Supplementary Information (SI) for ChemComm.

Defect-rich silver electrode with nickel hydroxide nanoparticles for alkaline hydrogen evolution reaction

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Experiment

Preparation of Ag nanoparticles

$NaBH_4$ reduction method was used to prepare Ag nanoparticles. A 0.025 mol/L $AgNO_3$ solution with a volume ratio of 5:2 was mixed with a 0.2 mol/L $NaBH_4$ solution under water bath conditions at 40 °C, taking care to pour the $AgNO_3$ solution into the $NaBH_4$ solution quickly. The liquid phase reaction was waited for 10 min, during which the water bath and stirring conditions were maintained at 40 °C. The reaction mixture with Ag precipitation was obtained and the resulting Ag product was washed 2-3 times with deionized water. After pre-freezing, it was placed in a freeze-dryer for 24 h to obtain dried Ag nanoparticles.

Preparation of Ag/Ni mixture

Ball milling method was used to mix Ag nanoparticles and Ni nanoparticles. The raw materials were lab-prepared Ag nanoparticles and commercial Ni nanoparticles, the purity of commercial Ni nanoparticle was 99.9%, and the average particle size was 30 nm. 0.233 g of commercial Ni nanoparticle was added into 180 ml of deionized water and dispersed uniformly by ultrasonication for 10 min, then added into 180 ml of 8 mM HCl solution and ultrasonically reacted for 10 min to remove Ni oxide impurities, the obtained product was denoted as solution A; Solution B was obtained by adding 1.404 g of Ag nanoparticles into 1440 ml of deionized water and dispersing for 10 min. Solution A was mixed with solution B and then centrifugally treated to obtain a mixed slurry of nano-Ag and nano-Ni with a Ni atomic number ratio of 20%. Put 1.5 g of the mixed slurry of nano-Ag and nano-Ni into a PTFE ball mill jar, and then 30 Zr ball mill beads with a diameter of 5 mm and 10 ml of deionized water were added in to the jar, the speed of the ball mill was set as 400 rpm, and 5 cycles were run, with each cycle consisting of a 1 h running time and a 0.5 h pause time.

The ball-milled slurry was collected in a centrifuge by deionized water rinsing, the centrifuge spend and time were set to 12,000 rpm and 10 min, respectively. After that, the mixed Ag nanoparticles and Ni nanoparticles was dried by freeze-drying.

Preparation of self-supported electrode

Ag-Ni self-supported electrodes were obtained by cold-press process. o.6 g mixture of Ag and Ni nanoparticles with 20% Ni atomic number ratio was pressed at10 MPa, and kept the pressure at room temperature for 10 min, the obtained Ag-Ni self-supported electrode possesses a diameter of 15 mm and a thickness of 0.4 mm. Pure Ag electrode (P-Ag) were obtained by same process and using the pure Ag nanoparticles instead of mixed metal powders, and pure Ni electrode (P-Ni) were obtained by cthe same process and using Ni foam instead of mixed metal powders.

Preparation of Ag/Ni(OH)$_2$ self-supported electrode

Electrochemical treatment was used to obtain Ag/Ni(OH)$_2$ self-supported electrodes with alkaline HER catalytic activity. In the electrochemical system, the saturated calomel electrode was used as the reference electrode, the carbon rod as the counter electrode, and the self-supported electrode as the working electrode. A cyclic voltammetry scan with potentials ranging from -1.8 V to -0.9 V was applied to the working electrode for 20 revolutions in a 1 M KCl electrolyte with a sweep rate of 0.05 V/s; then a cyclic voltammetry scan with potentials ranging from -0.8 V to 0.4 V was applied to the working electrode for 20 revolutions in a 0.1 M KOH electrolyte with a sweep rate of 0.05 V/s. Eventually an Ag/Ni(OH)$_2$ self-supported electrode was obtained.

