Supporting materials

1 Determination of NH_3

1.1 Indophenol blue method

The ammonia produced in the electrolyte was estimated by the indophenol blue method. In detail, 3 mL of 1 wt% sodium nitroprusside solution, 5 mL of 6.05 mol/L phenol and 6.5 mL of 6 mol/L NaOH were added into 100 mL of 1.5 mol/L sodium citrate solution. After stirring for 10 min, the mixed solution was stored in the refrigerator. To obtain a standard concentration-absorbance curve, a series of 10 mL standard ammonia chloride solutions with gradient concentration (0, 0.2, 0.4, 0.5, 0.8 and 1.0 μg/mL) were mixed with 1 mL of 0.05 mol/L NaClO and 1 mL of indophenol blue solution. After being stirred for 30 min, 2 mL of the above solution was drawn out for the UV-vis absorbance measurement at 639 nm. By 3 times repeated tests, the standard curve was plotted according to the standard gradient solution and their absorbance value and the fitting curve ($y=0.26577x+0.01235$, $R^2=0.999$) shows a good linear relation between absorbance value and NH_4Cl concentration. To quantify the NH_3 generated in NRR tests, 1 mL of 0.05 mol/L NaClO and 1 mL of indophenol blue solution were added into 10 mL of the reaction solution. After that, 2 mL of the above solution was drawn out for the UV-vis absorbance measurement at 639 nm. The ammonia concentration can be calculated according to its absorbance value and the standard curve.

1.2 Determination of N_2H_4

The N_2H_4 in the electrolyte was estimated by the Watt and Chrisp method. The p-$C_9H_{11}NO$ (5.99 g), HCl (concentrated, 30 mL) and C_2H_5OH (300 mL) were mixed as the color reagent. To obtain a standard concentration-absorbance curve of N_2H_4 gradient concentration, standard N_2H_4 solution of a series of concentration (0, 0.1, 0.3, 0.5, 0.8 and 1.2 μg/mL) were prepared. In detail, 5 mL of the solution above was added into 5 mL of the standard gradient solution. After stirring for 15 min at room temperature, 2 mL of the above solution was drawn out for the UV-vis absorbance measurement at 457 nm and the fitting curve is $y=0.627x+0.009$ ($R^2=0.999$). To measure the concentration of N_2H_4 in the reaction solution, the preceding steps were repeated and the N_2H_4 concentration can be calculated according to its absorbance value and the standard curve.

1.3 ^{15}N isotope labeling experiments

^1H nuclear magnetic resonance (NMR) method was carried out to measure the generation of NH_3 via the feeding gas $^{14}N_2$ and $^{15}N_2$. To plot the standard curve, 100 μL of 10 μg/mL of standard $^{14}NH_4Cl$ and $^{15}NH_4Cl$ was added into 0.6 mL of d6-DMSO respectively. Afterward, the electrolyte was bubbled with the purified $^{15}N_2$ gas for 30 min with a low-velocity gas flow. After NRR tests, the solution was measured by ^1H NMR spectroscopy to obtain the standard curves of $^{14}NH_4Cl$ and $^{15}NH_4Cl$. To further qualify the generated NH_3, 10 mL of after-NRR solution was added to sulfuric acid to adjust the pH value to 2 and then heated to concentrate to 100 μL. The same as the preceding operations, 0.6 mL of d6-DMSO was added into the solution followed by ^1H NMR spectroscopy.

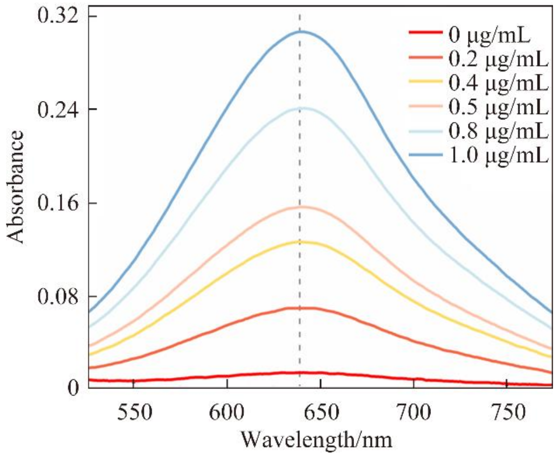

Figure S1 UV-vis spectra of standard gradient NH_4Cl solution using indophenol blue method for 30 min

