ELECTRONIC SUPPLEMENTARY INFORMATION

Modularly Aromatic-Knit Graphitizable Phenolic Network as a Tailored Platform for Electrochemical Applications

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Section S1. Materials

Tannic acid (TA, ACS reagent, Sigma-Aldrich), NiCl₂·6H₂O (≥ 98%, Sigma-Aldrich), CoCl₂·6H₂O

 $(\geq 98\%$, Sigma-Aldrich), FeCl₃·6H₂O ($\geq 98\%$, Sigma-Aldrich), SnCl₄·5H₂O ($\geq 98\%$, Sigma-Aldrich), ammonia solution (28 ~ 30%, Sigma-Aldrich), Si nanoparticles (CN Vision, 30 ~ 50 nm of diameter), 1.3 M LiPF₆ in EC/DMC 30/70 v/v% + 5% FEC (Panaxetec), KOH solution (Sigma-Aldrich), pitch-carbon precursor (Samsung SDI), (+)-glucose (ACS reagent, Sigma-Aldrich), graphite (Sigma-Aldrich), nickel nanoparticles (< 1 µm, Sigma-Aldrich), HCl solution (37%, ACS reagent, Sigma-Aldrich) were used. All chemicals were used as received without further purification.

Section S2. Synthetic methods

Synthesis of modularized TA (m-TA), metal/m-TA, and carbonized metal/m-TA

To synthesis metal-chelated m-TA (metal/m-TA), metal-chelated TA (metal/TA) complexes were firstly prepared by simple mixing of 10 ml of metal chloride solution and 10 ml of TA aqueous solution. On the basis of 0.5 g of TA dissolved in 10 ml of water (29.4 mM), solutions were mixed with varying the mixing molar ratio of 10:1, 3:1, 1:1, 1:3, and 1:10 (TA : hydrated metal chloride), followed by adding the ammonia solution to increase the pH to 10.5. Obtained metal/TA complexes in solution was placed on Teflon-lined autoclave and was subject to hydrothermal reaction at 180°C for 12 h. After hydrothermal reaction, black-brownish solution containing metal/m-TA was washed three times with aqueous solution using ultra-centrifugation separation process. In order to obtain metal/m-TA powders, the collected wet complexes after ultra-centrifugation were fully dried in vacuum at 80 °C for 3 h.

The m-TAs were prepared by following the same procedure of synthesizing metal/m-TA complexes, except for adding metal ions at the initial step. Finally, the synthesized m-TAs were vigorously washed five times with deionized-water, followed by vacuum drying at 80°C for overnight.

Carbonized metal/m-TA were synthesized by thermal carbonization of metal/m-TA using electrical tube furnace (R 50/250/13, Nabertherm) at 900°C for 2 h under argon-purged atmosphere. For the carbonization experiment at 2000°C, graphite furnace (Nasiltech) was used for 2 h under Ar-purged atmosphere.

Synthesis of Si@C/metal as an anode material for lithium-ion battery

First, 0.1 g of Si nanoparticles (CN Vision, $30 \sim 50$ nm of diameter) was dispersed in 10 ml of water with a concentration of 10 mg ml⁻¹. Next, to form metal/TA layers on the Si nanoparticles, the prepared 20 ml of metal chloride aqueous solution (10 mg ml⁻¹ of NiCl₂·6H₂O, FeCl₃·6H₂O and SnCl₄·5H₂O) and 10 ml of TA aqueous solution (20 mg ml⁻¹) were mixed with the solution of Si NPs using vortex mixer, followed by adding ammonia solution to adjust pH of the solution to basic condition. Then, to induce the oxidative coupling to a metal/TA film, the obtained Si@metal/TA was placed in Teflonlined autoclave and heated in oven at 180 °C for 12 h. When hydrothermal reaction is finished, resultant solution was washed three times with aqueous solution and the collected powder was dried for 1 h in vacuum oven at 80 °C. Finally, to obtain Si@C/metal, the dried Si@metal/m-TA powder was thermally carbonized in a furnace at 900 °C for 2 h under argon atmosphere. (ramping rate = 5°C min⁻¹). To the synthesis of Si@m-TA (without metal), the same procedure of synthesizing Si@C/metal was employed, except for adding metal ions at the initial step.

Synthesis of Si@carbon as a control sample for lithium-ion battery

Si/C composites with hard and soft carbon were prepared by ball-milling of Si nanoparticles with glucose or pitch (precursors for hard and soft carbons, respectively) with the weight ratio of 1:2 (Si : carbon precursor) for 30 min. After collecting ball-milled powders, obtained powder was annealed in an electric furnace at 900 °C under argon atmosphere.

Synthesis of carbonized bimetallic metal/m-TA as electrocatalysts for water splitting

All synthetic procedures for synthesizing bimetallic metal/m-TA are following those for the carbonized metal/m-TA except for the solution mixing step. In terms of bimetallic complexes, two different types of metal chloride solutions were utilized for mixing with 1:1.5:1.5 of the molar ratio (TA : metal 1 : metal 2) based on 0.5 g of TA dissolved in 10 ml of water (29.4 mM), wherein the bimetallic species were chosen in Ni, Co, and Fe.

Section S3. Characterizations of synthesized material

Instruments and measurements

To analyze the molecular structure, 700 MHz of ¹H and ¹³C nuclear magnetic resonance equipment (NMR, AVANCE III 700, Bruker Corporation), matrix-assisted laser desorption ionization mass spectrometer (MALDI-TOF, Voyager DE-STR, Applied Biosystems), and Fourier transform infrared spectroscopy (FT-IR, IFS-66/S, Bruker Corporation) were used. To determine the actual amount of carbon or residual carbon content in the composites, thermogravimetric analysis (TGA) (TG/DTA7300, SEICO Inst.) was employed under air or N₂ at a heating rate of 10 °C min⁻¹. Raman spectra were taken using a micro-Raman spectrometer system (ALPHA 300M, WITec). Powder X-ray diffraction (XRD) patterns were obtained (D8 Focus, Bruker AXS) using Cu Ka radiation ($\lambda = 1.5406$ Å) in the 20 range from 10° to 85° with a step size of 0.02°s⁻¹. Mechanical properties of electrodes were measured with nano-indenter (NanoTest Vantage Platform, Micro Materials). Film thicknesses, surface morphologies, and chemical compositions were observed by using high-resolution transmission electron microscopy (HR-TEM, JEM-3010, JEOL) and corresponding energy dispersive X-ray spectroscopy (EDS) for elemental analysis. Surface areas and corresponding porosity profiles were investigated by using Brunauer-Emmet-Teller (BET, ASAP2020 Plus, Micromeritics Instruments) surface area measurement apparatus.

