Supporting Information
for

Facile Tailoring of a Multi-Element Nanocomposite for Electrocatalysis.

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NAC Sample Synthesis

NAC Mixed Ions:

To prepare the NAC Mixed Ions, 0.126 mg/mL of anhydrous $PtCl_4$ (Sigma-Aldrich), 0.048 mg/ml of $NiCl_2$ hexahydrate (Sigma-Aldrich), 0.048 mg/ml of $CuCl_2$ dihydrate (Sigma-Aldrich), 0.048 mg/ml of $CoCl_2$ hexahydrate (Sigma-Aldrich), and 0.04 mg/ml of anhydrous VCl_3 (Sigma-Aldrich) was added to 10nm Au colloid solution (BBI Solutions). The Au colloid and metal chloride mixture was left on the shaker until the sample turned dark blue and the self-assembled chains were formed. 0.195 mg/ml of $NaBH_4$ (Sigma-Aldrich) was then added to the solution.

NAC Mixed Chains:

To prepare the NAC Mixed Chains, 0.63 mg/mL of anhydrous $PtCl_4$ (Sigma-Aldrich) was added to 10nm Au colloid solution (BBI Solutions), left on the shaker until the sample turned dark blue to prepare Au-Pt chains. Separately, 0.06 mg/ml of $NiCl_2$ hexahydrate (Sigma-Aldrich), 0.06 mg/ml of $CuCl_2$ dihydrate (Sigma-Aldrich), 0.06 mg/ml of $CoCl_2$ hexahydrate (Sigma-Aldrich), and 0.05 mg/ml of anhydrous VCl_3 (Sigma-Aldrich) was added to 10nm Au colloid solution (BBI Solutions). The Au colloid and metal chloride mixture was left on the shaker until the sample turned dark blue and self-assembled Au- Ni Cu Co V chains were formed. The Au-Pt and Au- Ni Cu Co V were mixed in a 1:4 ratio to form a 20% Au-Pt and 80% Au- Ni Cu Co V volume ratio. The solution was then reduced using 0.195 mg/ml of $NaBH_4$ (Sigma-Aldrich).

NAC in H_2O:

To prepare the NAC in H_2O sample, 0.126 mg/mL of anhydrous $PtCl_4$ (Sigma-Aldrich), 0.048 mg/ml of $NiCl_2$ hexahydrate (Sigma-Aldrich), 0.048 mg/ml of $CuCl_2$ dihydrate (Sigma-Aldrich), 0.048 mg/ml of $CoCl_2$ hexahydrate (Sigma-Aldrich), and 0.04 mg/ml of anhydrous VCl_3 (Sigma-Aldrich) was mixed in milli-Q water. 0.195 mg/ml of $NaBH_4$ (Sigma-Aldrich) was then added to the solution.

NAC without V:

To prepare the NAC without V, 0.126 mg/mL of anhydrous $PtCl_4$ (Sigma-Aldrich), 0.048 mg/ml of $NiCl_2$ hexahydrate (Sigma-Aldrich), 0.048 mg/ml of $CuCl_2$ dihydrate (Sigma-Aldrich), 0.048 mg/ml of $CoCl_2$ hexahydrate (Sigma-Aldrich), and 0.048 mg/ml of $FeCl_2$ (Sigma-Aldrich) was added to 10nm Au colloid solution (BBI Solutions). The Au colloid and metal chloride mixture (Au- Pt Ni Cu Co Fe) was left on the shaker until the sample turned dark blue and the self-assembled chains were formed. 0.195 mg/ml of $NaBH_4$ (Sigma-Aldrich) was then added to the solution.

NAC without Pt:

To prepare the NAC without Pt, 0.048 mg/ml of $NiCl_2$ hexahydrate (Sigma-Aldrich), 0.048 mg/ml of $CuCl_2$ dihydrate (Sigma-Aldrich), 0.048 mg/ml of $CoCl_2$ hexahydrate (Sigma-Aldrich), 0.04 mg/ml of anhydrous VCl_3 (Sigma-Aldrich), and 0.048 mg/ml of $FeCl_2$ (Sigma-Aldrich) was added to 10nm Au colloid solution (BBI Solutions). The Au colloid and metal chloride mixture (Au – Ni Cu Co V Fe) was left on the shaker until the sample turned dark blue and the self-assembled chains were formed. 0.151 mg/ml of $NaBH_4$ (Sigma-Aldrich) was then added to the solution.

