

Supporting Information

Self-assembled Ni(cyclam) -BTC network on ITO for oxygen evolution catalyst in alkaline solution

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Experimental

Chemicals: All solutions are prepared with deionized Milli-Q water. Nickel(II) perchlorate hexahydrate, $(\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O})$, reagent Grade), 1,4,8,11-tetraazacyclotetradecane ($\text{C}_{10}\text{H}_{24}\text{N}_4$, 98%), and 1,3,5-benzenetricarboxylic acid ($\text{C}_9\text{H}_6\text{O}_6$, 98%) were purchased from Alfa Aesar, potassium hydroxide (KOH , $\geq 85\%$) was purchased from Duksan chemicals (Ansan, Korea), and sulfuric acid (H_2SO_4 , 98 %) was purchased from Daejung Chemicals (Cheongwon, Korea). All reagents and solvents were used without further purification.

Materials: ITO ($10 \Omega/\text{cm}^{-1}$ conductivity, 100 nm thickness) glasses were purchased from Samsung Corning Co. An ITO glass was washed with three times by acetone (99.5%, Samchun chemicals, Korea) and by $3^\circ \text{H}_2\text{O}$ (Milli-Q, Millipore, $18 \text{ M}\Omega \cdot \text{cm}$) in an ultrasonication bath for 15 min.

Instruments and measurements: CHI-600e potentiostat (CH Instruments, Austin, TX) was used for all electrochemical measurements. Three electrodes were used in an electrochemical cell; a pristine and modified ITO with a self-assembled Ni(cyclam)-BTC with various deposition time as working electrodes, Ag/AgCl (1 M KCl) as a reference electrode, and Pt wire as a counter electrode. Ag/AgCl (1 M KCl) and Pt wire electrodes were purchased and used from CH Instruments. For all electrochemical measurements, 1 M KOH solutions were deaerated with Ar. The UV-Visible spectrum of Ni(cyclam)-BTC-5hrs was measured by a single beam CARY-100 UV-Vis spectrophotometer (Agilent Technologies, CA, USA). X-ray photoelectron spectroscopy (XPS) measurements were taken using a K-alpha spectrometer with an X-ray source of Al $\text{K}\alpha$ and at a pass energy level of 40 eV (ThermoFisher scientific, MA, USA). Inductively coupled plasma-mass spectrometry (ICP-MS) was measured using Thermo X series II (Thermo Electron, Bremen, Germany). Topographical images of a pristine ITO and Ni(cyclam)-BTC-5h were obtained by SPA-300HV atomic force microscopy (AFM, SII Technology, Japan) with non-contact mode.

Supporting figures

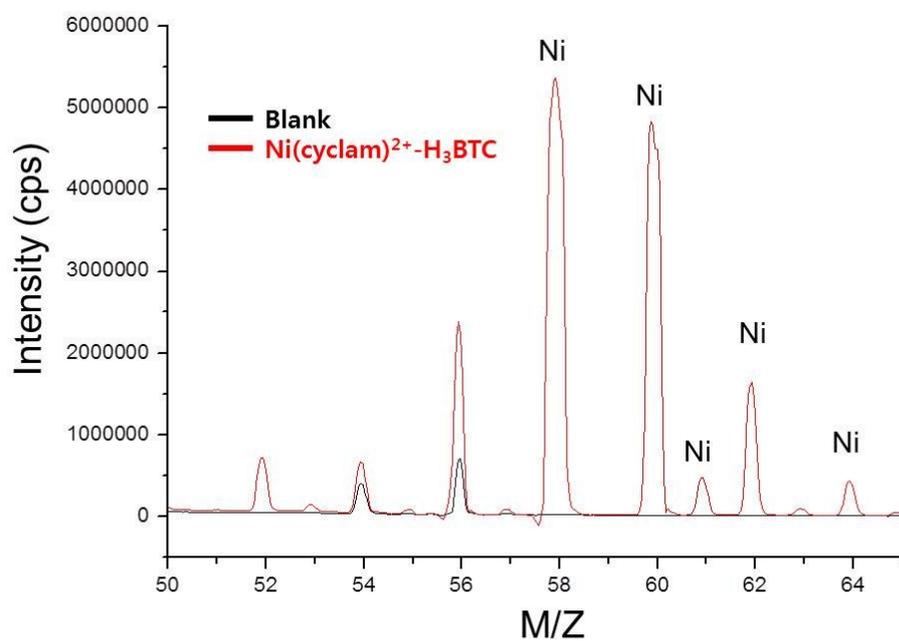


Figure S1. ICP-MS of Ni(cyclam)-BTC-5h on ITO.