MALDI-TOF measurement

The samples for MALDI-TOF MS analysis were prepared as follows. 1 μ l of sample solution (dissolved in DMSO) and 1 μ l of matrix solution (2,5-Dihydroxybenzoic acid (DHB) dissolved in THF) was mixed. Samples were then air-dried at room temperature for a characterization.

Nano-indentation measurement

Nano-indentation measurements were performed using samples prepared as thin films. All films were deposited on the Cu foil substrate, with a weight ratio of 85 : 15 for carbon sample vs PAA binder, followed by a roll pressing for eliminating the pores in the film. Final film thickness of the electrodes was set to 62 µm. Thin films were characterized with a sharp Berkovich pyramidal diamond tip (Z resolution/travel of 0.02 µm/50 mm). The indentations were performed with a constant loading rate of 0.1 mN/s and a dwell period of 5 s at the maximum applied load. The penetration depth was set to 10%

of the thickness of the films. The indentations were repeated more than 10 times for each film sample.

Section S4. Electrochemical characterizations

Electrode preparation and measurement for lithium ion battery

In the case of Li ion half-cells, electrochemical properties of the as-prepared samples were measured using coin cells (CR2032-type). For the preparation of the working electrodes, Si@C/metal samples were mixed with conductive carbon black (DB 100) and poly(acrylic acid) (PAA; 250 000 Mw, 35 wt% in H₂O, Sigma-Aldrich) in ethanol at a mass ratio of 70 : 15 : 15 to form a homogeneous slurry with a mortar and pestle. The resultant slurry was then uniformly coated on a Cu foil with a doctor blade and dried at 120 °C under vacuum. The loading mass of the active materials was controlled to

be ~1.5 mg cm⁻² with a film thickness of 44 μ m. Electrochemical cells were assembled with the composite as the anode, Li metal as the counter electrode, and a microporous polypropylene (PP) (Celgard 2400, Celgard) film as the separator. A 1.3 M LiPF₆ solution in a 3:7(v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as the electrolyte. In addition, fluoroethylene carbonate (FEC) was added into the electrolyte as an additive. These cells were assembled in a glovebox at a humidity of ≤ 1 ppm and galvanostatically charged and discharged in the potential range between 0.02 and 1.0 V (vs Li/Li⁺) at current densities ranging from 100 to 10 000 mA g⁻¹ using a multichannel potentiostat/galvanostat (WMPG 1000, WonATech). The specific capacity values were estimated based on the total amount of active materials in the electrodes. Cyclic voltammetry was carried out in the potential range between 0.02 and 1.0 V at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS, CHI6143E, CH Instruments, Inc.) measurements were performed at 5 mV ac oscillation amplitude over the frequency range between 100 kHz and 0.01 Hz. Fitting of the impedance data settings and simulations were performed by using the Zview software. For galvanostatic intermittent titration technique (GITT) analyses, the cells were utilized for GITT at 3rd cycle followed by cycled for 2 cycles in advance. Employed voltage window for GITT was 0.01 - 1.5V (vs Li/Li⁺) at 0.1 C of current density, and duration time for each galvanostatic current and rest was 10 min and 1 h, respectively.

Graphite anode preparation for lithium ion battery (operated under standard condition for industrial production)

Graphite-mixed anode was fabricated with a mixture of carboxymethyl cellulose (CMC) and styrenebutadiene rubber (SBR) binder with water as the solvent, and their composition was adjusted to 87 : 9 : 1 : 1.5 : 1.5 of a weight ratio for graphite : Si@C/metal : Super P : CMC : SBR. The loading level was 7.26 mg cm⁻² with 45 μ m of the electrode thickness including 18 μ m of copper foil for all electrodes.

In the case of full cell fabrication, commercialized lithium nickel cobalt aluminum (NCA) cathode (specific capacity = 196 mA/g) was used as the counter electrode instead of Li metal. Electrochemical cells (CR2032-type coin cells) were assembled with the composite as the anode, and a microporous polypropylene (PP) (Celgard 2400, Celgard) film as the separator. Here, the ratio of loading level between anode and cathode was maintained to 1.1 : 1. A 1.3 M LiPF₆ solution in a 3:7 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as the electrolyte. In addition, fluoroethylene carbonate (FEC) was added into the electrolyte as an additive. These cells were assembled in a glovebox at a humidity of \leq 1ppm and galvanostatically charged and discharged in the potential range between 2.5 and 4.2 V at 0.1 C of current density for 1st cycle, 0.2 C of current density

for 2nd cycle followed by 0.5 C current density from 3rd cycle using a multichannel potentiostat/galvanostat (WMPG 1000, WonATech, Korea).

Electrode preparation and measurement for electrocatalytic testing

In the case of electrocatalytic measurements, catalysts were evaluated in 1 mol L⁻¹ KOH solution using a CH instrument (CHI600D). The measurements were conducted by following standard protocols. Hg/HgO saturated with NaOH and Pt wire were respectively used as reference and counter electrodes. Carbon fibre paper (CFP, 1×1 cm²) was used as the working electrode. The catalyst, polyvinylidene fluoride (PVDF, binder), and Ketjenblack (conductive agent) were mixed in a 70 : 20 : 10 weight ratio. N-Methyl-2-pyrrolidone (NMP) was added to the mixture to make a slurry. The prepared slurry was uniformly coated on CFP and dried at 80°C for 12 h in a vacuum oven. The catalysts were deposited on CFP with a loading of ~ 1 mg cm⁻². Then, the OER activities of the as-prepared electrodes were measured in 1 mol L⁻¹KOH solution using the LSV method with 95% *iR* compensation at the scan rate of 5 mV s⁻¹. The durability of the as-prepared electrode was measured using a chronoamperometric (CA) method on the working electrode. The double-layer capacitances (Cdl) of the catalysts were determined in the non-faradaic potential region at various scan rates of 50, 100, 150, 200, and 250 mV s⁻¹. Potentials were expressed relative to the reversible hydrogen electrode (RHE). Electrochemical impedance spectroscopy (EIS, CHI6143E, CH Instruments, Inc.) measurement were performed at 5 mV ac oscillation amplitude over the frequency range between 100 kHz and 0.01 Hz. Fitting of the impedance data settings and simulations were performed by using the Zview software. The electrochemical surface area (ECSA) was calculated using the following formula: ECSA = $C_{\rm dl}/C_{\rm s}$, taking C_s (specific capacitance) equal to 0.040 mF cm⁻², as adopted from a previous study on OER catalysts.

