

Supporting Information

Synthesis and Application of Hexagonal Perovskite BaNiO₃ with Quadrivalent Nickel at Atmospheric and Low-Temperature Conditions

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Experimental Section

Materials synthesis: Ba(NO₃)₂ (0.26 g) and Ni(NO₃)₂·6H₂O (0.29 g) were dissolved in distilled water (50 mL). The precursor solution was stirred with nitric acid (3 mL) at 70 °C for 30 min. Citric acid (4 g) and ethylene glycol (4 g) were added to the solution, and the solution was further stirred at 70 °C for 1 h. The different amount of ethylenediamine was slowly dropped into the solution to control pH values. The pH was measured by hand held pH meter (DKK-TOA, HM-30P model). After change of the solution to black-like gel, the temperature rose to ~300 °C. The grey-colour powders were calcined at 900 °C for 1 h with a heating rate of 10 °C min⁻¹.

Materials characterizations: XRD measurements were performed using a D/MAX-2500H (Rigaku) with Cu K α radiation ($\lambda=0.15418$ nm) in the 2 θ -80° window in the 2 θ range. UV/vis spectroscopy (MECASYS, Optizen 2120UV) was used to measure UV spectra. Field emission scanning-electron microscopy (FE-SEM) (JSM-7001F) was used to observe the morphologies of the BaNiO₃ particles. The weight loss and heat flow was detected by TGA/DSC (METTLER TOLEDO, 1100SF model) at heating rate of 10 °C min⁻¹ in O₂/N₂ mixture gas (6:4). Particle size distributions were detected by using Microtrac Nanotrac Wave Nanotechnology Particle Size Analyzer (Microtrac). Energy-dispersive X-ray spectroscopy (EDX) was measured to confirm the compositions of the BaNiO₃ depending on pH values. FT-IR spectra were obtained by using FTS-3500 Excalibur FT-IR Series Spectrometer (BIORAD). Specific surface area was determined for the synthesized BaNiO₃ through Brunauer-Emmet-Teller (BET) analysis. The BET was measured using BELSORP-mini II (BEL Japan Inc.), flowing N₂ gas.

Electrochemical measurements: Electrode was prepared by drop-casting a catalyst ink. The catalyst ink consisted of the BaNiO₃ (2 mg), carbon black (8 mg, VULCAN® XC72R,

surface area: $\sim 220 \text{ m}^2 \text{ g}^{-1}$), and Nafion (80 μL , 5 wt. %, Sigma Aldrich). The catalyst ink was sonicated for 3 min, and then stirred for 30 min. The mixing process was repeated more than 3 times. The catalysts ink (6 μL) was drop-cast onto a glassy carbon electrode (0.196 cm^2 , Pine Instruments), yielding a total loading of 0.295 mg cm^{-2} . OER measurements were performed with a rotating disk electrode setup. Pt and Hg/HgO in saturated 1 M NaOH ($\sim 0.14 \text{ V}$ versus reversible hydrogen electrode (RHE) for Pt) were used as a counter and reference electrodes, respectively. A 0.1 M KOH (99.99 %, Sigma Aldrich) electrolyte was prepared with DI water. The potential calibration of the reference electrode was performed in a high-purity hydrogen-saturated 0.1 M KOH solution. The Pt wire was used as the working electrode. Cyclic voltammetry (CV) was measured at a scan rate of 1 mV s^{-1} and the average of the two potentials where the current crossed zero was obtained to be the thermodynamic potential for the hydrogen electrode reaction. To evaluate ECSA, cyclic voltammograms were obtained in N_2 -saturated 0.1 M KOH at different scan rates from 2.5 to 40 mV s^{-1} . Electrochemical surface areas (ECSAs) were estimated by measuring the electrochemical capacitance of the electrode-electrolyte interface in the double-layer regime of the voltammograms.

