Size-controlled synthesis of CuFe, CuRu alloy nanoparticle catalysts for electrochemical nitrogen reduction reaction

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NH_3 is the main source of fertilizer and carbon-free energy carrier. Electrochemical nitrogen reduction reaction attracts increasing attention because it can be realized under ambient temperature and pressure, which is more advantageous than traditional Haber-Bosch process. However, it is still impeded by the low active site density and sluggish kinetics, leading to a low NH_3 yield rate. To enhance catalytic activity and selectivity, in this study, alloy nanoparticles of Cu which is not an ideal electrocatalyst for HER and Fe, Ru which is favorable to NRR were originally synthesized. CTAB was first used in the size-controlled synthesis of CuFe, CuRu alloy to investigate the effect of nanoparticle size on catalytic performance.

The alloy nanoparticles were synthesized via hydrothermal process with metal chlorides and hydrazine. Surfactant CTAB was added at different molar ratios to control nanoparticle size. Catalysts were characterized by EXAFS, XRD and TEM. A three-electrode configuration was used in an H-type electrochemical cell and ammonia concentration was estimated using the indophenol blue method during UV-Vis measurements.

Compared with previous studies, as shown in Fig.1, Cu_1Fe_2 achieved the Faradaic efficiency (20.81%) and the ammonia yield rate (50.18 μg mg^{-1}cat. h^{-1}), which is better than the previous study (2.94% and 29.13 μg mg^{-1}cat. h^{-1}). [1] With Cu_1Ru_3, the Faradaic efficiency (22.06%) and the ammonia yield rate (46.52 μg mg^{-1}cat. h^{-1}) were obtained, which are also superior to the previous study. [2] It was also discovered that the smaller alloy nanoparticles exhibited better catalytic performances.

The introduction of Fe, Ru to fabricate CuFe, CuRu alloys enhanced electrochemical performance by changing the electronic structure of Cu, promoting NRR while restraining HER. The tailored atomic ratio of Cu to Fe, Ru also had an influence on electronic structure. Moreover, with the addition of CTAB, alloy nanoparticle size was reduced, which displayed large surface area for high active site density. Size-controlled alloy strategy could be used to design efficient catalysts for other important reactions.

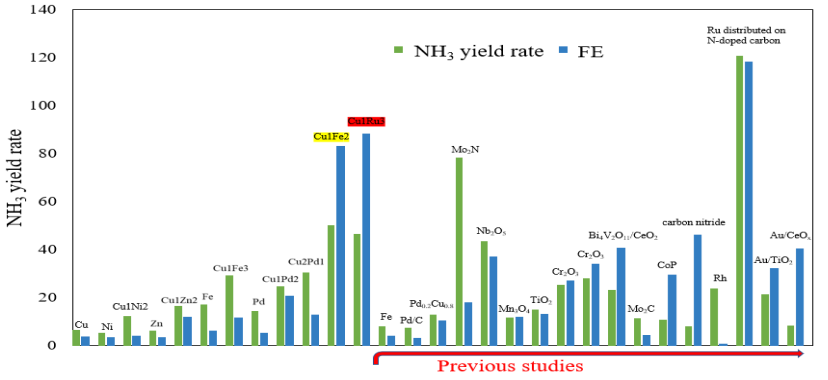

Fig1. Ammonia formation rate and Faradaic efficiency for synthesized nanoalloy catalysts in this and previous research

[1] X. Wang et al., Adv. Mater., 2020, 32, 2004382.
[2] C. Kim et al., Adv. Mater., 2022, 34, 2205270.