Determination of diffusion coefficient using electrochemical impedance spectroscopy (EIS)

The diffusion coefficient of lithium ions is calculated from EIS analysis by using following equation (Figure S10).¹

$$D_{Li} = R^2 T^2 / 2A^2 n^4 F^4 C^2 \sigma_{\omega}^2$$
 (Equation S1)

where σ_{ω} is the Warburg factor, R is the gas constant, A is the area of the electrode, F is the Faraday constant, C is the concentration of lithium ions in the electrode material and n is the number of electrons involved in the reaction. Here, EIS test was conducted before charge/discharge cycling to exclude the effect of solid electrolyte interphase (SEI) layer formation. The Warburg factor (σ_{ω}) is obtained from the slope of the linear plot between the real part of impedance (Z') and the inverse square root of the frequency (Figure S10e and S10f) at low frequency regions using the following relation,

$$Z' = R_s + R_{ct} + \sigma_\omega \omega^{-1/2}$$
 (Equation S2)

Determination of diffusion coefficient using galvanostatic intermittent titration technique (GITT)

The diffusion coefficient of Li-ions is calculated from voltage profiles using following relation (Figure S11).²

$$D_{Li} = \frac{4}{\pi t} \left(\frac{m_B V_m}{M_B S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 (t \ll L^2 / D_{Li})$$
(Equation S3)

where $m_{\rm B}$, $M_{\rm B}$, $V_{\rm m}$ and S denote the molecular weight, mass amount, molar volume of active material, and the electrode area, respectively. $\Delta E_{\rm S}$ is the steady state voltage change ascribed by the current pulse, and ΔE_t is the voltage change upon applying the constant current. Also, t is the duration time for applying the current, and L is the length of diffusion pathway of Li-ions.

Determination of diffusion coefficient using chronoamperometric (CA) technique

The diffusion coefficient of hydroxyl ions is calculated from CA measurements. For an electroactive material, with a diffusion coefficient of D, the current for the electrochemical reaction at a mass transport limited rate is described by the Cottrell equation (Figure S14).³ $I = nFAD^{1/2}C_b/\pi^{1/2}t^{1/2}$ (Equation S4)

where A is the area of the electrode, F is the Faraday constant, C_b is the bulk concentration of hydroxyl ions in the electrode material and n is the number of electrons involved in the reaction. Under diffusion control, a plot of I versus $t^{-1/2}$ will be linear, from which the slope value of D can be obtained.

Determination of electrochemically active surface area (ECSA)

Cyclic voltammetry (CV) method is used to calculate the ECSA. The double-layer capacitance of the electrodes in a non-Faradaic potential region (0.1 V window about OCP) was identified from CV graph. Then, the following formula is used to calculate ECSA.⁴

$$ECSA = C_{dl} / C_s$$
 (Equation S5)

Taking C_s (specific capacitance) equal to 0.040 mF cm⁻², as adopted from a previous study on OER catalysts.

Section S5. Density functional theory (DFT) calculations

1) Gaussian

Two structures (trimerized C-C coupled intermediate and modularized TA) are relaxed with B3LYP/6-31 + G(d,p) and wB97XD/6-31 + G(d,p) methods, using Gaussian16 program package. ⁵⁻⁸ Calculations for both gas phase and solvated case are done by implementing polarizable continuum model (PCM).9 For B3LYP calculations, correction for van der Waals force is taken into account with D3 correction.¹⁰ Vibrational frequency is calculated for each molecule to obtain the Gibbs reaction energy for formation of 3 ester bonds within the m-TA molecules, calculated at ambient and high temperature/pressure conditions.

2) VASP

For the calculation of electrocatalysts, Vienna Ab-initio Software Package (VASP) is used.¹¹ Generalized gradient approximation (GGA) functional parametrized by Perdew, Burke and Ernzerhof (PBE) is used to treat electronic exchange-correlation interactions, in conjunction with projector augmented wave (PAW) potentials. Energy cutoff value for the plane-wave basis function is set to 400 eV.¹²⁻¹⁴ For all calculations, Monkhorst-Pack k-point mesh of $3 \times 3 \times 1$ is used.¹⁵

Bulk configurations of BCC FeCo, FCT NiCo, and FCT NiFe are adapted from materials project database.¹⁶ Six layered slabs with c(2x2) surfaces facing (110), (111) and (111) are constructed for FeCo, CoNi, and NiFe and relaxed with the bottom three layers fixed to their bulk positions using the python library Pymatgen.¹⁷ To find the most stable position of carbon layer on each surface, a single layer of carbon is then positioned on different surface sites. Work by Swart *et al.* define four different carbon layer adsorption for FCC (111) surfaces, and we have tested similar positioning for the similar FCT lattices.¹⁸ The most stable positioning is chosen for further calculations as following; center of carbon ring positioned on long bridge site for FeCo (ring-Long_Bridge), center of carbon ring at FCC site (ring-FCC) for NiCo (111), and center of carbon ring at HCP site (ring-HCP) for NiFe (111) surface. Note that the final geometry of graphene layer on FeCo and NiCo is much more distorted relative to NiFe due to difference in bulk lattice constants.