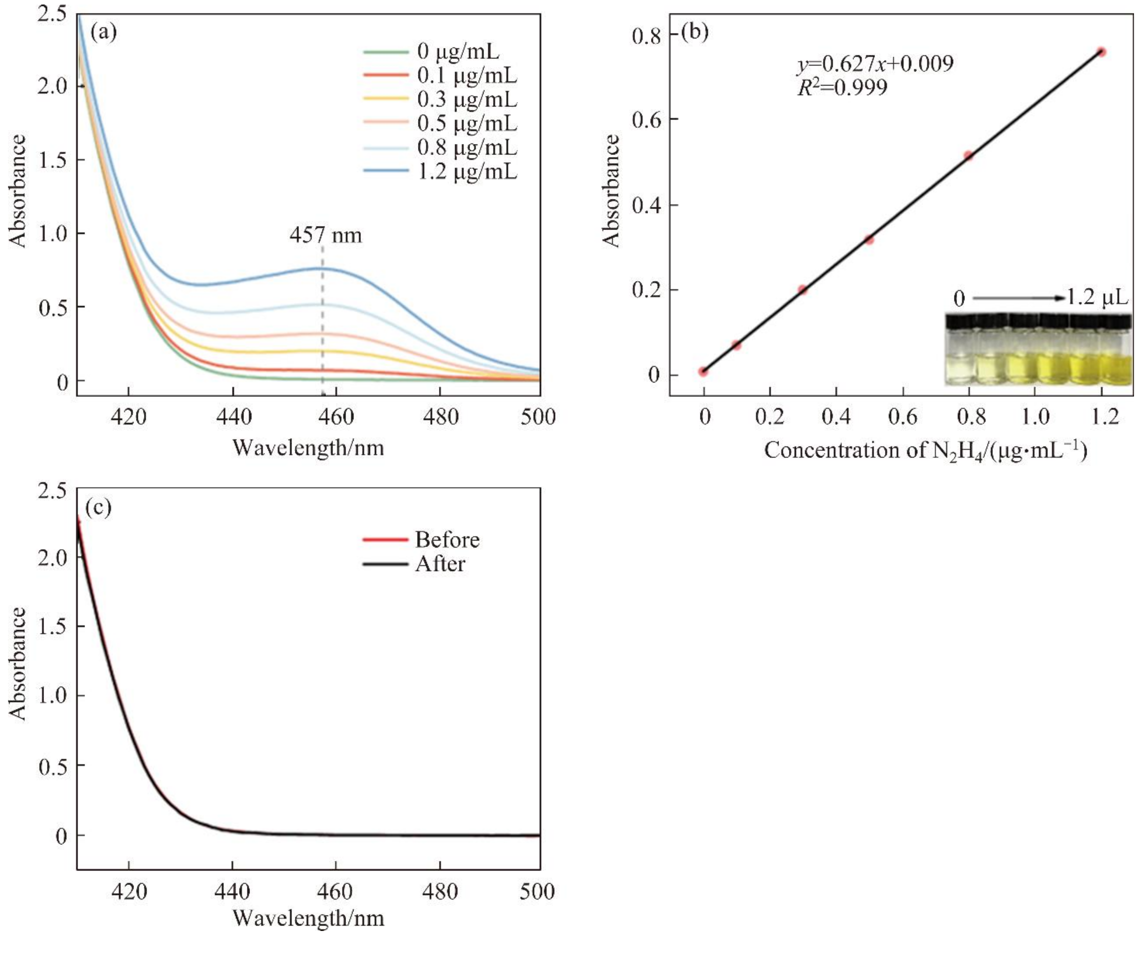

Figure S2 (a) UV-vis spectra of standard gradient NH_4Cl solution using Watt and Chrisp method and (b) the corresponding calibration curve of the estimation of NH_4Cl; (c) UV-vis spectra of $(FeCoNiMoCr)_9S_8$ before and after NRR