Material characterization

The material was analyzed using an X-ray diffraction (Bruker D8 Advanced) with Cu as the target, a rotary-target X-ray generator with a power of 16 kW, a minimum step of 0.0001°, a scanning angle range of 10° to 90°, and a scanning speed of 10°/min. Secondary electron images, backscattered electron images and elemental surface distribution scans of H-Ag/Ni and control samples were observed by scanning electron microscope (Hitachi S-4800). Defect analysis and phase analysis were performed using a transmission electron microscope (JEM F200). Elemental valence analysis was performed by X-ray photoelectron spectroscopy (ESCALAB 250Xi). Elemental valence bonding was analyzed by in situ Raman (Labram HR Evolution).

Electrochemical tests

The electrochemical tests were performed using a standard three-electrode system with a saturated calomel electrode as the reference electrode, a carbon rod as the counter electrode, and a self-supporting electrode as the working electrode in a 1 M KOH electrolyte. All self-supporting electrodes were half submerged in the electrolyte and facing the counter electrode with a catalytic area of 0.88 cm^{-2}. The electrochemical tests were carried out on a CHI601E working station at room temperature.

TOF test

Pb underpotential deposition (UPD) was used to determine the transition frequency (TOF) of Ag-Foil, P-Ag, P-Ni and H-Ag/Ni. Prior to Pb deposition, the electrode was cyclically scanned for 20 turns from -0.5 V to -0.25 V in pure 0.1 M CH_3COOK as a background, and then the solution was exchanged for 0.1 M CH_3COOK + 1 mM $(CH_3COO)_2Pb$ and cyclically scanned between -0.5 V to -0.25 V for 20 turns for the underpotential deposition test. The charge deposited by Pb (Q_{Pb}) was obtained by subtracting the background current from the underpotential deposition current and integrating over the abscissa. Accordingly, the TOF of the self-supported electrode can be calculated by the following equation:

$$TOF = \frac{I}{2F_n} = \frac{I}{Q_{Pd}}$$

where Q_{Pd} is the total charge due to Pd adsorption and desorption in the cyclic voltammetry, and I is the current at which the sample was subjected to LSV test.

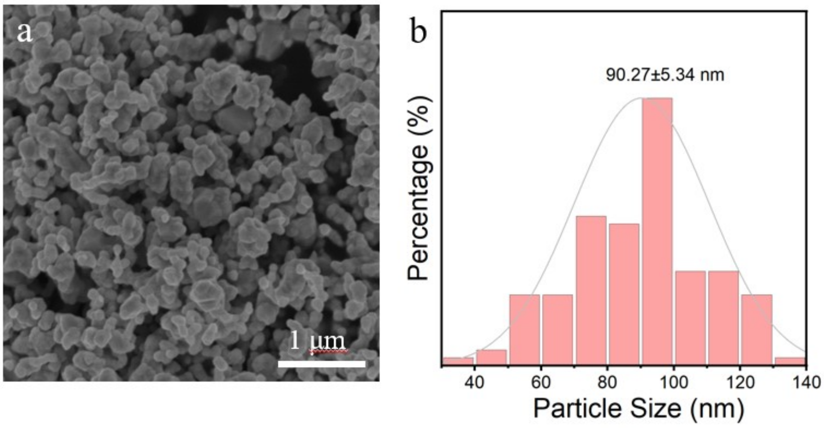

Figure S1. (a) SEM image of Ag nanoparticles. (b) Histogram of particle size distribution of Ag nanoparticles.

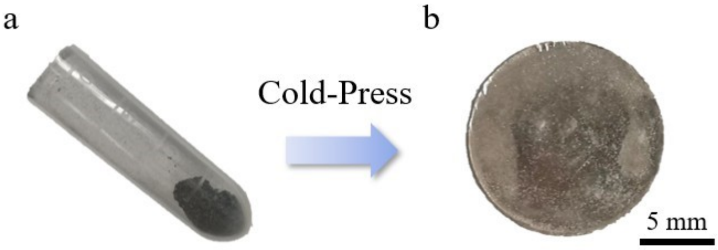

Figure S2. (a) Ag-Ni metal powder after ball milling and mixing. (b) Ag-Ni self-supported electrode sheet obtained by cold-press.

