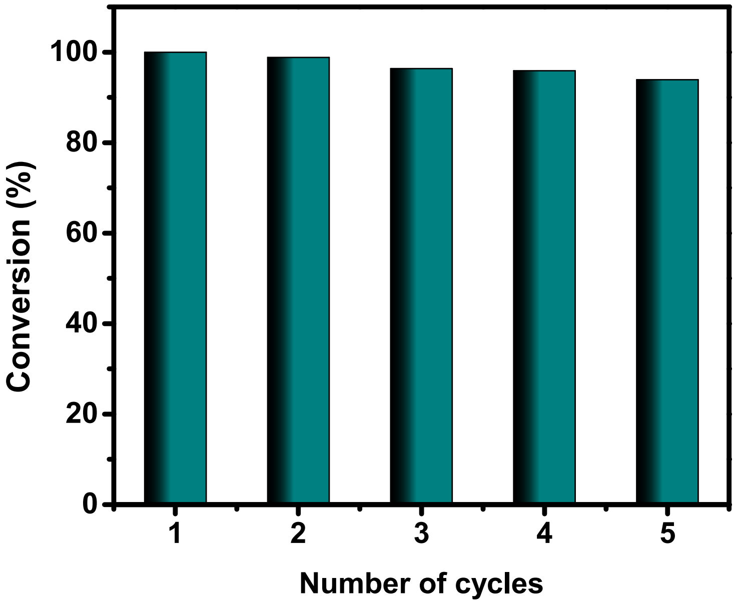


Fig. S5 Recyclability of Au@NiCoLDH-EG catalyst for the reduction of 4–NP.

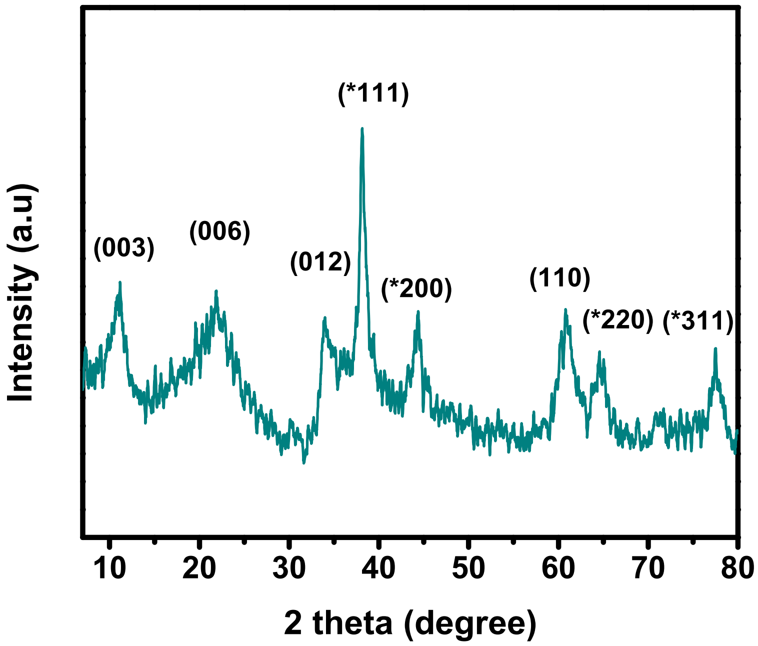


Fig. S6 XRD pattern of Au@NiCoLDH-EG after the catalytic reduction of 4-NP.

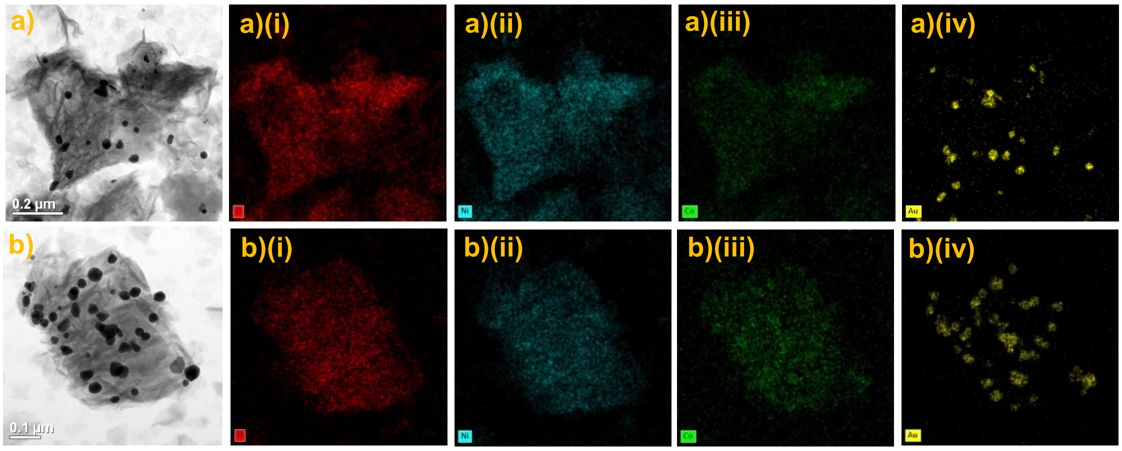


Fig. S7 (a)(i–iv) TEM image of Au@NiCoLDH-EG with EDS mapping after first cycle reduction of 4-NP. (b) (i–iv) TEM image of Au@NiCoLDH-EG with EDS mapping after second cycle reduction of 4-NP.