The overall HER mechanism is evaluated with a three-state diagram consisting of an initial H⁺ state, an intermediate H* state, and 1/2 H₂ as the final product. The free energy of H* (ΔG_{H*}) is proven to be a key descriptor to characterize the HER activity of the electrocatalyst. A electrocatalyst with a positive value leads to low kinetics of adsorption of hydrogen, while a catalyst with a negative value leads to low kinetics of release of hydrogen molecule. The optimum value of $|\Delta G_{H*}|$ should be zero. The ΔG_{H*} is calculated as¹⁹

$$\Delta G_{H*} = E_{H*} + \Delta E_{ZPE} - T\Delta S_H (Equation S6)$$

where $E_{\text{H*}}$ is the binding energy of adsorbed hydrogen, and ΔE_{ZPE} and ΔS_{H} are the difference in zeropoint energy and entropy between the adsorbed hydrogen and hydrogen in the gas phase, respectively. As the contribution from the vibrational entropy of hydrogen in the adsorbed state is negligibly small, the entropy of H₂ in the gas phase at the standard conditions. Therefore, Eq. S6 can be rewritten as²⁰

$$\Delta G_{H*} = E_{H*} + 0.24 \ eV \ (Equation \ S7)$$

Three adsorbates are chosen, namely O, OH, OOH, which are known to be key intermediates in oxygen evolution reaction (OER). Different adsorption sites are tested on top, bridge, and hollow sites of the carbon layers. Most adsorbates placed on hollow sites result in migration to nearby bridge or top sites, and are neglected from further investigation. The sites fully investigated for all adsorbates are shown in Fig. S24a. The sites are named according to the position of surface carbon relative to the bimetallic catalysts underneath.

Reaction energies are calculated against $H_2O(g)$ and $H_2(g)$, using the computational hydrogen electrode (CHE) model.

$$E_{0H} = E_{surf + *0H} - E_{surf} - E_{H_20} + \frac{1}{2}E_{H_2} (Equation S8)$$
$$E_0 = E_{surf + *0} - E_{surf} - E_{H_20} + E_{H_2} (Equation S9)$$

$$E_{OOH} = E_{surf + *OOH} - E_{surf} - 2E_{H_2O} + \frac{3}{2}E_{H_2}(Equation \,S10)$$

To account for the Gibbs free energy difference between the reaction steps, the following equations as implemented by Rossemeisl *et al.* is used.²¹

 $\Delta G_{1} = E_{OH} + \Delta E_{ZPE} - T\Delta S - eU (Equation S11)$ $\Delta G_{2} = E_{O} - E_{OH} + \Delta E_{ZPE} - T\Delta S - eU (Equation S12)$ $\Delta G_{3} = E_{OOH} - E_{O} + \Delta E_{ZPE} - T\Delta S - eU (Equation S13)$ $\Delta G_{4} = 4.92 - E_{OH} + \Delta E_{ZPE} - T\Delta S - eU (Equation S14)$

where E_{ZPE} is the zero point energy correction, and U is the applied potential. Zero point energies and entropic corrections are taken from reference.²²

From the above equations, overpotential can be obtained by using the following relationship, and results of OER steps according to the potentials are shown in Figure 5h and Table S7.

$$\eta^{OER} = \frac{\left|\max\left\{\Delta G_{1}, \Delta G_{2}, \Delta G_{3}, \Delta G_{4}\right\}\right|}{e} - 1.23 V (Equation S15)$$

Section S6. Figures and Tables



Figure S1. Chemical structure of tannic acid (TA).



Figure S2. Proposed possible coupling pathway starting from C-C coupled intermediate to the modularized TA (m-TA) molecules. Total Gibbs free energy of formation is calculated by adding up each Gibbs energy of the step 1, 2, and 3 (Table 1).



Figure S3. Indexing of ¹³C NMR spectra of C-C coupled intermediate (orange) and modularized TA (m-TA, green).



Figure S4. Theoretically estimated ¹³C NMR and ¹H NMR data using ChemDraw. Predictions for (ab) hexahydroxydiphenic acid (HHDP), (c-d) ellagic acid (EA), (e-f) m-TA without carboxyl groups, and (g-h) m-TA with carboxyl groups.



Figure S5. Proposed fragmentation pathways interpreted from MALDI-TOF characterization data.



Figure S6. Thermogravimetric analysis (TGA) curves of metal/m-TA (Ni/m-TA) with various complexation ratios under (a) N_2 and (b) air atmosphere.

As shown, according to the variation of initial molar complexation ratio between TA and metal ions over a wide range, the residual metal content can be controlled from 10 to 70 wt%. As expected, with lowering the TA complexation ratio in forming metal/m-TA, a greater amount of metal content could be attained after the pyrolysis.



Figure S7. BET surface area characteristics of the carbon samples derived from various precursors, including (a) graphite, (b) carbonized pitch@900°C, (c) carbonized TA@900°C, (d) carbonized m-TA@900°C, and (e-h) corresponding pore size distributions.



Figure S8. Comparative Raman spectra of the pyrolyzed carbons from various precursors, including (a) carbonized TA @ 2000°C, (b) carbonized m-TA @ 2000°C, (c) graphite (d) carbonized pitch @ 900°C, (e) carbonized glucose @ 900°C, (f) carbonized metal/TA @ 900°C, and (g) carbonized metal/m-TA @ 900°C.

All Raman spectra are fitted and the ratios of corresponding I_D / I_G have been carefully estimated by following method reported by Kouketsu *et al.* (*Island Arc*, **23**, 33-50, 2014 & *Carbon*, **85**, 147-158, 2015), wherein not only main D peak (D1 ~ 1350 cm⁻¹) and G peak (~ 1580 cm⁻¹) but also other D peaks (D2, D3 and D4) stem from amorphous nature of the carbon structure were collectively considered. In particular, the D1 and D2 bands are regarded as the vibration mode of micro-crystallite domains of graphite and the disordered graphitic lattice, respectively. The D3 and D4 bands are ascribed to the existence of amorphous region. Especially, the D3 band is relavant to the presence of substantial amounts of amorphous carbon, whereas the D4 band is associated with C-H terminated functional groups (adsorbed molecules or molecular fragments). As shown in Figure S8, each peak is separately marked with the assigned colour.