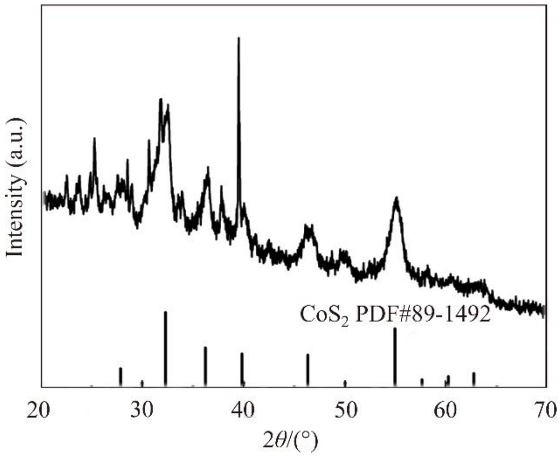

Figure S3 XRD pattern of (FeCoNiMoCr)S$_x$ after the NRR test

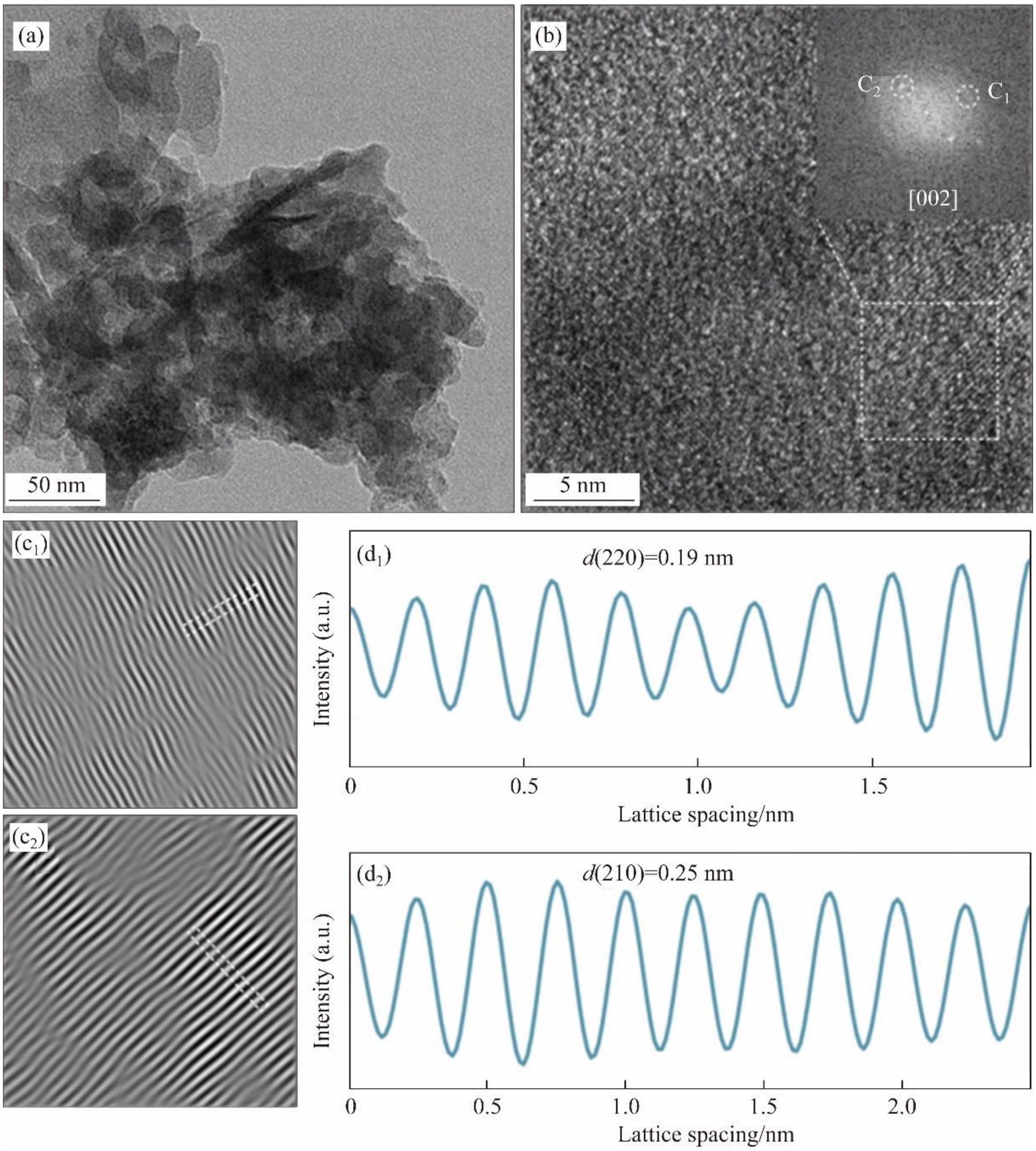

Figure S4 (a) TEM and (b) HRTEM images of (FeCoNiMoCr)S$_x$ after the NRR test(inset is the FFT pattern of the dashed white area); (c$_1$, c$_2$) Corresponding IFFT pattern; (d$_1$, d$_2$) Intensity profiles from the dashed white areas in (c$_1$, c$_2$)