For all samples prepared with 10nm Au colloid solution, a redshift to around 630nm was observed due to Au's surface plasmon resonance (**Figure S5**).

Sample Preparation

Samples are prepared for electrical measurements by centrifuging the samples and resuspending in Milli-Q water for two times to wash away any salts in solution. 15ul are then drop-casted on a 3mm diameter glassy carbon electrode (GCE) and coated with 3ul of 5 wt. % Nafion™ perfluorinated resin solution (Sigma-Aldrich).

Samples were prepared for TEM by diluting 1:2 in ethanol and drop-casted on lacey carbon TEM grids.

Samples prepared for XPS and XRD by centrifuging and resuspending in Milli-Q water for two times to wash away any salts in solution, then centrifuged and dispersed in ethanol and drop-casted on a Si substrate for XPS and glass substrate for XRD.

Sample Characterization

TEM characterization was conducted using a JEOL JEM-F200 TEM at an acceleration voltage of 200 kV. EELS was conducted using a ThermoFisher Scientific Talos F200X S/TEM. XRD was conducted using a PANalytical Xpert Pro MRD with Cu Kα radiation ($\lambda = 1.54$ Å). XPS was conducted using a VGS ESCALab 250.

Electrochemical Measurements

Electrochemical measurements were performed using an Ivium multi-channel Ivium-n-Stat potentiostat in a standard three-electrode system using the GCE as a working electrode, a Pt wire counter electrode, and a glassy carbon reference electrode. Samples were conditioned for at least 30 cycles at a scan rate of 100mV/s until cyclic voltammetry curves were stable. Linear sweep voltammetry was then conducted at a scan rate of 50mV/s. EIS was conducted in 0.5M H_2SO_4. Using frequencies of 10 MHz to 1Hz with an amplitude of 20 mV, and an overpotential of 10 mV (-0.250V vs SCE).

Figures

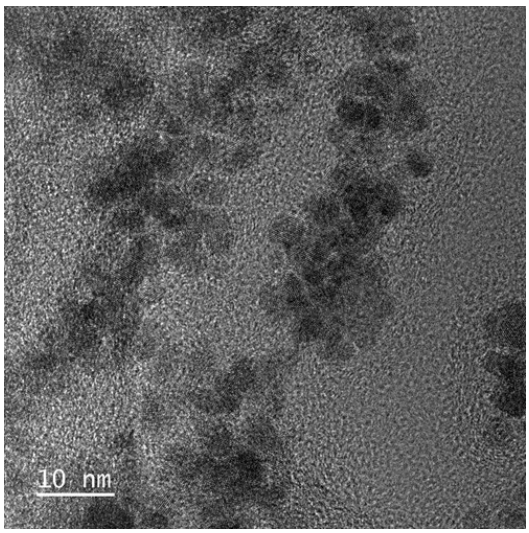

Figure S1. TEM of NAC sample made in H_2O without the Au chain template. 3-5 nm size nanoparticles are observed without any specific large scale organization.