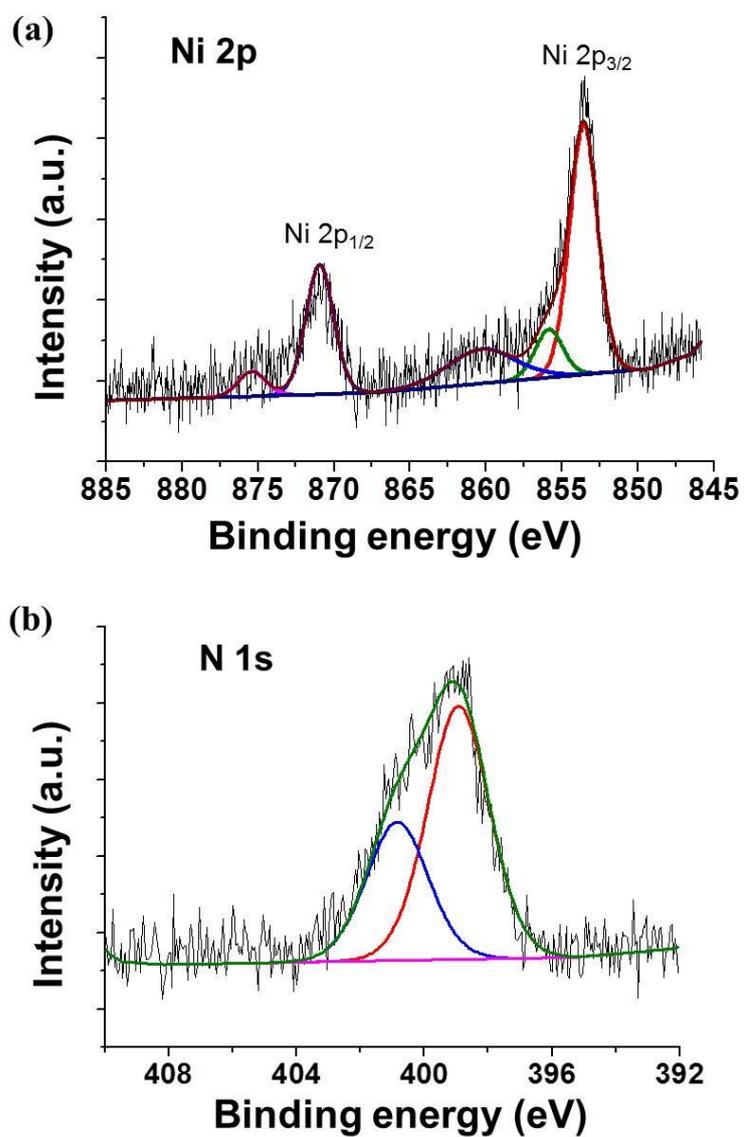


Figure S2. The high-resolution XPS spectra of (a) Ni 2p and (b) N 1s region from Ni(cyclam)-BTC-5h.