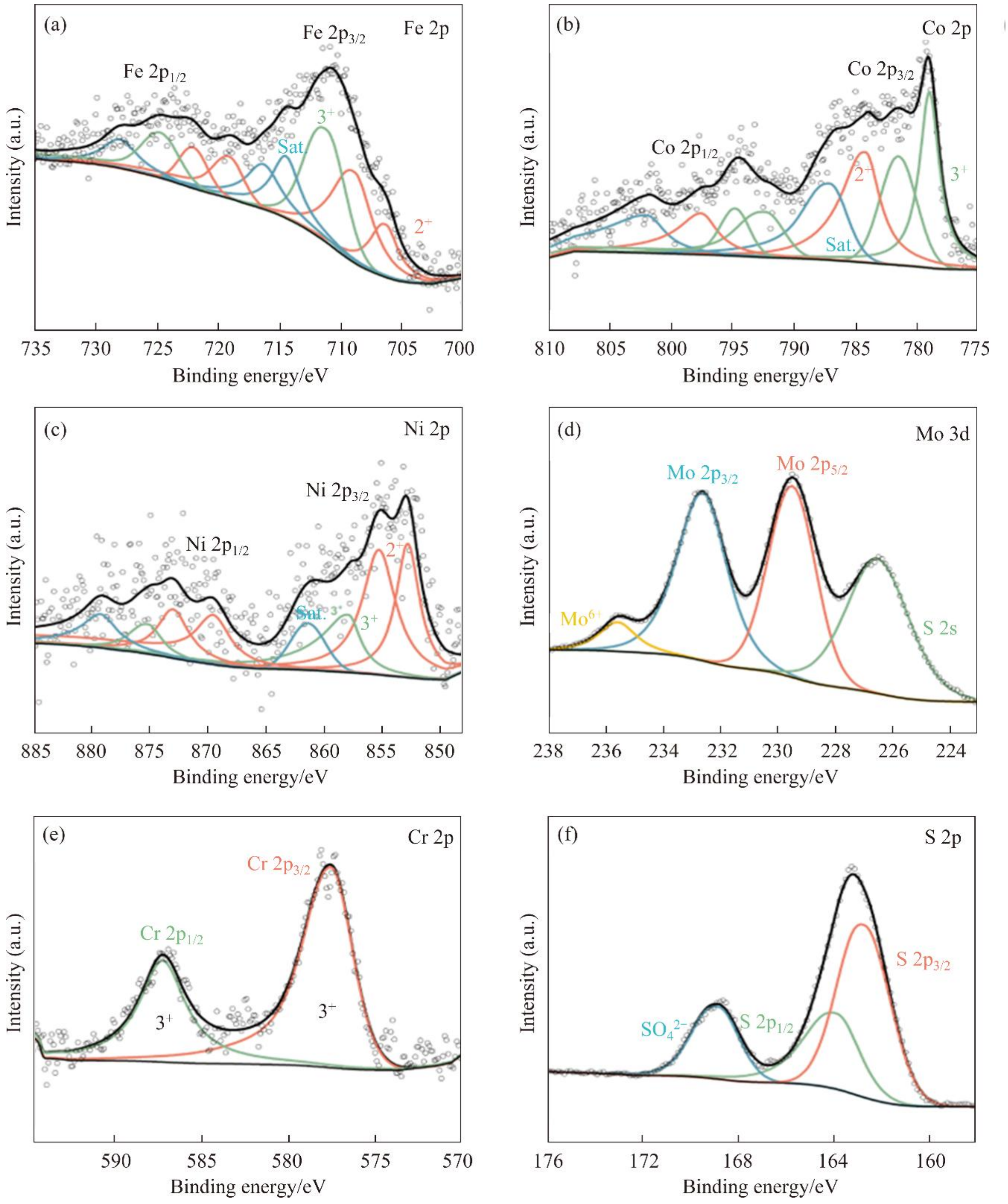

Figure S5 XPS spectra of (a) Fe 2p, (b) Co 2p, (c) Ni 2p, (d) Mo 3d, (e) Cr 2p and (f) S 2p for (FeCoNiMoCr)S_x after the NRR test

Figure S6 pH value of electrolytes before and after the NRR tests