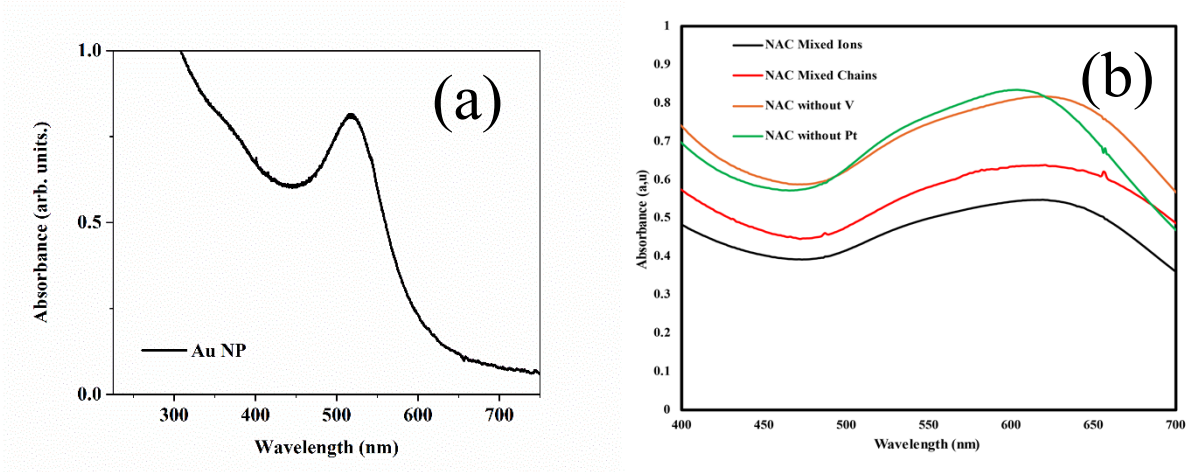

Figure S2. UV-Vis absorbance spectra of: (a) Au nanoparticles showing the plasmon resonance peak at 525 nm. (b) of different NACs made with the Au chain template where the plasmon resonance peak is red shifted to ~620-640 nm due to the formation of chain like structures.

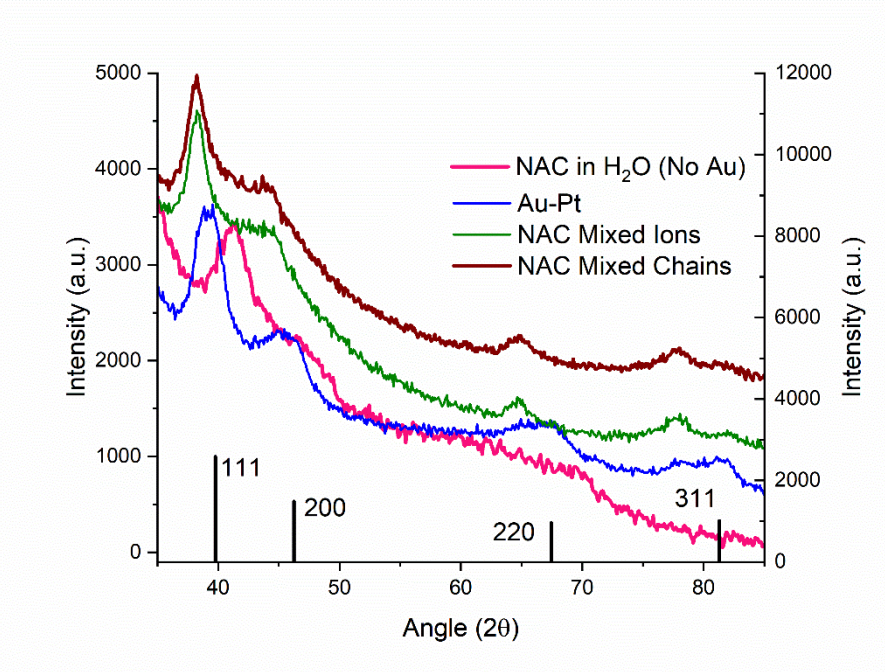

Figure S3. GIXRD of NAC Mixed Ions, NAC Mixed Chains, AuPt chains, NAC in H_2O (without Au chain template). The XRD peak locations for an Pt standard is also shown.

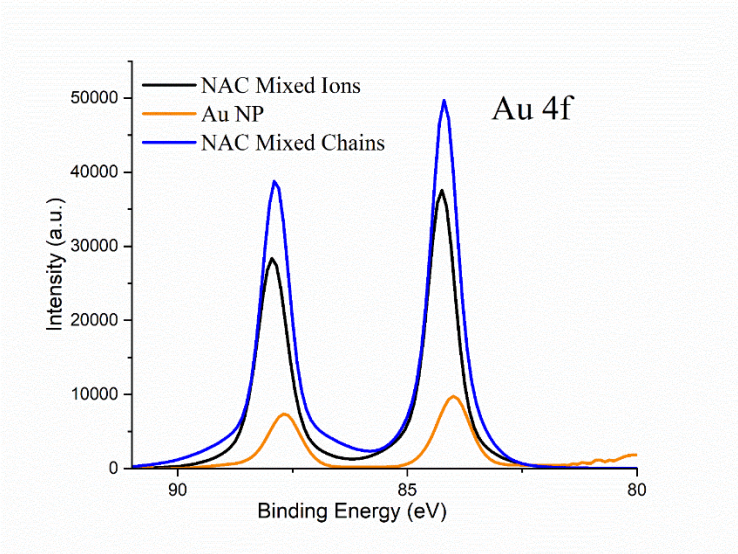

Figure S4. XPS spectra of the Au 4f regions for the NAC Mixed Ions, NAC Mixed Chains and Au nanoparticles.