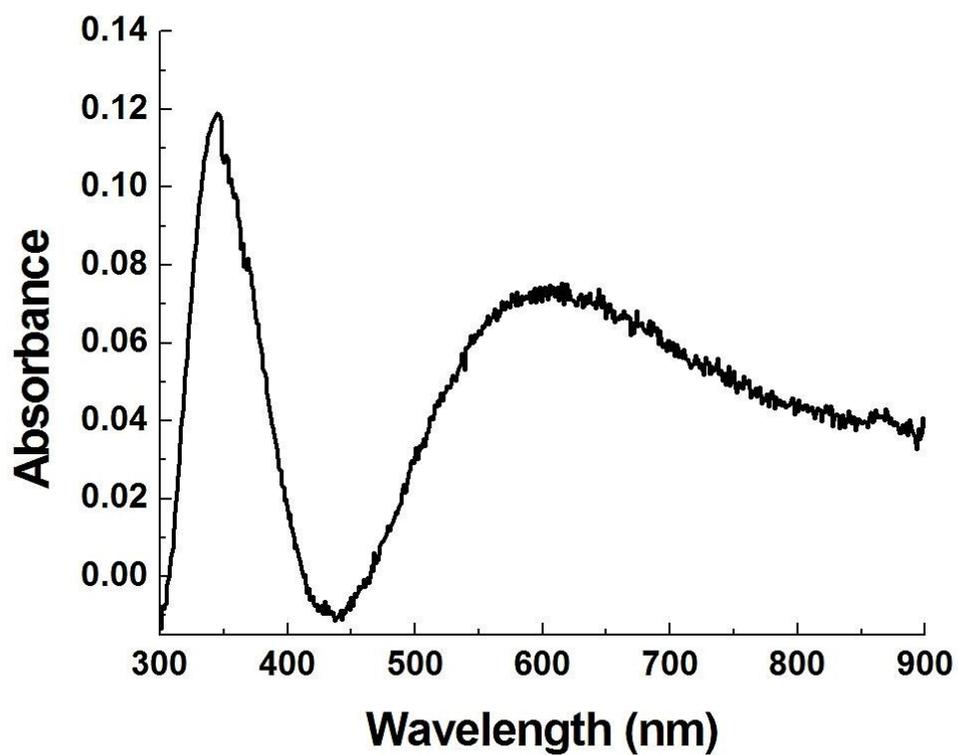


Figure S3. The baseline corrected UV-Vis spectrum measured from Ni(cyclam)-BTC-5h.

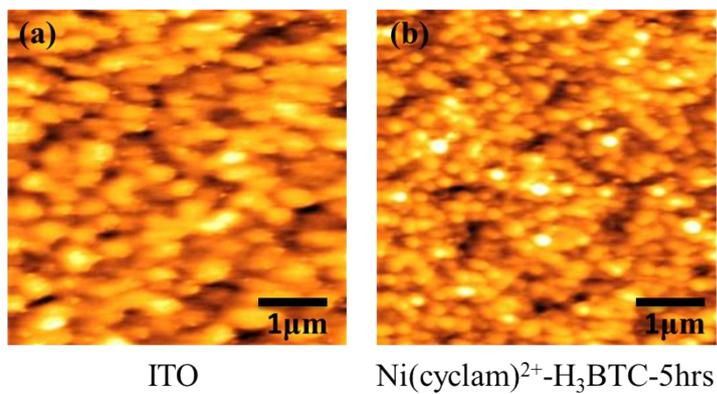


Figure S4. AFM images from (a) a pristine ITO and (b) Ni(cyclam)-BTC-5h.