$$i_{\text{DL}} = C_{\text{DL}} \times v$$

$$\text{ECSA} = C_{\text{DL}}/C_s$$

where i_{DL} is the capacitive current, C_{DL} is the specific capacitance of the electrode double layer, v is the scan rate, and C_s is the specific capacitance. Anodic currents measured at 0.14 V were plotted as a function of scan rate. All OER activities on the catalysts were measured in O_2 -saturated during OER cycling due to O_2/HO^- equilibrium at 1.23 V versus RHE. The potential was measured by using a potentiostat (Biologic VSP model) at a scan rate of 10 mV s^{-1} and a rotation speed of 1600 rpm. The chronopotentiometric responses were obtained at a rotation speed of

1600 rpm and a constant current density of $10 \text{ mA cm}^{-2}_{\text{disk}}$ in O_2 -saturated 0.1 M KOH for 20 h. All potentials represent iR-corrected potentials.

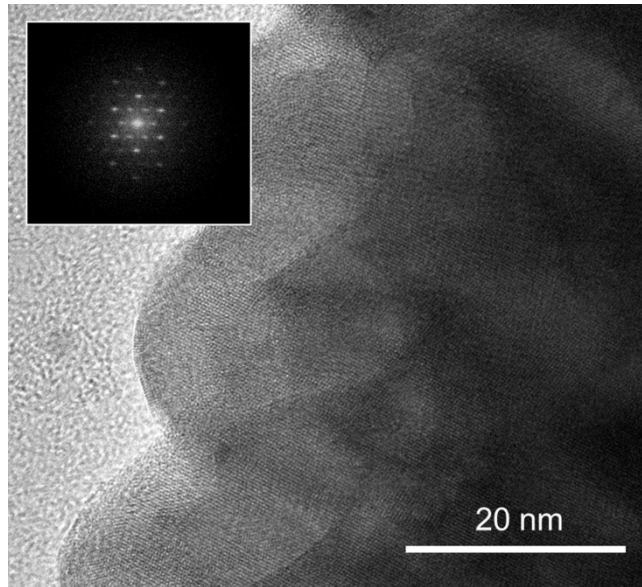


Figure S1. TEM image of the BaNiO₃ synthesized by ED-derived sol-gel methods at pH 10.

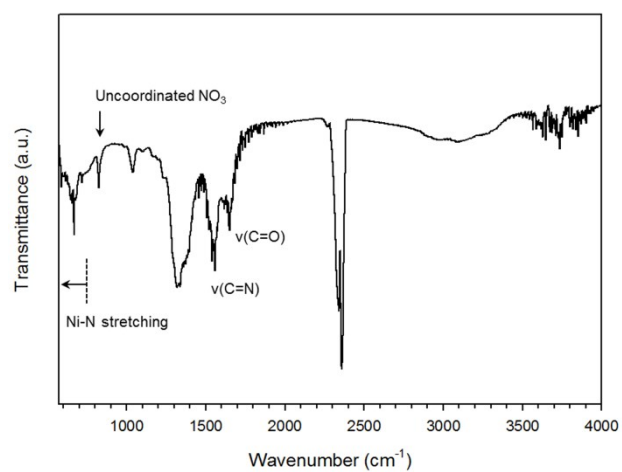


Figure S2. FT-IR spectrum of the precipitated products at pH 10.