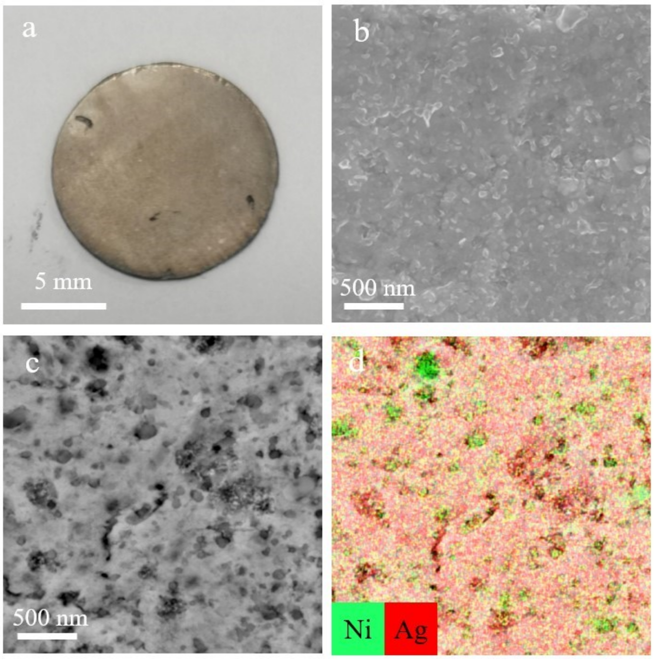

Figure S3. Characterizations of H-Ag/Ni electrode. (a) optical image. (b) Secondary electron image. (c) Backscattered electron image. (d) EDS elemental mapping.

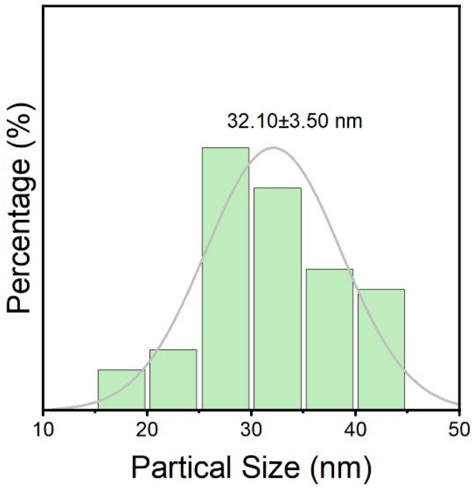

Figure S4. Histogram of particle size distribution of $Ni(OH)_2$ nanoparticles in H-Ag/Ni.