Catalyst	**Specific surface area (m^2/g)**	**Rate constant (min^{-1})**	**Ref.**
Au-Ag NPs	35.4	2.85×10^{-2}	1
Pt@Co-Al LDH	35	0.96	2
Ni-Co LDH		0.03	3
CuO/Cu_2O	15.4	0.42	4
Ag NPs	60	0.28	5
AuNPs/rGO	230.4	0.1176	6
Au/PDA	14.53	0.51	7
NiMn LDH	56	0.231	8
$Ag/NiOH_2$	-	0.28	9
NiCoLDH-EG	280	0.21	This work
Au@NiCoLDH-EG	60	0.65	This work

Table S1. Comparison table of catalysts used for reduction of 4-NP.

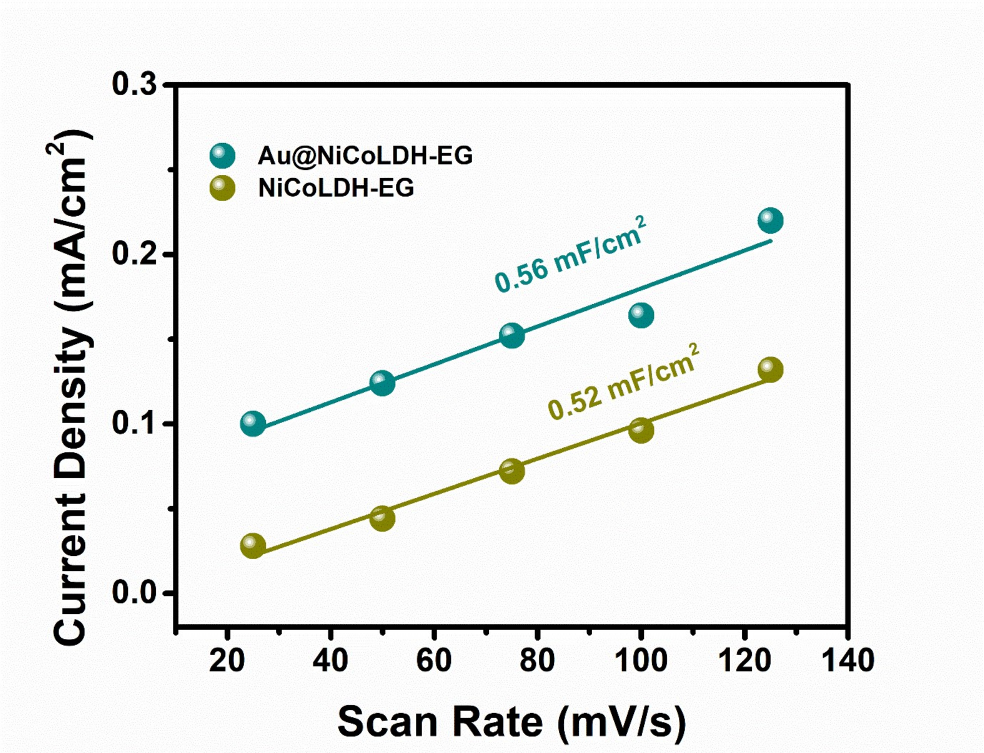


Fig. S8 Linear fit for double-layer capacitance of Au@NiCoLDH-EG and NiCoLDH-EG.

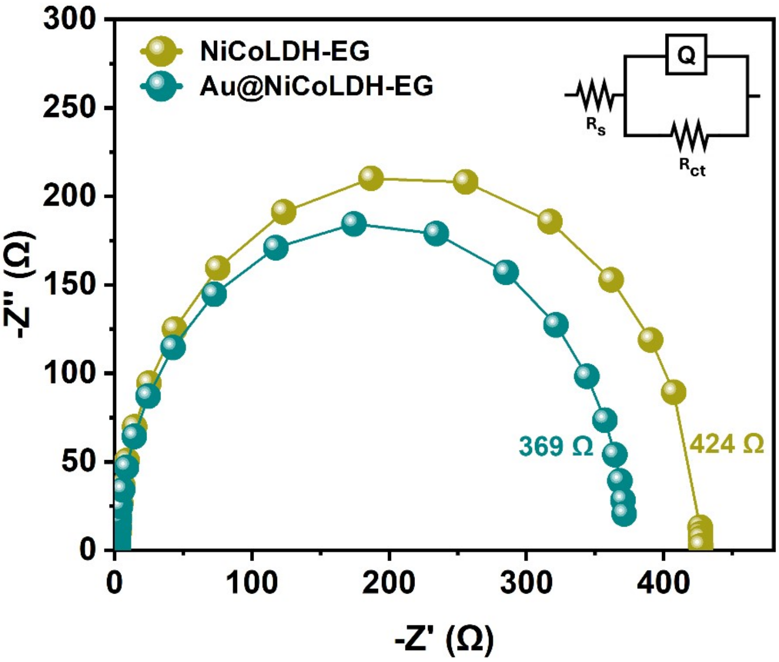


Fig. S9 EIS of Au@NiCoLDH-EG and NiCoLDH-EG.

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