Figure S9. Load-displacement curves of (a) graphite, (b) soft carbon, (c) hard carbon, and (d-h) carbonized metal/m-TA (Ni/m-TA) with different complexation ratios. The reduced Young's modulus (E_r) of films were evaluated from the load-displacement curves using the Oliver and Pharr method.²³ The effective Young's modulus was then calculated using following equation:

$$\frac{1}{E_r} = \frac{1 - v_s^2}{E} + \frac{1 - v_i^2}{E_i}$$

where *E* is Young's modulus of the sample, E_i is Young's modulus of the diamond indenter tip ($E_i = 1140$ GPa), v_s and v_i are the Poisson's ratio of the sample (v_s) and the diamond indenter tip ($v_i = 0.07$), respectively. Results are summarized in Table S2.



Figure S10. Comparison of Nyquist plots (fitting results are summarized in Table S3) measured in 1.3 M LiPF₆ electrolyte for different carbon (hybrid) materials. (a) Nyquist plots for carbonized metal/m-TA (Ni/m-TA) with different complexation ratios (C/Ni, 1:10 to 10:1) and corresponding (b) Warburg impedance and Li diffusion coefficient. (c) Nyquist plots for carbonized Ni/m-TA (3:1) compared to different types of carbon/metal hybrids including Ni nanoparticles mixed with graphite and pitch carbon having the same weight composition ratio and corresponding (d) Warburg impedance and Li diffusion coefficient. Inset shows equivalent circuit model of electrochemical system (R_s : solution resistance, R_{sf} and CPE_{sf}: resistance and capacitance). (e-f) Corresponding Randles plots between real part of impedance vs. the inverse square root of frequency derived from electrochemical impedance spectroscopy (EIS) analyses.



Figure S11. Results of galvanostatic intermittent titration technique (GITT): charge/discharge GITT profiles obtained from 2nd cycle, potential profile with respect to the time, and GITT curve at a rate of 0.1 C. (a-c) graphite, (d-f) soft carbon (pitch), (g-i) hard carbon (glucose), and (j-l) carbonized Ni/m-TA (3:1).

As shown, the carbonized metal/m-TA have exhibited the lowest overpotential value during the resting time between pulsed currents while retaining a similar slope value in voltage changes to that of the hard carbon despite its higher crystallinity, thereby supporting the superior ionic diffusivity of the carbonized metal/m-TA.



Figure S12. Nyquist plots (fitting results are summarized in Table S4) measured in 1.0 M KOH electrolyte for carbonized metal/m-TA (Ni/m-TA) with different complexation ratios (C/Ni, 1:10 to 10:1). Inset shows the equivalent circuit model of electrochemical system (R_s : solution resistance, R_{sf} and CPE_{sf}: resistance and capacitance of the interfacial layer, R_{ct} and CPE_{ct}: charge-transfer resistance and double-layer capacitance).



Figure S13. Cyclic voltammograms (CV) measured at different scan rates of (a-h) carbonized metal/m-TA (C/Ni) with different complexation ratios, different types of carbon/metal hybrids including Ni nanoparticles mixed with (f) graphite, (g) pitch carbon and (h) Vulcan-carbon (XC-72). Current measured in the non-faradaic region was due to capacitive charging. (i) Corresponding double-layer capacitance measurements (plots of scan rate vs. current density) in 1.0 M KOH used to determine ECSA for various catalysts. (j) Summarized values of ECSA for a comparison.



Figure S14. Comparison of chronoamperograms measured in 1.0 M KOH for (a) carbonized Ni/m-TA (3:1) with different types of carbon/metal hybrids including Ni nanoparticles mixed with graphite, pitch carbon and Vulcan-carbon (XC-72) with the same weight composition ratio and corresponding (b) Cottrell plot for the data from chronoamperograms.



Figure S15. (a) Schematic illustration of preparing the Si@carbon/metal anodes. (b-d) Corresponding transmission electron microscopic (TEM) images for each step.



Figure S16. Energy-dispersive X-ray spectroscopy (EDS) elemental mapping of (a) Si@C/Sn and (b) Si@C/Fe particles.



Figure S17. Thermogravimetric analysis (TGA) curves of Si@C/Ni, Si@C/Fe, and Si@C/Sn particle under air atmosphere.



Figure S18. (a-b) Cyclic voltammetry (CV) and (c-d) galvanostatic charge-discharge profiles of Si@C/Fe and Si@C/Sn at a current density of 100 mA/g.



Figure S19. Cycling performances and Coulombic efficiencies of m-TA coated Si NPs (Si @ m-TA) anode (measured at 0.1 C of current density for 1st cycle and 0.5 C of current density for further cycles.)



Figure S20. OER electrocatalytic performances of carbonized metal/m-TA (3:1) compared to (a) different types of carbon/metal hybrids including Ni nanoparticles mixed with graphite, pitch carbon, and Vulcan-carbon (XC-72) with the same weight composition ratio. (b) Comparison with different complexation ratios (tannic acid : Ni) in forming the carbonized metal/m-TA (Ni/C hybrid).



Figure S21. X-ray diffraction (XRD) patterns of FeCo/C, NiFe/C, and CoNi/C alloy hybrids.



Figure S22. Energy-dispersive X-ray spectroscopy (EDS) elemental mapping of the (a) FeCo/C and (b) CoNi/C alloy hybrids.



Figure S23. Size distribution of metal nanoparticles and carbon shell thickness variation of the carbonized metal/m-TA according to the initial complexation ratio (TA : metal).



Figure S24. Theoretical interpretation of OER over alloy/carbon hybrids. (a) Definition of possible adsorption sites for each alloy hybrid, a single graphitic carbon layer placed on (i) FeCo BCC (110) plane, (ii) CoNi FCT (111) plane, and (iii) NiFe FCT (111) plane. Subscript "b" means a bridge site between C atoms and "t" means a single C atom site. (b) Schematic illustration of possible adsorption of intermediates (*OH, *O and *OOH) at each reaction step. It is hypothesized that adsorption sites are freely moved to other sites during OER to minimize overpotentials.



Figure S25. Gibbs free energy (ΔG) profiles for the OER on various catalysts. (a) Ideal case, (b) FeCo/C, and (c) CoNi/C at zero potential (U = 0, black color), equilibrium potential for oxygen evolution (U = 1.23 V, pink color), and minimum potential (cyan color) where all steps run downhill. Schematic illustrations show the adsorption of each intermediate, where a single graphitic carbon layer placed on alloy crystal plane. Blue, white, light brown, and dark brown colours represent Co, Ni, Fe, and C atoms, respectively.