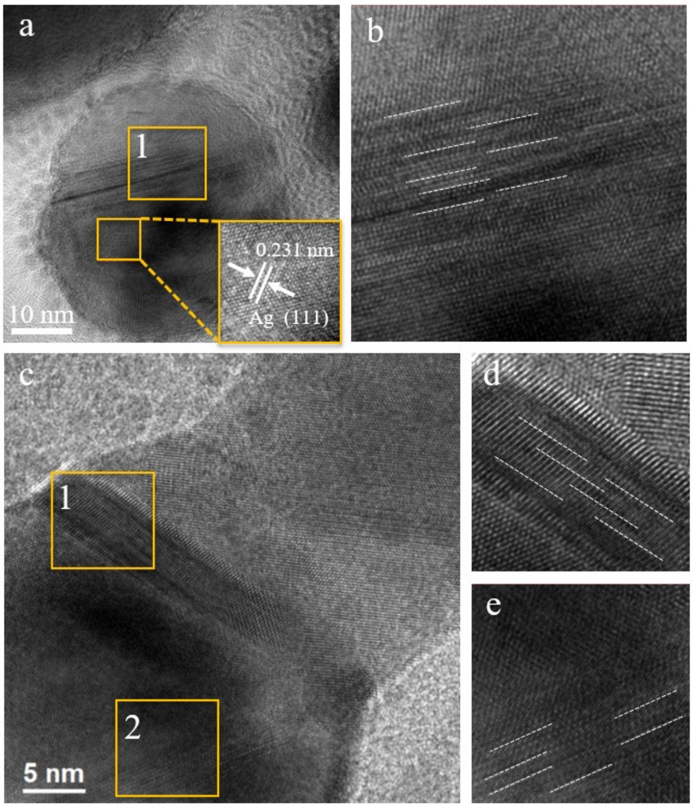

Figure S5. TEM images of H-Ag/Ni. (a) High-resolution TEM image. (b) Zoom-in image of zone 1 in Fig. a. (c) High-resolution TEM image. (d) Magnified image of zone 1 in Figure. c. (e) Magnified image of zone 2 in Figure c.

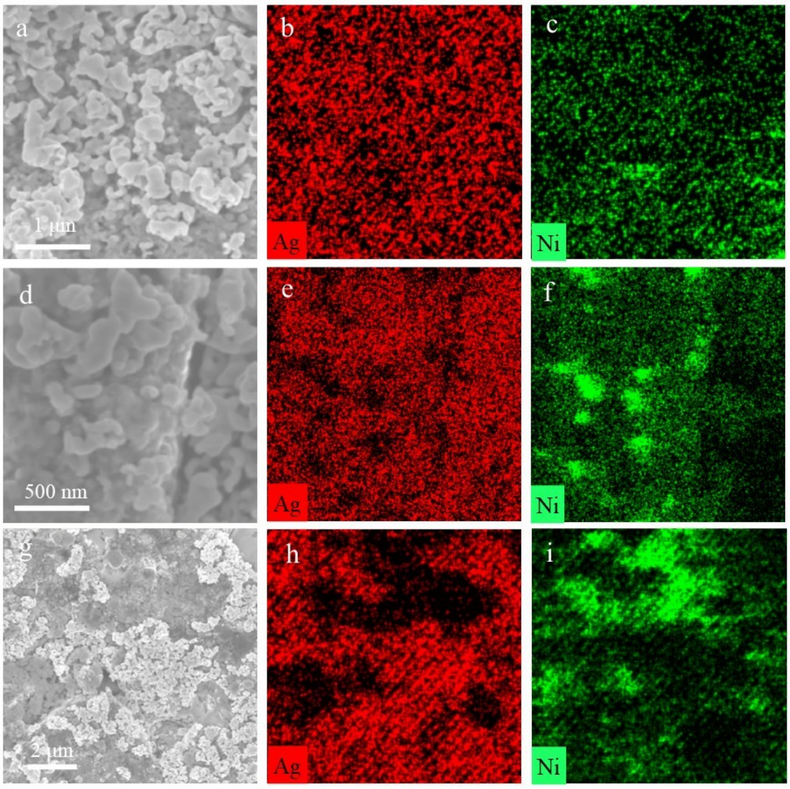

Figure S6. SEM images of H-Ag/Ni-10%, H-Ag/Ni, and H-Ag/Ni-30%. (a)(b)(c) H-Ag/Ni-10%. (d)(e)(f) H-Ag/Ni. (g)(h)(i) H-Ag/Ni-30%.