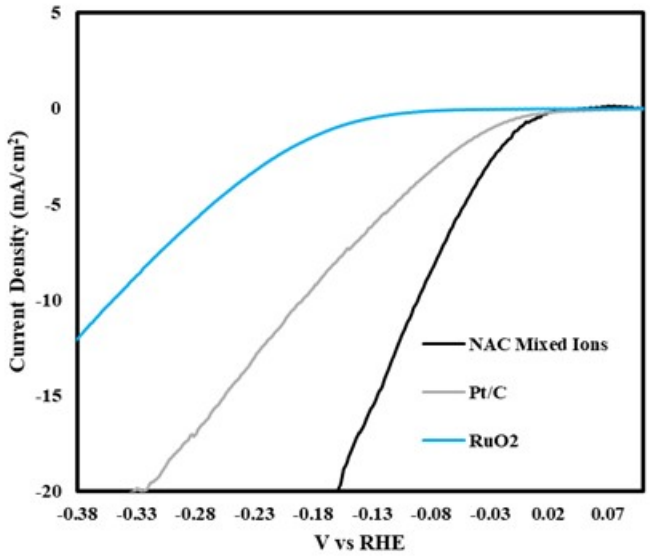

Figure S5. HER polarization curves of NAC Mixed Ions, Pt/C and RuO_2 in 0.1M KOH. The NAC Mixed Ions sample has the best performance.

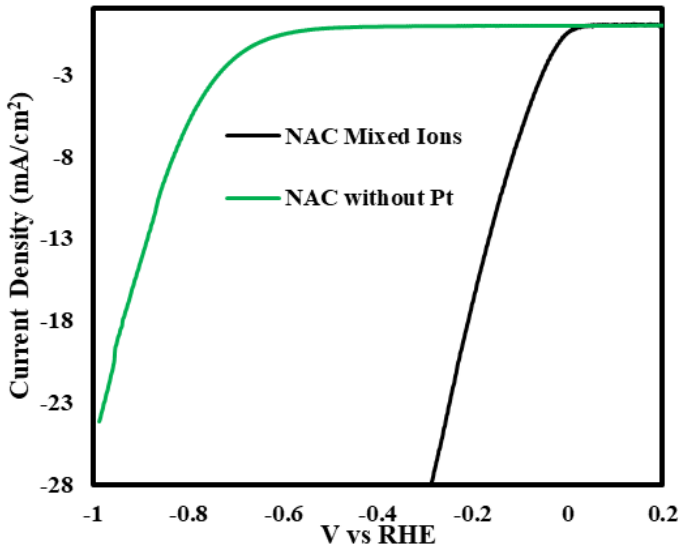

Figure S6. HER polarization curves of NAC Mixed Ions, and NAC made without Pt in 0.1M KOH. The absence of Pt in the NAC sample leads to very high overpotentials.