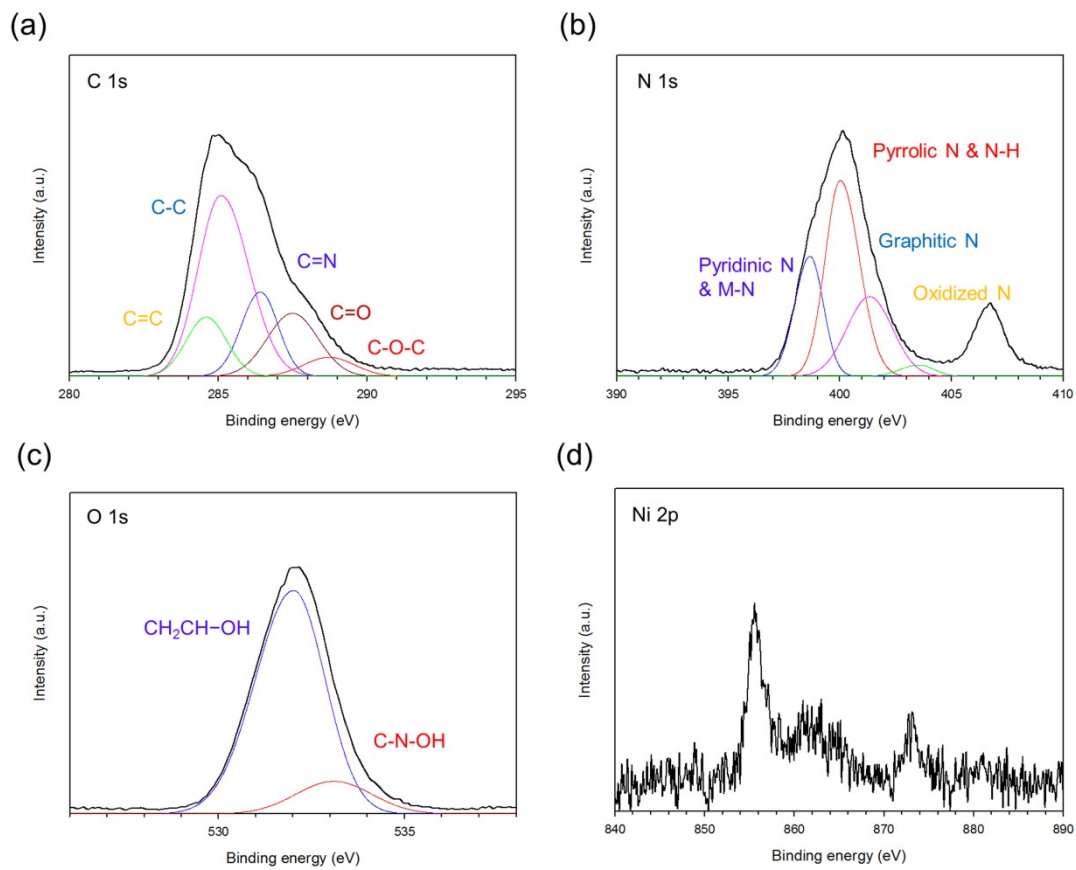


Figure S3. XPS spectra of the precipitated products at pH 10.

