Supplementary Information

Dual-Atom-Site Cu@PCN Photocatalyst Selectively Produces Ethane from CO_2 Reduction

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Supplementary Notes

In-situ EPR measurements

Before testing, it was necessary to create a 2 mg/mL DAS-Cu@PCN suspension (dispersed into methanol). Following argon bubbling, aqueous methanol solution dispersions were analyzed in sealed quartz tubes for the "before photoactivation sample." After argon bubbling, the sealed quartz tube designated as the "after photoactivation sample" was exposed to Xe lamp radiation for 30 minutes. O_2 gas was purged for 30 minutes into the "after photoactivation sample" to create the "after regeneration sample." Before conducting EPR measurements, all quartz tubes were frozen and kept in liquid nitrogen to maintain 77 K.

Tauc calculation formula

$$(\alpha h v)^{1/n} = B(h v - Eg)$$

Where α is the absorption coefficient, hv is the photon energy, h is the Planck constant ($h \approx 4.13567 \times 10^{-15}$ eV·s), v is the incident photon frequency ($v = c / \lambda$, where c is the speed of light, $c \approx 3 \times 10^8$ m/s, λ is the wavelength of the incident light), B is the proportional constant, and Eg is the band gap width of semiconductor materials.

The band edge positions of catalyst can be calculated using the following equation:

$$E_{CB} = (V\ vs.\ NHE) = E_{fb}(V\ vs.\ AgCl/Ag) + 0.197 - X$$

$$E_{VB} = E_{CB} + E_g$$

Where E_{VB} and E_{CB} stand for the valence band edge potential and conduction band edge potential, respectively; $E_{Ag/AgCl}$=0.197 V (saturated potassium chloride) vs. NHE; X is the voltage difference between the conduction band value and the flat potential value, generally 0.1-0.2 eV (the conduction bands of n-type semiconductors are normally 0.1-0.2 eV deeper than the flat-band potential), which is set as 0.2 eV in this work.
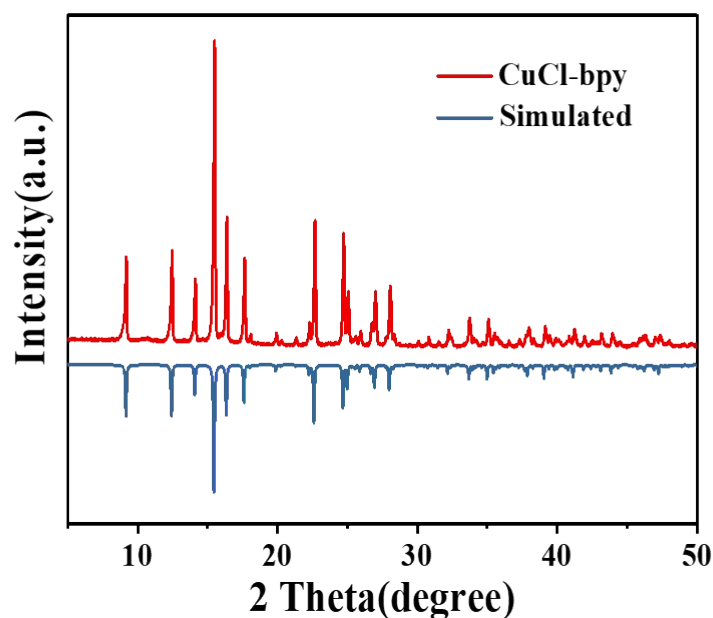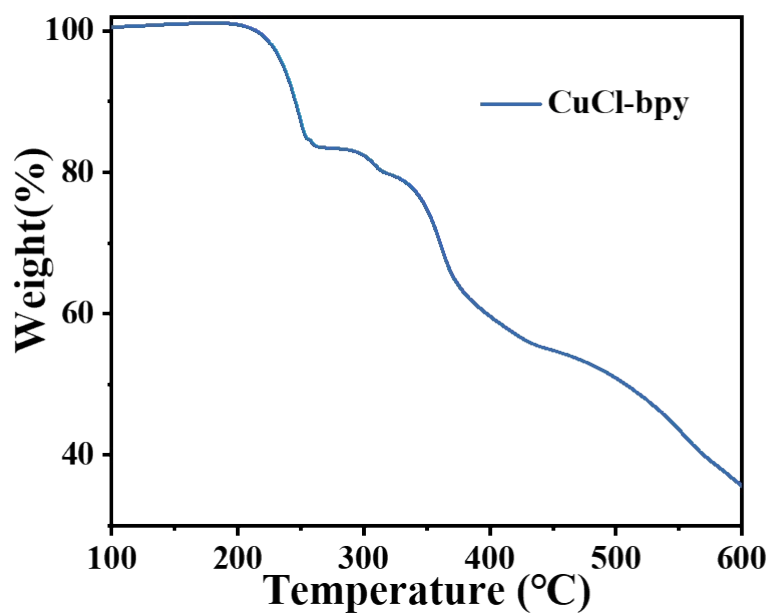