Figure S26. Tafel plots of FeCo/C, NiFe/C, and CoNi/C alloy hybrids for OER reaction.



Figure S27. Electrocatalytic HER performances of different bimetallic alloy/C electrocatalysts for FeCo, CoNi, and NiFe. (a) LSV profiles (iR-compensated) in 1.0 M KOH at a scan rate of 5 mV s⁻¹, (b) and the corresponding Tafel plot, (c) comparative HER performances for various catalysts in terms of required overpotentials at a current density of 10 mA cm⁻² and the corresponding Tafel slopes. (d) Theoretical DFT calculations for estimating HER activity trends with respect to the types of bimetallic alloy catalysts.



Figure S28. (a) Chronoamperometric (CA) stability responses (i –t) of FeNi/C for OER and FeCo/C for HER at an overpotential ($\eta@10 \text{ mA/cm}^2$) in 1.0 M KOH electrolyte. (b) LSV profiles (*iR*-compensated) of NiFe/C before and after 10000 cycles of CV (500mV s⁻¹) in OER region in 1.0 M KOH at a scan rate of 5 mV s⁻¹.



Figure S29. Two-electrode polarization curves (*iR*-compensated) for overall water splitting in 1.0 M KOH, scanned from 1.0 to 2.0 V at the scan rate of 5 mV s⁻¹.



Figure S30. X-ray diffraction (XRD) patterns of Si@C/Ni, Si@C/Fe, and Si@C/Sn particles.



Figure S31. Comparison of Nyquist plots (fitting results are summarized in Table S5) measured in 1.3 M LiPF₆ electrolyte for different Si@carbon (hybrid) anodes. (a) Nyquist plots compared between various SiO_x anodes including carbon layers from carbonized metal/m-TA with different weight composition ratio (C/Ni, 1:1 and 1:0.5) and soft carbon (pitch). (b) Nyquist plots compared between various Si anodes including carbon layers from carbonized metal/m-TA (C/Ni, 1:1), reduced graphene oxide (rGO), soft carbon (pitch) and hard carbon (glucose). (c) Nyquist plots compared between various Si anodes including C/metal layers from different types of carbonized metal/m-TA (Ni, Fe, and Sn) and bare Si.

In addition to cyclic tests using half cells, EIS analyses were carried out for the samples of Si@C/metal and Si/C hybrids with varying the type of carbons (Figure S19 and Table S5). As compared to Si/C hybrids with rGO, soft, or hard carbons (39.7, 33.0, and 51.8 Ω , respectively), Si@C/metal complexes exhibited substantially reduced surface resistance by a factor of around three. (17.4, 22.8, and 18.2 Ω for Si@C/Ni, Si@C/Fe and Si@C/Sn, respectively.) Furthermore, the carbonized metal/m-TA were successively coated on ceramic type of active materials, SiO_x, which also be utilized for measuring EIS spectra with various metal contents. As above-mentioned EIS trend, the electrical conductivity increased with increasing the amount of metal contents in carbonized metal/m-TA shell, which was superior to those of soft carbon-coated SiO_x (21.69, 27.84 and 31.61 Ω for 1:1 and 1:0.5 samples of SiO_x@C/Ni and SiO_x@soft carbon sample, respectively). Based on these EIS results related to cell operations, it was strongly expected that the carbonized metal/m-TA shell would act as an excellent supporting platform for securing active core materials thanks to the superior transportation ability of ionic species and electrons.



Figure S32. (a) Comparison of reduced Young's moduli of Si@C/Ni, Si@Soft carbon, and Si@Hard carbon. Load-displacement curves of (b) Si@C/Ni, (c) Si@Soft carbon and (d) Si@Hard carbon films. The reduced Young's modulus (E_r) of films were evaluated from the load-displacement curves using the Oliver and Pharr method [10]. The effective Young's modulus was then calculated using following equation:

$$\frac{1}{E_r} = \frac{1 - v_s^2}{E} + \frac{1 - v_i^2}{E_i}$$

where *E* is Young's modulus of the sample, E_i is Young's modulus of the diamond indenter tip ($E_i = 1140$ GPa), v_s and v_i are the Poisson's ratio of the sample (v_s) and the diamond indenter tip ($v_i = 0.07$), respectively. As a result, the effective Young's modulus is 4.90 GPa (Si@C/Ni), 0.93 GPa (Si@soft carbon), 0.22 GPa (Si@hard carbon) with a standard deviation of 1.65, 0.09, and 0.16, respectively (results are summarized in Table S6).

Supplementary Tables

Table S1: A comparison of D/G ratio of carbon/metal hybrids with recently reported materials.

Materials	Annealing temperature (°C)	D/G ratio	Reference
Carbonized Ni/m-TA (3:1)	900	0.657	This work
FeNiP/C from BMM-10 MOFs	900	0.97	Nano Energy, 2019 , 62, 745
Ni-doped FeP/C	800	0.75	Sci. Adv., 2019 , 5, eaav6009
Carbonized Ni-MOF (Ni-C)	700	0.63	Nat. Commun., 2018, 7, 10667
NiCo ₂ O ₄ @graphene from ZIF-67@Ni-BTC	500	1.02	J. Mater. Chem. A, 2018 , 6, 19604
Ni@N-CNCs	800	0.96	Adv. Mater., 2017, 29, 1605083
Ni@NC with CNT	700	1.00	Energy Environ. Sci., 2016 , 9, 123
Ni/CoNC from Ni/Co-MOFs	800	0.71	Adv. Sci., 2016 , 3, 1500265

Materials	(Calculated) Poisson's ratio	Reduced Young's modulus, E (GPa)	Standard deviation
Graphite	0.2	1.11	0.54
Soft carbon (Pitch @ 900° C)	0.2	3.14	1.02
Hard carbon (Glucose @ 900 ℃)	0.2	2.88	0.65
Carbonized Ni/m-TA (10:1)	0.24301	6.09	2.07
Carbonized Ni/m-TA (3:1)	0.22068	3.99	1.46
Carbonized Ni/m-TA (1:1)	0.20770	3.27	1.20
Carbonized Ni/m-TA (3:1)	0.20649	2.88	0.93
Carbonized Ni/m-TA (1:10)	0.20264	1.75	0.28

Table S2: A summary of mechanical properties of different carbon/metal hybrids materials obtained by nanoindentation tests in Figure S9.