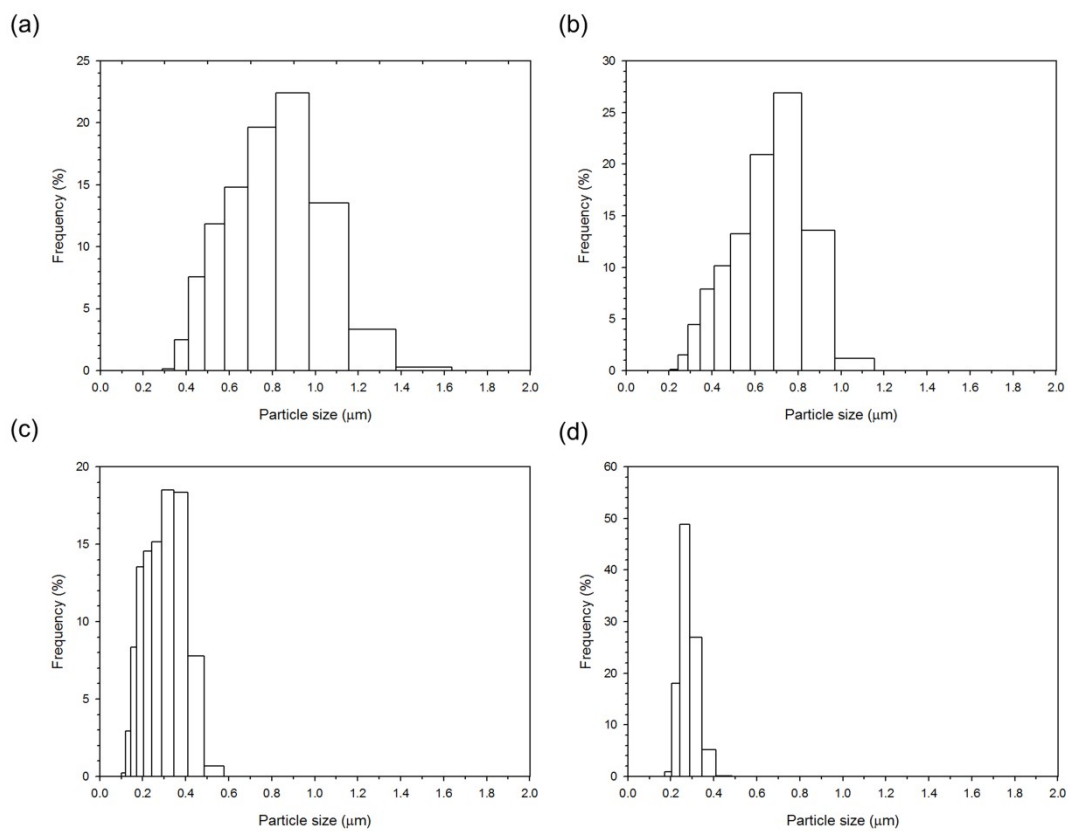


Figure S4. Particle size distribution of the BaNiO_3 synthesized at (a) pH 0.03, (b) pH 3.5, (c) pH 7, and (d) pH 10.