Fig. S1 XRD of CuCl-bpy

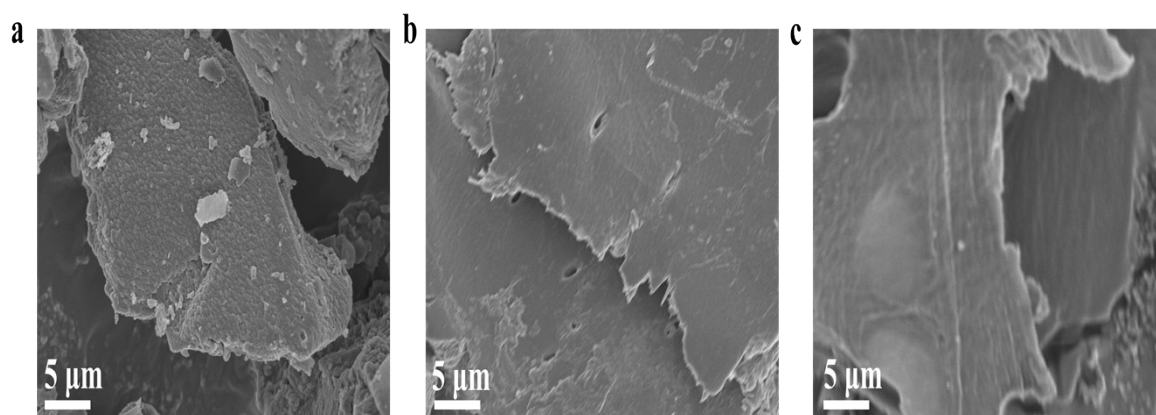Fig. S2 TGA for CuCl-bpy under N_2 atmosphere.

Fig. S3. SEM images of (a) PCN, (b) SA-Cu@PCN, (c) DAS-Cu@PCN

Table S1. ICP of the DAS-Cu@PCN catalyst

Catalyst	Sample quality m_0 (g)	Test element	Test solution element concentration C_0 (mg/L)	Sample element content Wt (%)
DAS-Cu@PCN	0.0370	Cu	1.342	0.9068
	0.0370	Cu	1.353	0.9142
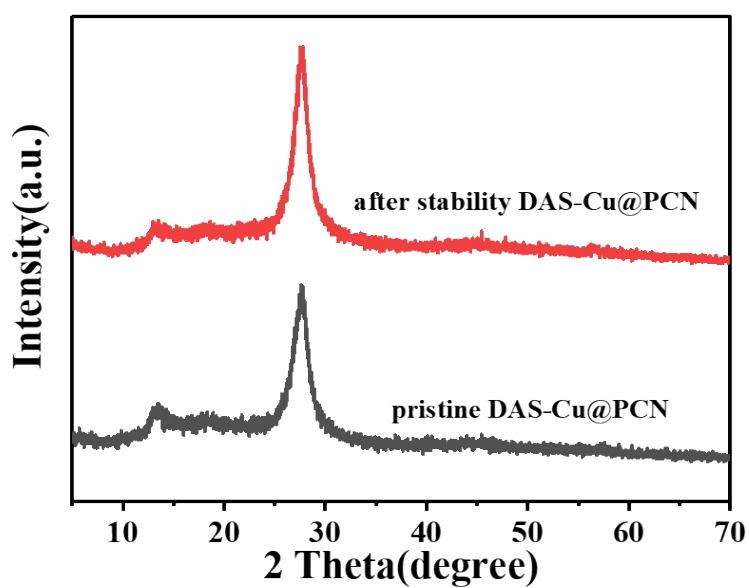
Figure S4. Comparison of XRD before and after reaction

Table S2. Surface composition of the PCN support and its Cu-containing derivatives DAS-Cu@PCN derived from XPS spectra