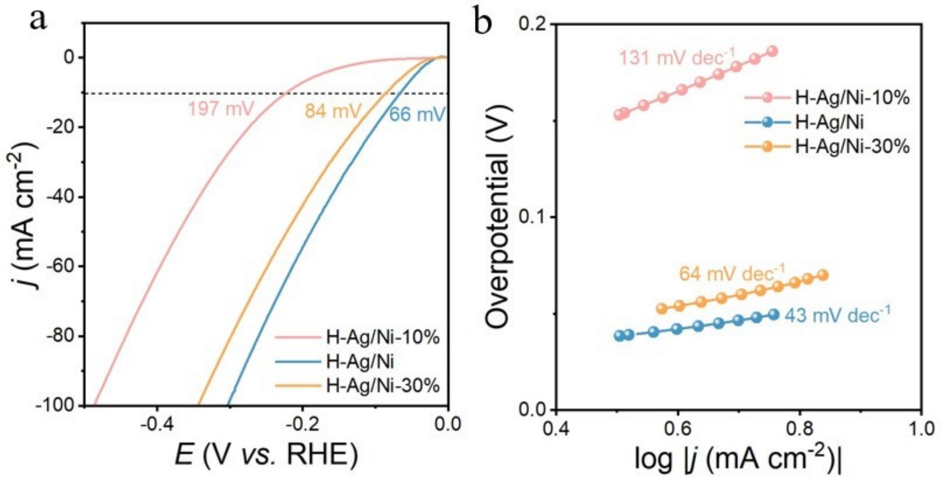

Figure S7. HER performance of different catalysts in 1 M KOH. (a) LSV curves of H-Ag/Ni-10%, H-Ag/Ni and H-Ag/Ni -30%. (b) Tafel slope plot based on the LSV curves in Figure. a.

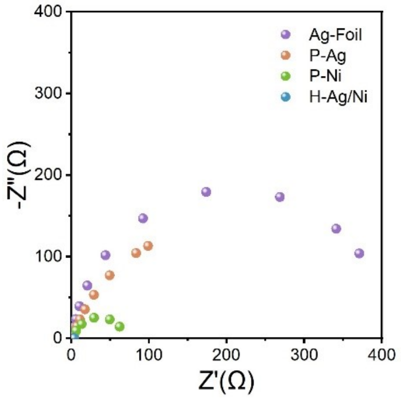

Figure S8. Nyquist plots of Ag-Foil, P-Ag, P-Ni and H-Ag/Ni.

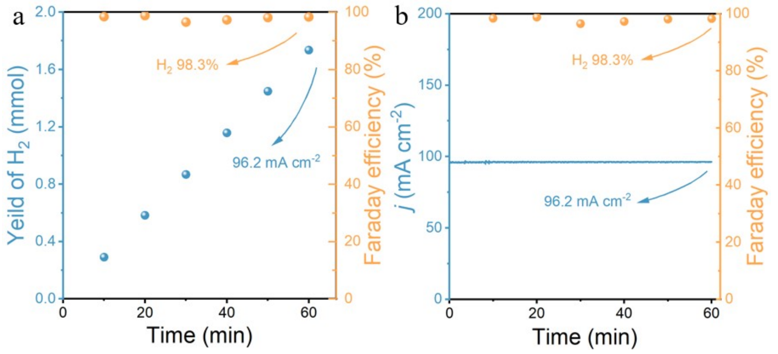

Figure S9. Alkaline HER Faraday efficiency of H-Ag/Ni.