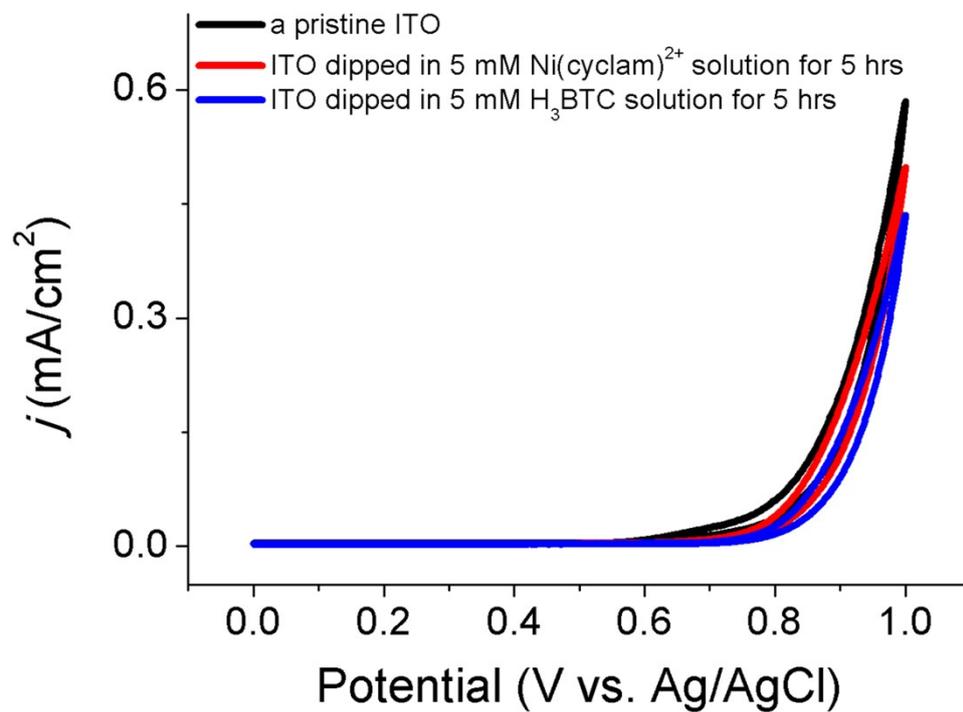


Figure S5. The steady state CVs after 10 successive potential cycles measured in an alkaline solution with 1 M KOH on ITO electrodes which were dipped in 0.5 M H₂SO₄ aqueous solutions containing either 5 mM Ni(cyclam)²⁺ (red) or the same concentration of H₃BTC (blue), respectively.

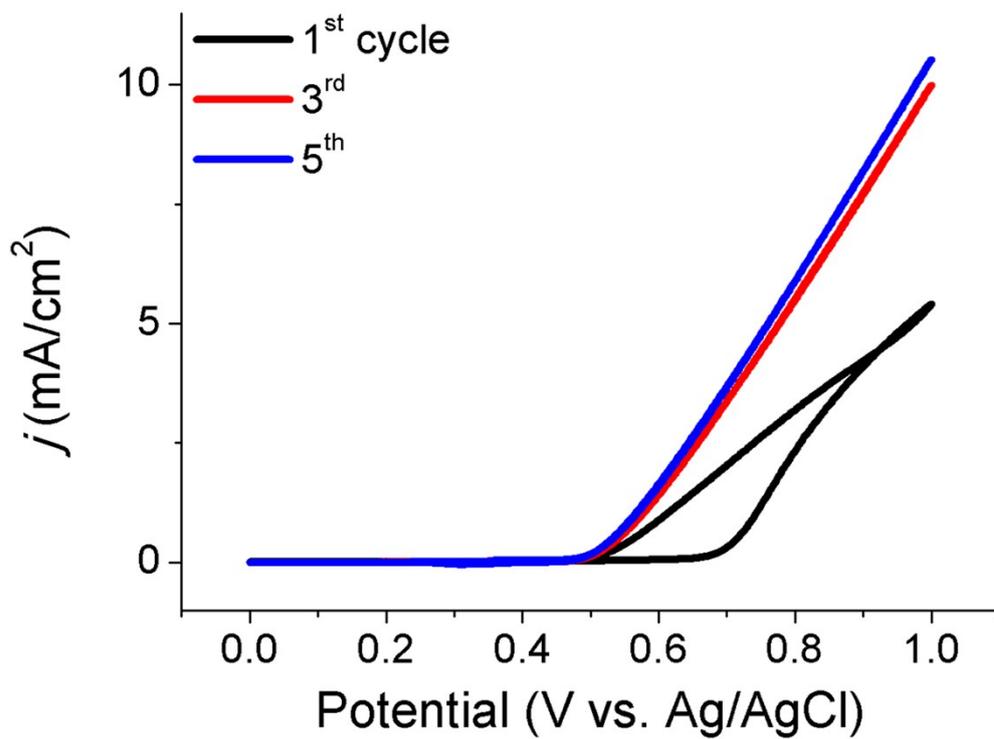


Figure S6. The 1st, 3rd and 5th cycle CVs from Ni(cyclam)-BTC-5h in 1 M KOH solution.