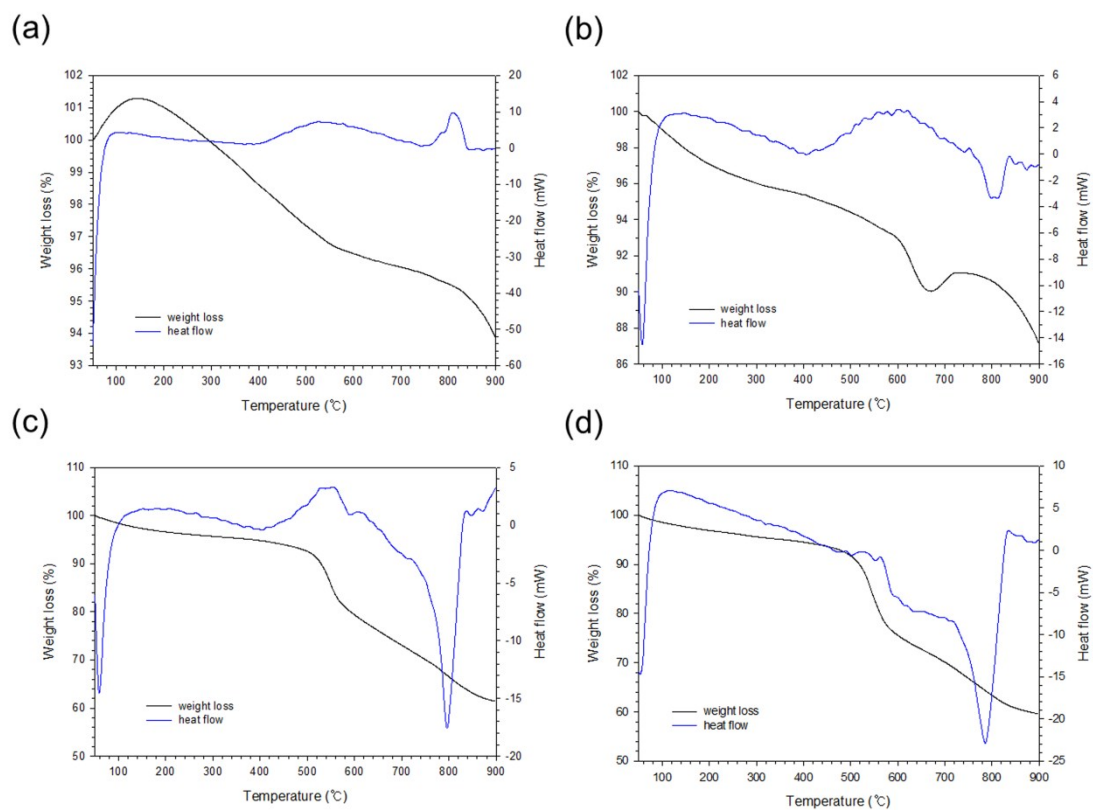


Figure S5. TG/DSC curves of the as-prepared BaNiO₃ depending on pH values. (a) pH 0.03, (b) pH 3.5, (c) pH 7, and (d) pH 10.

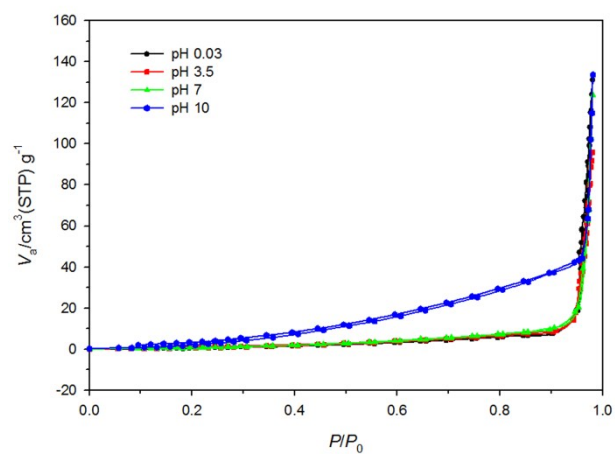


Figure S6. Nitrogen adsorption-desorption isotherm curves of the BaNiO₃ catalysts. The BET surface areas were increased with increase pH values.

