Supporting Information

Regulation of d-band electrons to enhance the activity of Co-based non-noble bimetal catalysts for hydrolysis of ammonia borane

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Number of figures: 7

Calculation method

The catalytic performance of the catalyst was evaluated using hydrogen generation rate (HER) and turnover frequency (TOF) value. HER and TOF value are calculated by typical formulas:

$$HER = V_{H2} / (m_{metal} \times t) \tag{S1}$$

$$TOF = n_{H2} / (n_{metal} \times t) \tag{S2}$$

in which V_{H2} and n_{H2} are the volume and mole number of generated H_2, respectively; m_{metal} and n_{metal} is the total mass and mole number of metals, respectively; t is the reaction time (min).

The position of the d-band center (ε_d) is calculated from the valence band spectrum (VBS) measured by X-ray photoelectron spectroscopy (XPS). Because the energy of the excited electron is low in the binding energy range of the VBS, it can correspond to the outermost electron of the sample element. The origin of the binding energy E_b was set to the Fermi energy E_f of the Ni plate. The Shirley background is subtracted from the measured spectra. The ε_d of the VBS is given by $\int R(\varepsilon)\varepsilon d\varepsilon/\int R(\varepsilon)d\varepsilon$, in this work, the $R(\varepsilon)$ is the XPS-intensity after background subtraction. The ε_d of the state density of structure obtained by theoretical calculation is also calculated according to this method. the $R(\varepsilon)$ is the DOS-intensity after background subtraction.
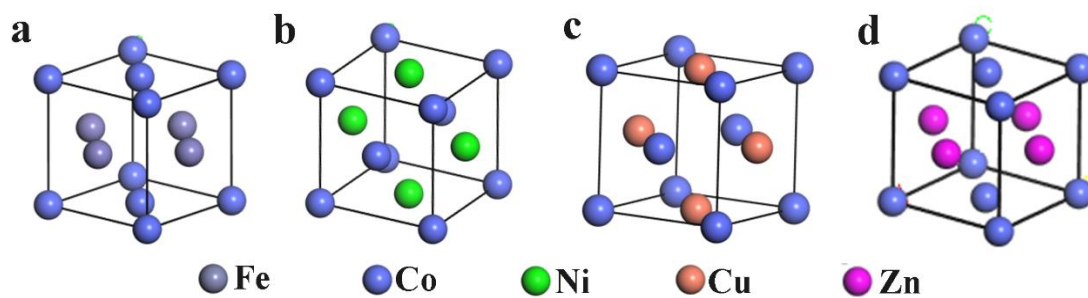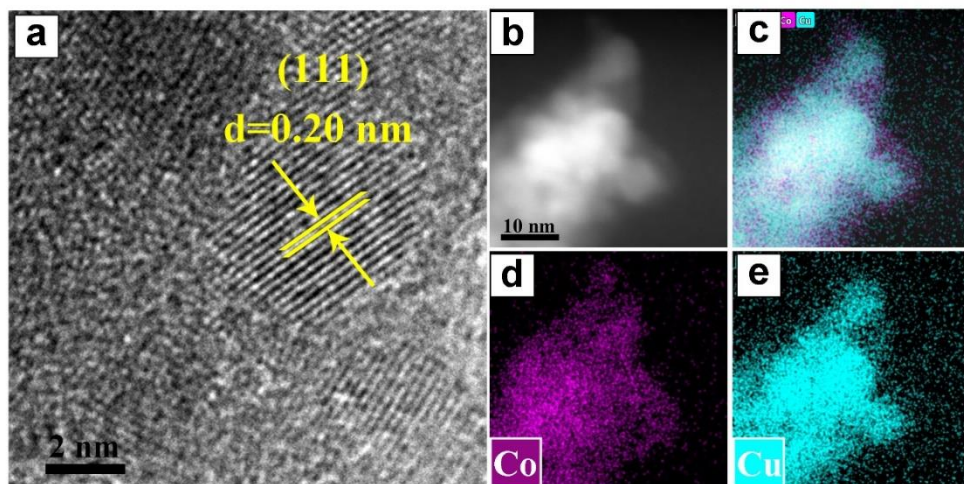
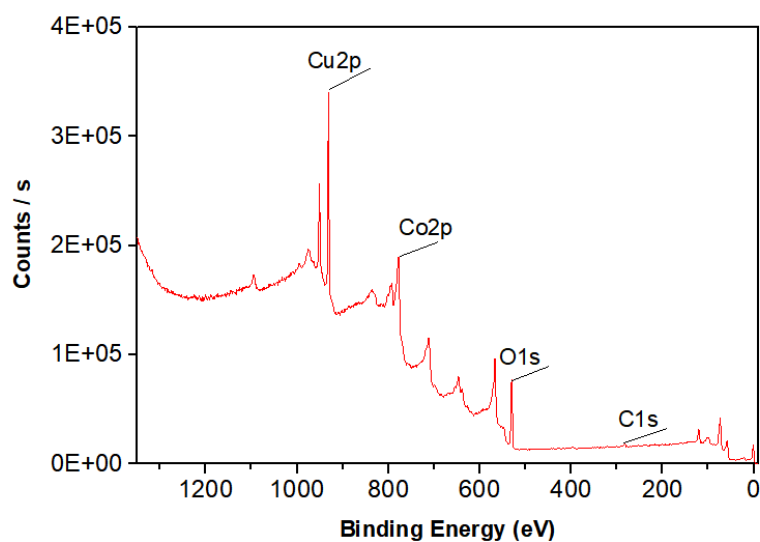**Figure S1** Calculated models for CoFe (a), CoNi (b), CoCu (c), and CoZn (d)
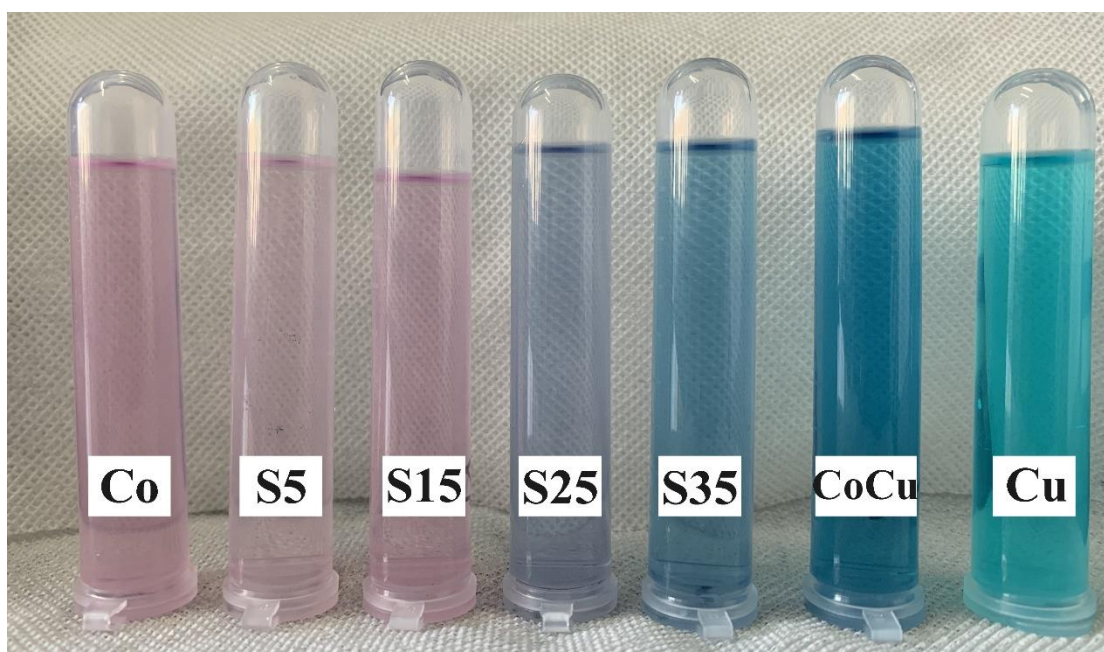
Figure S2 Acetic acid solution of pure metal Co, Cu and CoCu alloy and supernatant of SCoCu.
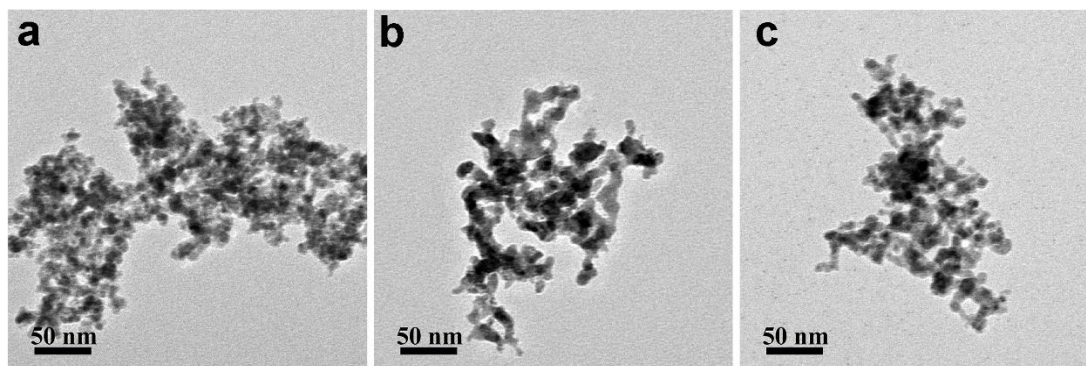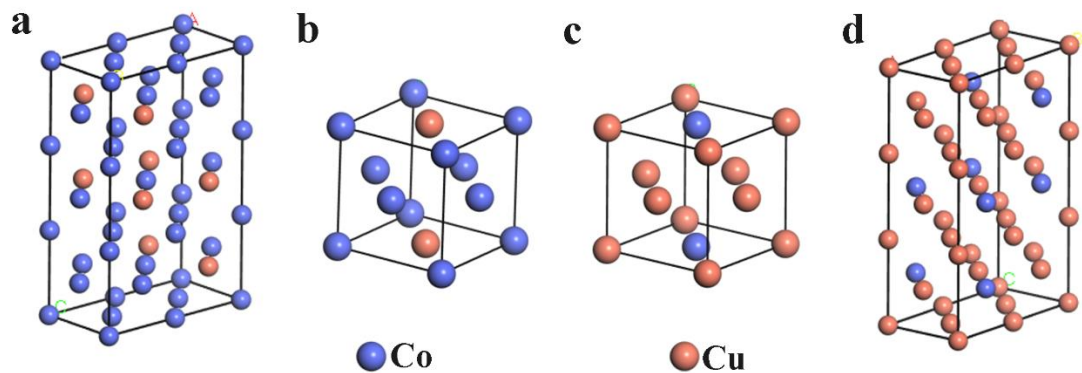