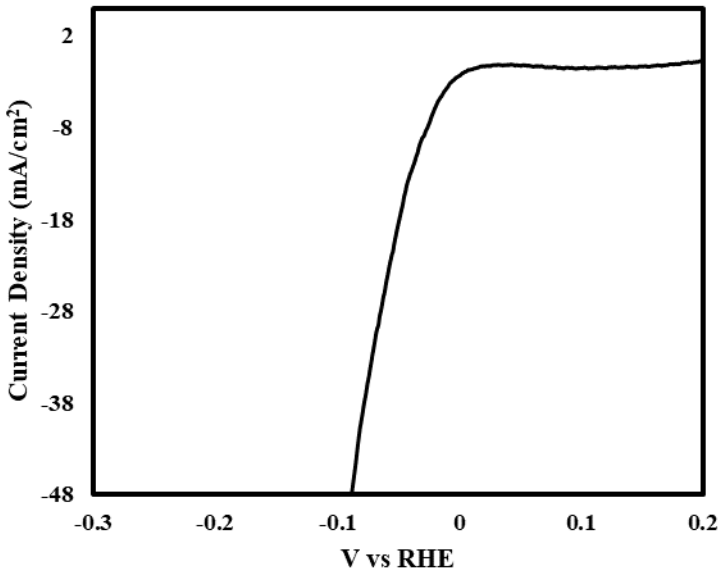

Figure S7. HER polarization curve of NAC Mixed Ions in 0.5M H_2SO_4. The sample shows a low overpotential of 33 mV at 10 mA/cm^2.

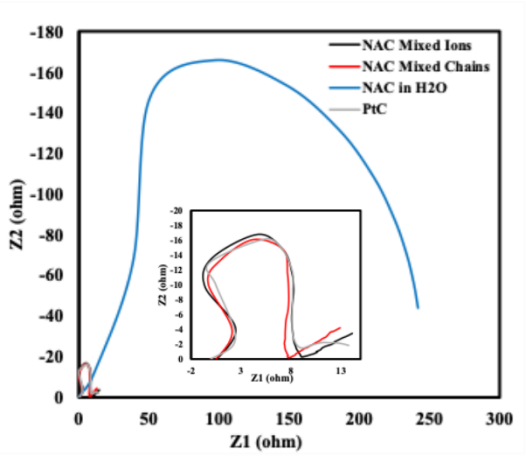

Figure S8. Electrochemical impedance spectroscopy results for the NAC samples and Pt/C. In the sample made without the Au chain template NAC H_2O a much higher charge transfer resistance is observed.

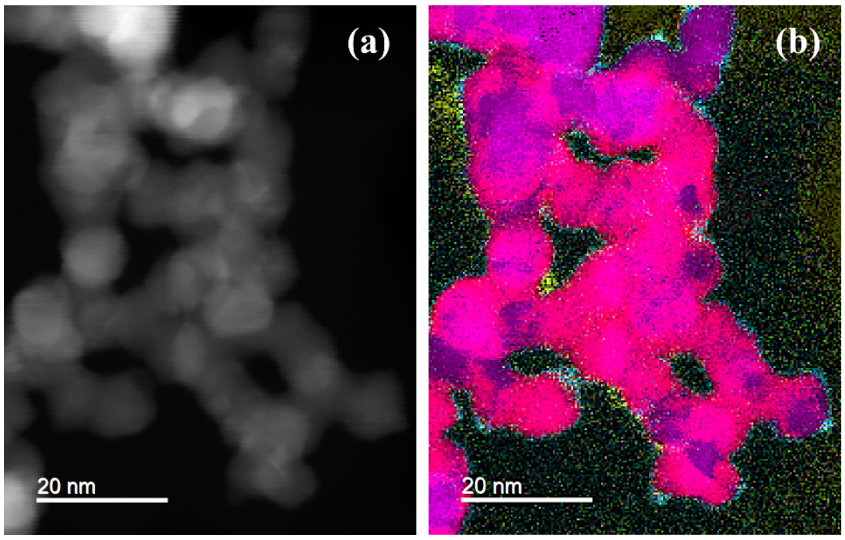

Figure S9. Image of NAC Mixed Ions from TEM analysis, (a) Annular dark field and (b) EELS composite image of the elements, with Au in magenta, Pt in blue, V in red, Cu in yellow, Ni in purple and Co in green.

Table S1: The ratio of metallic/oxidized states for each transition metal in the NAC's based on XPS analysis.

Element	**Ratio of (metallic/oxidized) state**	
Vanadium	NAC Mixed Chains	0.22
	NAC Mixed Ions	0.16
	NAC without Pt	0
	NAC H_2O	0.06
Cobalt	NAC Mixed Chains	0.34
	NAC Mixed Ions	0.07
	NAC without Pt	0
	NAC H_2O	0.03
Copper	NAC Mixed Chains	1.33
	NAC Mixed Ions	1.52
	NAC without Pt	1.31
	NAC H_2O	0.74
Nickle	NAC Mixed Chains	0.7
	NAC Mixed Ions	0.3
	NAC without Pt	0.0
	NAC H_2O	0.0