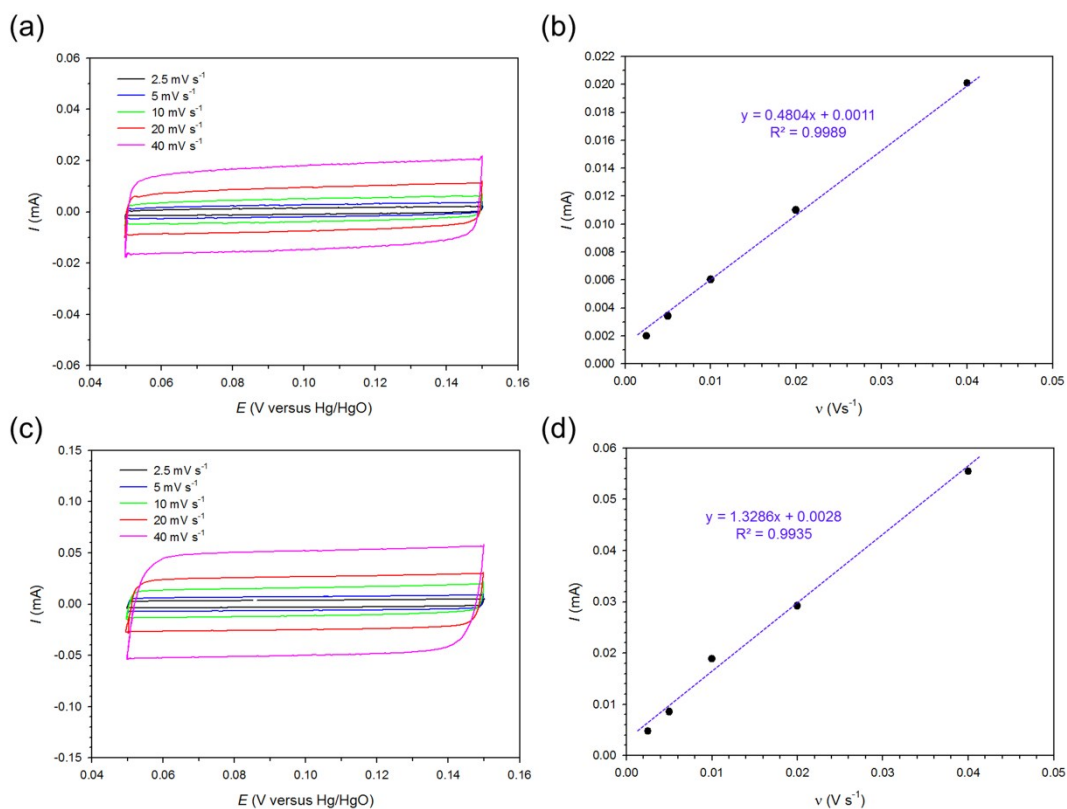


Figure S7. Cyclic voltammetry curves of the BaNiO₃ synthesized by different methods. (a) cyclic voltammograms measured for the BaNiO₃ catalysts synthesized by flux-mediated crystal growth in N₂ saturated 0.1 M KOH at different scan rates from 2.5 to 40 mV s⁻¹. (b) a plot of anodic current measured at 0.14 V as a function of scan rate. (c) cyclic voltammograms measured for the BaNiO₃ catalysts synthesized by ED-derived sol-gel method in N₂ saturated 0.1 M KOH at different scan rates from 2.5 to 40 mV s⁻¹. (d) a plot of anodic current measured at 0.14 V as a function of scan rate.

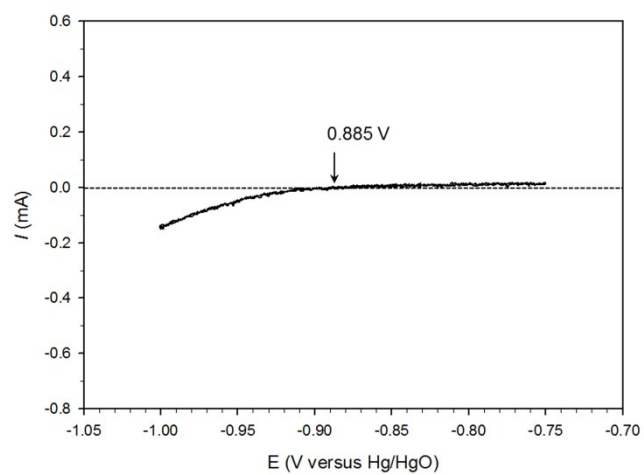


Figure S8. Potential calibration of the Hg/HgO reference electrode in 0.1 M KOH. In 0.1 M KOH solution, $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.885 \text{ V}$.

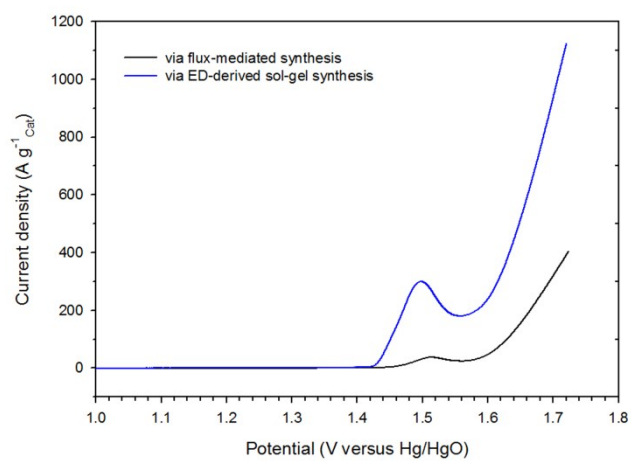


Figure S9. Specific OER activity of the BaNiO₃ synthesized by different methods. The specific activities were normalized to the mass of the catalysts.