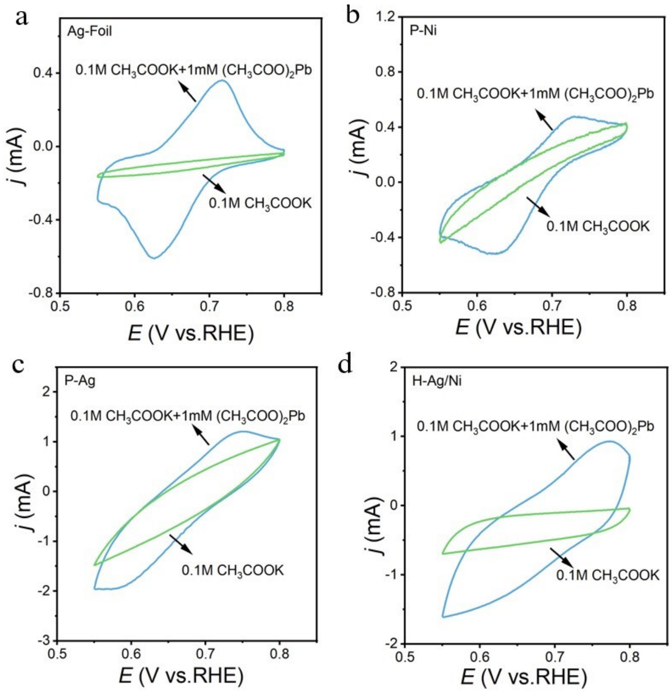

Figure S10. Pb adsorption-desorption voltammograms of (a) Ag-Foil, (b) P-Ag, (c) P-Ni and (d) H-Ag/Ni in 0.1 M CH_3COOK +1 mM $(CH_3COO)_2Pb$.

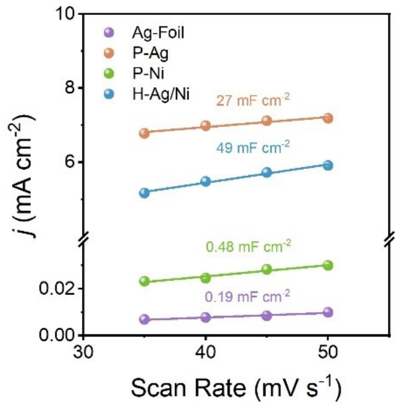

Figure S11. Electric double layer capacitance values (C_{dl}) of Ag-Foil, P-Ag, P-Ni and H-Ag/Ni.

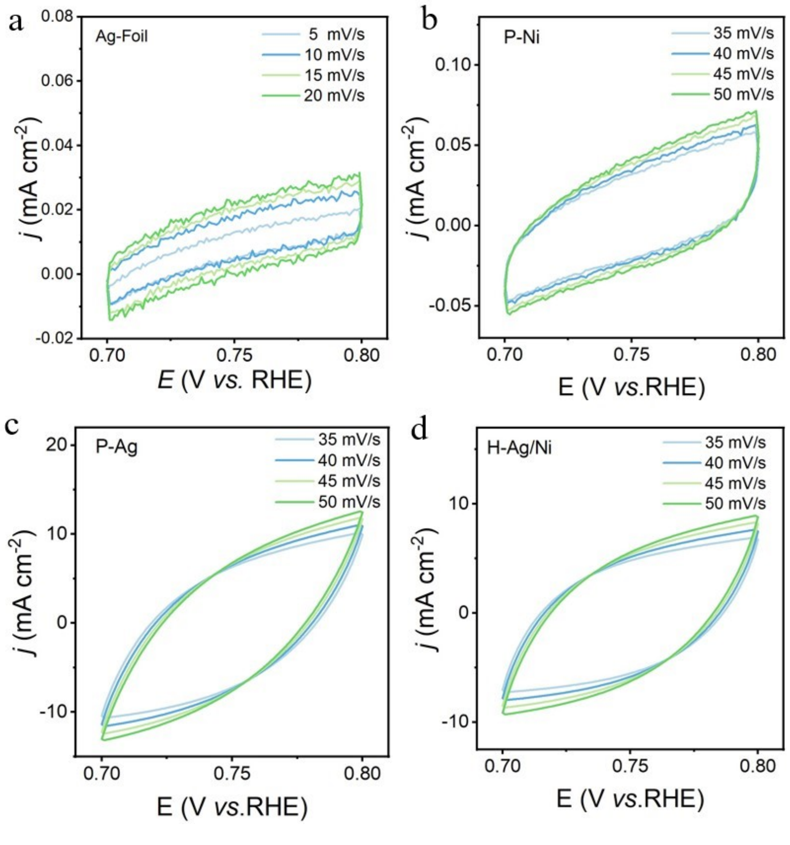

Figure S12. (a-d) Cyclic voltammetry curves at 5, 10, 15, and 20 mV s^{-1} scan rates in the 0.7 V~0.8 V vs. RHE potential range. (a) Ag-Foil. (b) P-Ag. (c) P-Ni. (d) H-Ag/Ni.