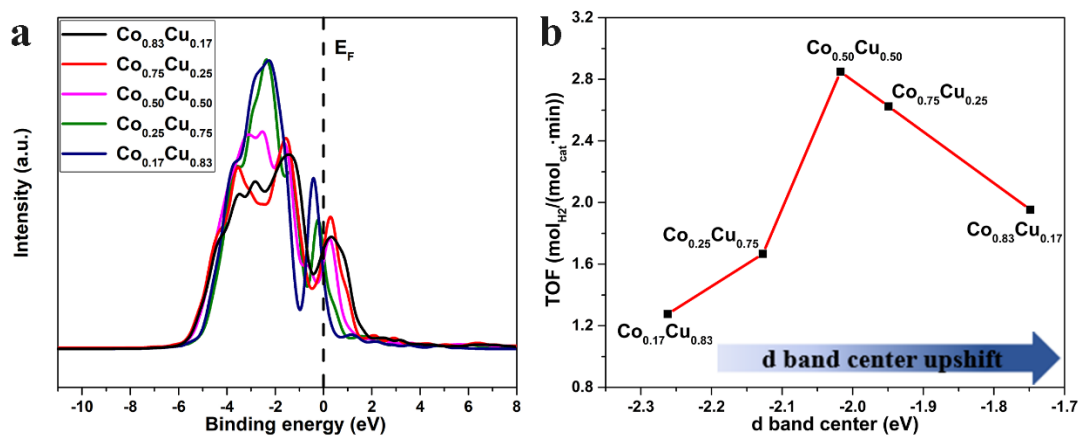**Figure S3** TEM image of S15 (a), S25 (b), S35 (c).

Figure S4 HRTEM image (a), HADDF image (b) and elements mapping analysis (c-e) of S0.

Figure S5 XPS full spectrum analysis of S5.

Figure S6 Calculated models for $Co_{0.83}Cu_{0.17}$ (a), $Co_{0.75}Cu_{0.25}$ (b), $Co_{0.25}Cu_{0.75}$ (c), and $Co_{0.17}Cu_{0.83}$ (d).

Figure S7 VBS of the Co_xCu_{1-x} as calculated by DFT (a) and relationships between TOF versus the ε_d position for Co_xCu_{1-x} (b).