Materials	$R_s(\Omega)$	$R_{sf}(\Omega)$	$R_{ct}(\Omega)$	$\sigma_{\omega} \left(\Omega / s^{1/2} \right)$	D _{Li} (cm²/s) (Warburg)	D _{Li+} (cm ² /s) (GITT) ^{b)}	D _{Li+} (cm ² /s) (GITT) ^{c)}
Graphite	1.98	41.88	229.52	33.93	7.22 × 10 ⁻¹¹	1.97×10^{-10}	1.55×10^{-12}
Soft carbon (Pitch @ 900°C)	1.91	51.96	83.53	13.93	4.29×10^{-10}	3.16×10^{-10}	4.33×10^{-10}
Hard carbon (Glucose @ 900° C)	2.42	53.10	71.09	11.85	5.92×10^{-10}	2.59×10^{-10}	6.75×10^{-10}
Carbonized Ni/m-TA (10:1)	1.55	29.05	44.90	10.25	7.92×10^{-10}	-	-
Carbonized Ni/m-TA (3:1) ^{a)}	2.40	43.55	29.16	4.33	4.44×10^{-9}	1.28×10^{-9}	6.77 × 10 ⁻¹⁰
Carbonized Ni/m-TA (1:1)	1.63	51.64	41.39	5.65	2.61×10^{-9}	-	-
Carbonized Ni/m-TA (1:3)	1.61	53.34	44.84	6.30	2.09×10^{-9}	-	-
Carbonized Ni/m-TA (1:10)	2.79	132.33	61.02	7.98	1.31×10^{-9}	-	-
Graphite + Ni NPs ^{a)}	3.36	46.68	449.33	252.18	1.31×10^{-12}	-	-
Pitch + Ni NPs ^{a)}	1.92	43.23	67.61	10.45	7.62×10^{-10}	-	_

Table S3: A summary of impedance parameters of carbon/metal hybrids in 1.3M LiPF₆ electrolyte obtained by fitting the experimental data in Figure 3e and S9 and S10.

a) Same weight ratio composition.

b) During lithiation.

c) During delithiation.

Warburg impedance (σ_{ω}), which is the scale of ionic mobilities in active material during electrochemical reaction, is estimated from EIS spectra (Table S3). Similar to aforementioned results, graphite carbon indicates the highest σ_{ω} value (33.93 Ω s^{-1/2}) due to its fine structure with high crystallinity, acting as a hindrance factor to active electrochemical reactions. By contrast, in the case of carbonized metal/m-TA (3:1), the lowest σ_{ω} value (4.33 Ω s^{-1/2}) is observed among all types of carbons, implying a strong potential for the facilitated ionic transportation. Likewise, σ_{ω} values of the carbonized metal/m-TA with varied metal contents are also investigated. With increasing the metal contents in the carbonized metal/m-TA, R_{sf} values gradually decrease with the enlargement of metallic domains. However, for the cases of R_{ct} and σ_{ω} , these values are optimally minimized at 3:1 of the mixing ratio (metal : TA), indicative of the fact that excessive inclusion of metals and accordingly increased crystallinity would rather mitigate ionic mobilities and retard electrochemical reactions. Instead, homogeneously hybridized metal species in the carbonized metal/m-TA with proper composition of 3:1 would synergistically promote the electrochemical reactions due to concurrently enhanced electronic and ionic mobilities.

Table S4: A summary of impedance parameters of carbon/metal hybrids in 1M KOH electrolyte obtained by fitting the experimental data in Figure 3h and S12.

Materials	$R_s(\Omega)$	$R_{sf}(\Omega)$	$R_{ct}(\Omega)$
Carbonized Ni/m-TA (10:1)	1.97	0.96	6.79
Carbonized Ni/m-TA (3:1) ^{a)}	2.22	1.13	1.47
Carbonized Ni/m-TA (1:1)	2.65	1.43	2.43
Carbonized Ni/m-TA (1:3)	2.24	1.38	7.37
Carbonized Ni/m-TA (1:10)	2.30	1.10	8.39
Graphite + Ni NPs ^a)	3.06	2.01	11.10
Pitch + Ni NPs ^a)	2.31	1.69	6.45
XC-72 + Ni NPs ^{a)}	2.19	1.53	3.79

a) Same weight ratio composition.

Materials	η _{OER(@10mAcm⁻²)} (mV)	Tafel slope _{OER} (mV dec ⁻¹)	2C _{dl} (mF/cm ²)	ECSA (cm²)
Carbonized Ni/m-TA (10:1)	340	87.24	17.93	224.13
Carbonized Ni/m-TA (3:1) ^{a)}	288	58.52	25.78	322.25
Carbonized Ni/m-TA (1:1)	312	92.70	21.73	271.63
Carbonized Ni/m-TA (1:3)	354	84.41	21.14	264.25
Carbonized Ni/m-TA (1:10)	363	71.67	13.71	171.38
Graphite + Ni NPs ^{a)}	357	129.39	9.22	115.25
Pitch + Ni NPs ^{a)}	384	116.49	7.05	88.13
XC-72 + Ni NPs ^{a)}	344	129.16	25.33	316.63

Table S5: A summary of OER performances, C_{dl} and ECSA for different electrocatalysts measured in 1 M KOH.

a) Same weight ratio composition.