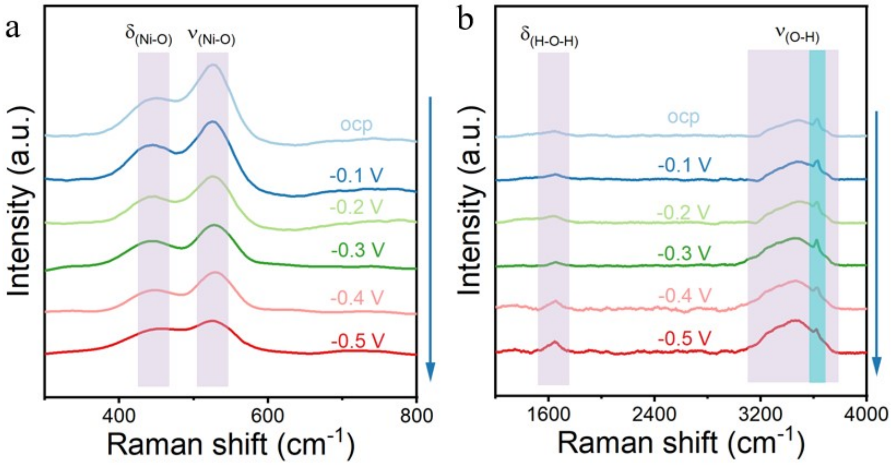

Figure S13. In situ Raman spectra of the H-Ag/Ni collected at different potentials within the range of 0 mV~ -500 mV in 1 M KOH electrolyte.

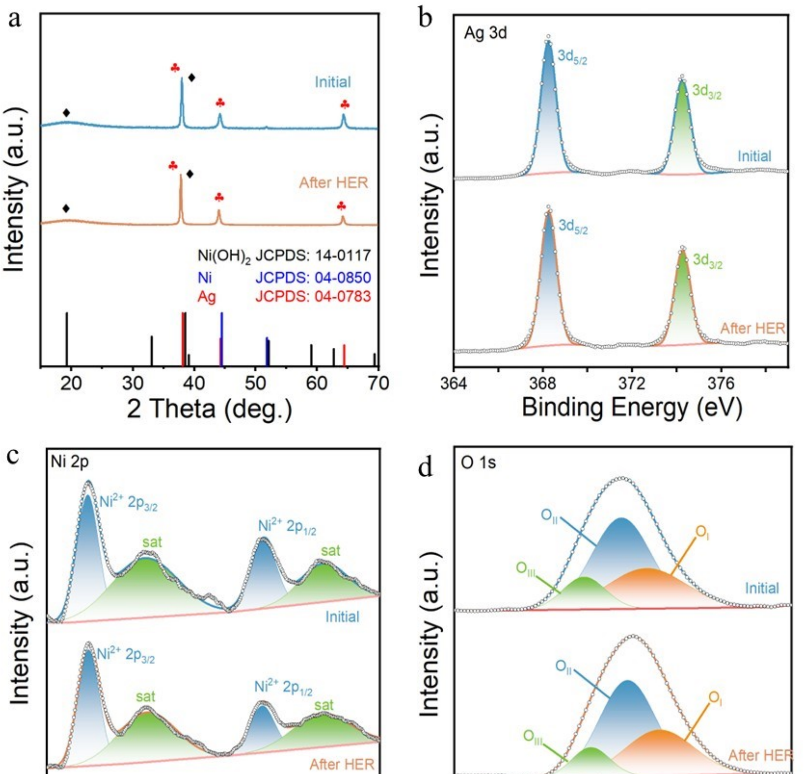

Figure S14. XRD and XPS characterizations of H-Ag/Ni initial and after stability test. (a) XRD. (b) XPS spectra of Ag 3d. (c) XPS spectra of Ni 2p. (c) XPS spectra of O 1s.