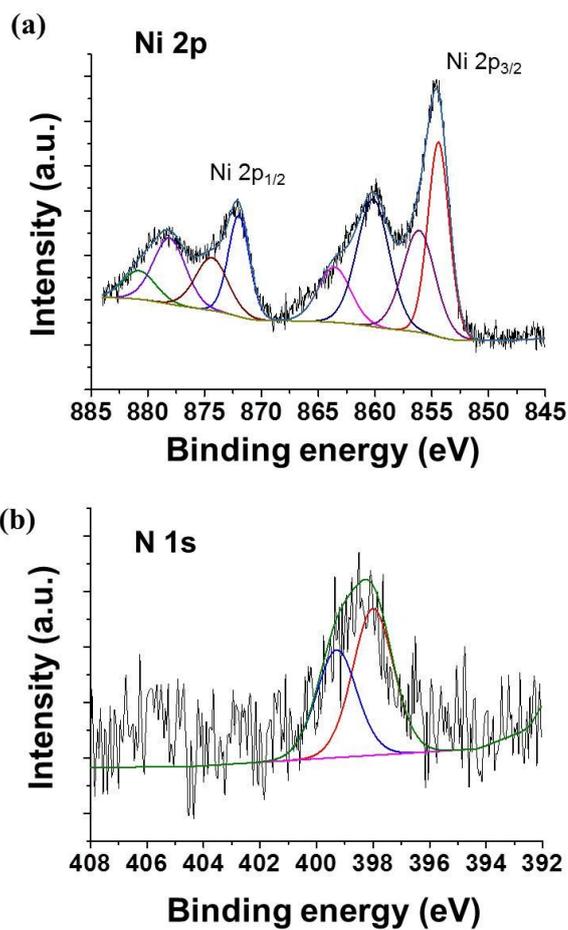


Figure S7. The high-resolution XPS spectra of (a) Ni 2p and (b) N 1s region from Ni(cyclam)-BTC-5h prepared after the successive ten potential cycles from 0 to 1.0 V in 1 M KOH solution.

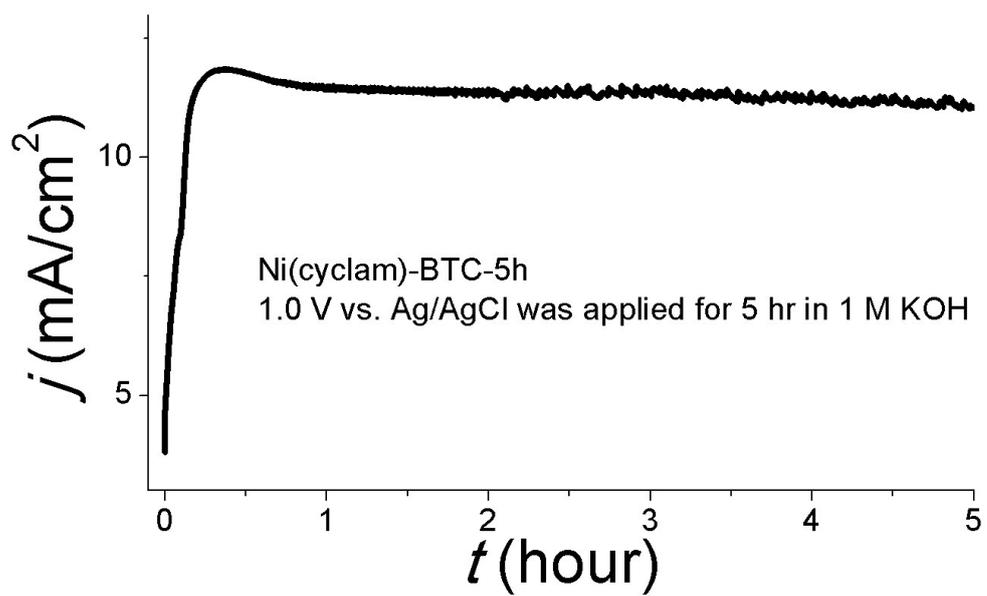


Figure S8. Chronoamperogram measured from Ni(cyclma)-BTC-5h in 1 M KOH aqueous solution at applied constant 1.0 V for 5 h.