Mat	erials	ΔE _{OH}	ΔE _O	ΔE _{OOH}
	μ_{t_Fe}	4.10	7.04	5.57
	μ_{t_Co}	3.94	8.80 ^{b)}	4.77
E ₂ C ₂ /C	μ_{b_Fe2}	3.97 ^{a)}	3.96	6.29 ^{a)}
reco/c	μ_{b_Co2}	4.31 ^{a)}	3.02	4.48 ^{a)}
	μ_{b_FeCo}	3.16 ^{a)}	7.84 ^{b)}	6.27 ^c)
	Optimized E ^{d)}	3.16	3.02	4.77
	μ_{t2_Co}	0.76	0.59	4.04
	μ_{t1_Co}	0.76	2.07	4.06
CoNi/C	μ_{t2_Ni}	0.74	2.10	3.99
	μ_{t1_Ni}	0.80	-1.83 ^{b)}	4.01
	Optimized E ^{d)}	0.80	2.10	3.99
	μ_{t_Fe}	1.54	2.89	5.82
	μ_{t_Ni}	1.39	4.54	6.43
N:E ₂ /C	$\mu_{t_FCC_Ni}$	2.68	2.67	5.03
NIF e/C	$\mu_{t_FCC_Fe}$	3.01	3.81	6.19
	μ_{b_Ni}	1.94 ^{a)}	2.76	5.20 ^{a)}
	Optimized E ^{d)}	1.39	2.67	5.03

Table S6: The binding energies for intermediates HO*, O*, HOO* at different adsorption sites for different electrocatalysts.

a) Relocation to another site.

b) Surface reconstruction.

c) Unstable for hydroperoxyl adsorption, dissolving to *O and *OH.d) It is hypothesized that adsorption sites can be freely moved to other sites during OER to minimize overpotentials.

Materials	ΔG _{OH} (eV)	$\Delta G_0(eV)$	ΔG _{OOH} (eV)	η (V)
FeCo/C	3.55	3.04	4.90	2.32
CoNi/C	1.19	2.12	4.41	1.06
NiFe/C	1.78	2.69	5.45	1.52

Table S7: The free energies for intermediates HO^{*}, O^{*}, HOO^{*} and calculated overpotentials (η) for different electrocatalysts.

 Table S8: A comparison of carbonized metal/m-TA (NiFe / C) OER performance with recently reported electrocatalysts in alkaline medium.

Electrocatalysts	Electrolyte	η _{OER(@10mAcm⁻²)} (mV)	Tafel slope _{OER} (mV dec ⁻¹)	Reference
FeNi/C (Carbonized FeNi/m-TA)	1M KOH	260	43.2	This work
FeNi/N-CNT	0.1M KOH	290	79	Nano Energy, 2020 , 68, 104293.
10at% S doped-NiFe LDH	0.1M KOH	286	82	Energy Environ. Sci., 2020 , advanced article (DOI: 10.1039/C9EE03573G)
fcc-NiFe@NC	1M KOH	292	61	Angew. Chem. Int. Ed., 2019, 58, 6099
TA-NiFe	1M KOH	290	28	Angew. Chem. Int. Ed., 2019, 58, 3769
NiFe@oxidized carbon cloth (OCC)	1M KOH	281	64	ChemElectroChem, 2019, 6, 2497
NiFe-LDH from mixed MOFs	1M KOH	275	56.7	Small, 2019 , 15, 1903410
Monolayer NiFe-LDH	1M KOH	272	54	Adv. Energy Mater., 2019, 9, 1900881
NiFe-Heteroatom-doped graphene (HG)	1M KOH	310	39	Sci. Adv., 2018, 4, eaap7970
Fe@NiFe LDH	1M KOH	269	48.3	Nat. Commun., 2018, 9, 2609
Ni-Fe LDH hollow nanoprisms	1M KOH	280	49.4	Angew. Chem. In. Ed., 2018, 57, 172
FeNi@NC/RGO	1M KOH	261	40	Chem. Sci., 2018, 9, 7009
NiFe ultrathin MOFs nanosheets (UMNs)	1M KOH	260	30	Nano Energy, 2018, 44, 345
Exfoliated NiFe LDH nanosheets	1M KOH	270	89	Adv. Mater., 2017, 29, 1700017
Hierarchically porous graphitized carbon (HPGC) supported NiFe	1M KOH	265	56	Nanoscale, 2017 , 9, 11596
NiFe-LDH/Co,N	0.1M KOH	312	60	Adv. Energy Mater., 2017, 7, 1700467
2at% Fe doped-Ni ₃ C	1M KOH	275	62	Angew. Chem. In. Ed., 2017, 56, 12566
NiFe-PVP	1M KOH	297	48	Adv. Energy Mater., 2017, 7, 1700220
Ni ₃ FeN NPs	1M KOH	280	46	Adv. Energy Mater., 2016, 6, 1502585
FeNi@NC	1M NaOH	280	70	Energy Environ. Sci., 2016, 9, 123
Exfoliated monolayer NiFe-LDH	1M KOH	302	40	Nat. Commun., 2014, 5, 4477

Sample	E (eV)	ZPE (eV)	TΔS (eV)
HO*	-	0.35	0
0*	-	0.05	0
HOO*	-	0.41	0
H_2	-6.76	0.27	0.41
H ₂ O	-14.23	0.56	0.67
O_2	-9.86	0.10	0.64

Table S9: The DFT calculated zero-point energy corrections and entropic contributions to the free energies.

Table S10: A summary of impedance parameters of Si@carbon/metal hybrids in 1.3M LiPF₆ electrolyte obtained by fitting the experimental data in Figure S31.

Materials	$R_s(\Omega)$	$R_{sf}(\Omega)$	$R_{ct}(\Omega)$
Bare Si	3.79	68.17	34.76
Si @ rGO	4.46	39.72	11.55
Si @ Soft carbon (Pitch @ 900°C)	4.55	33.01	8.47
Si @ Hard carbon (Glucose @ 900 ℃)	4.98	51.84	60.48
Si @ C/Ni (Carbonized Ni/m-TA)	3.97	17.44	16.91
Si @ C/Fe (Carbonized Fe/m-TA)	2.77	22.81	9.91
Si @ C/Sn (Carbonized Sn/m-TA)	3.47	18.23	15.71
$SiO_x @ C/Ni (Si : Ni = 1:1 (wt\%))$	2.94	21.69	5.42
SiO _x @ C/Ni (Si : Ni = 1:0.5 (wt%))	3.87	27.84	4.96
SiO_x @ Soft carbon (Pitch @ 900 °C)	5.47	32.61	18.31

Table S11: A summary of mechanical properties of different Si composite materials obtained by nanoindentation tests in Figure S	32.
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Materials	(Calculated) Poisson's ratio	Reduced Young's modulus, E (GPa)	Standard deviation
Si @ Ni/C (Carbonized Ni/m-TA)	0.252	4.90	1.65
Si @ Soft carbon	0.252	0.93	0.09
Si @ Hard carbon	0.252	0.22	0.16

Section S7. References

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