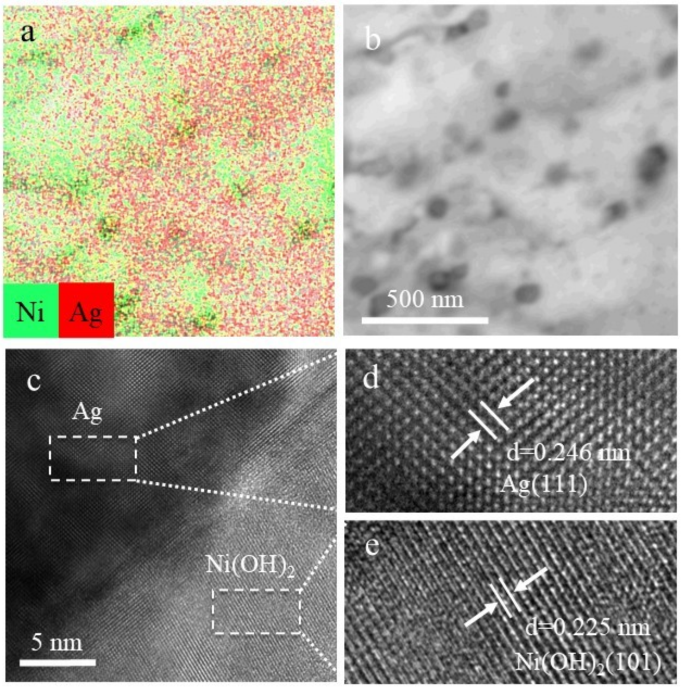

Figure S15. SEM and TEM images of H-Ag/Ni self-supported electrode after stability test. (a) EDS mapping image. (b) Backscattered electron image. (c) HRTEM image. (d-e) Zoom-in images of the selected zone in Fig. c.

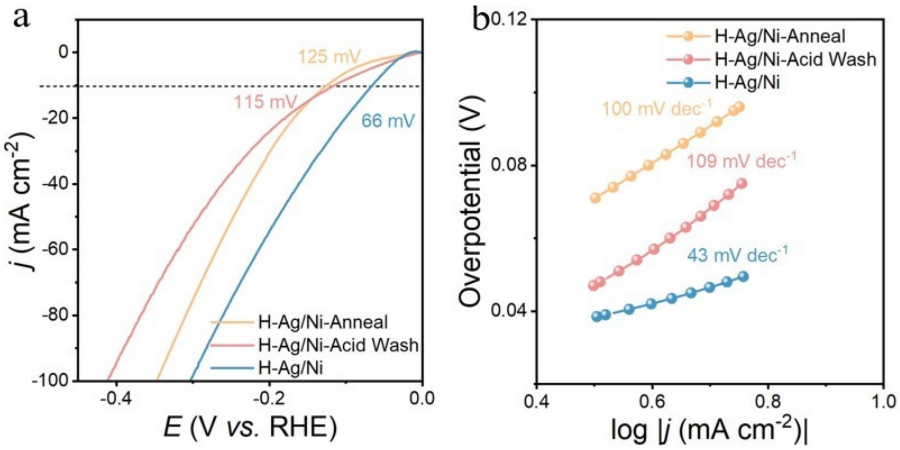

Figure S16. HER performance of different catalysts in 1 M KOH. (a) LSV curves of H-Ag/Ni-Anneal, H-Ag/Ni-Acid Wash and H-Ag/Ni. (b) Tafel slope plot based on the LSV curves in a.