Catalyst	C/%	N/%	Cu/%	Cl/%
PCN	43.4	56.6	0	0
DAS-Cu@PCN	44.35	55.52	0.08	0.05
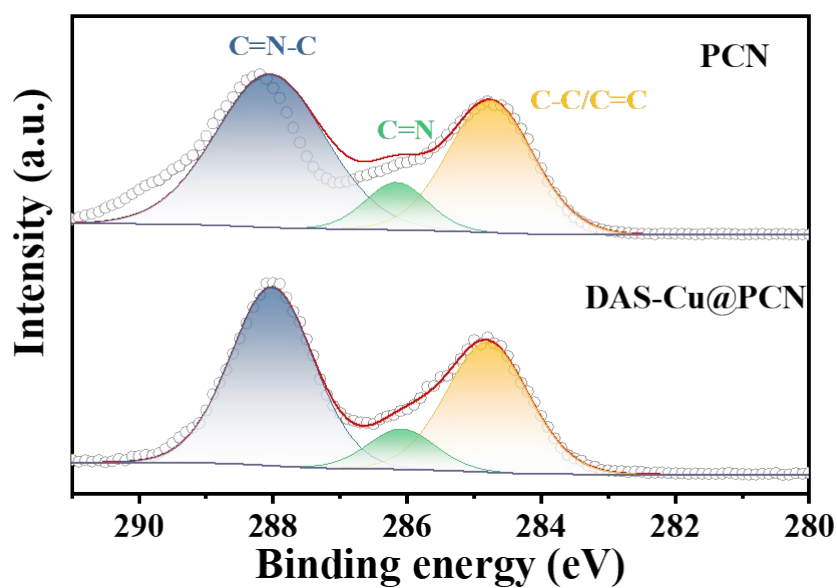
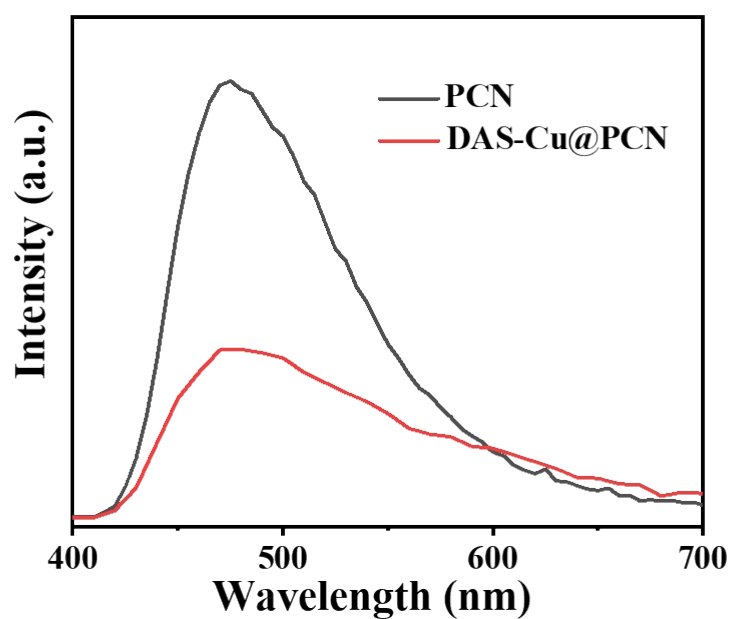Fig. S5 The C 1s high-resolution XPS pattern of PCN and DAS-Cu@PCN

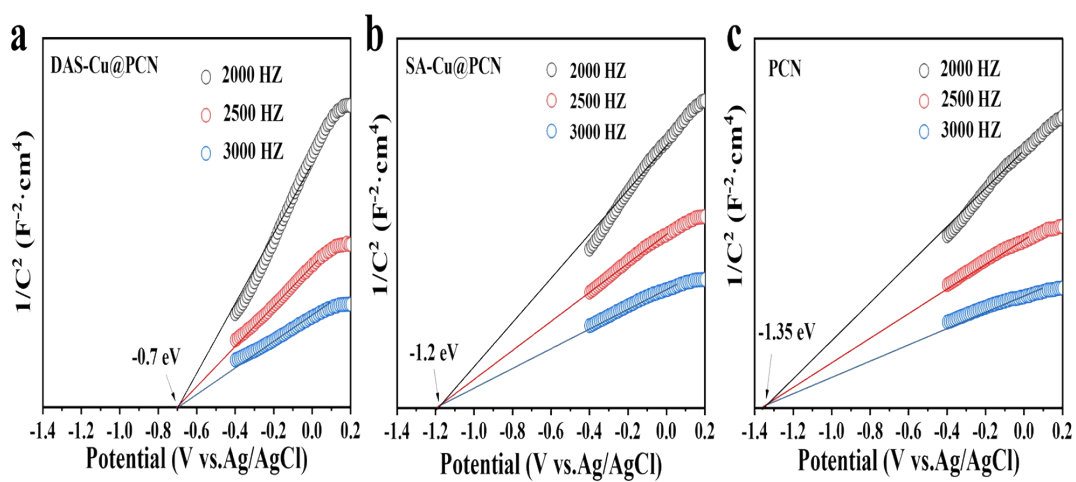Fig. S6 Photoluminescence (PL) emission spectra of different samples (λex = 375 nm)

Fig. S7 Mott-Schottky plots of the (a) DAS-Cu@PCN, (b) SA-Cu@PCN, (c) PCN
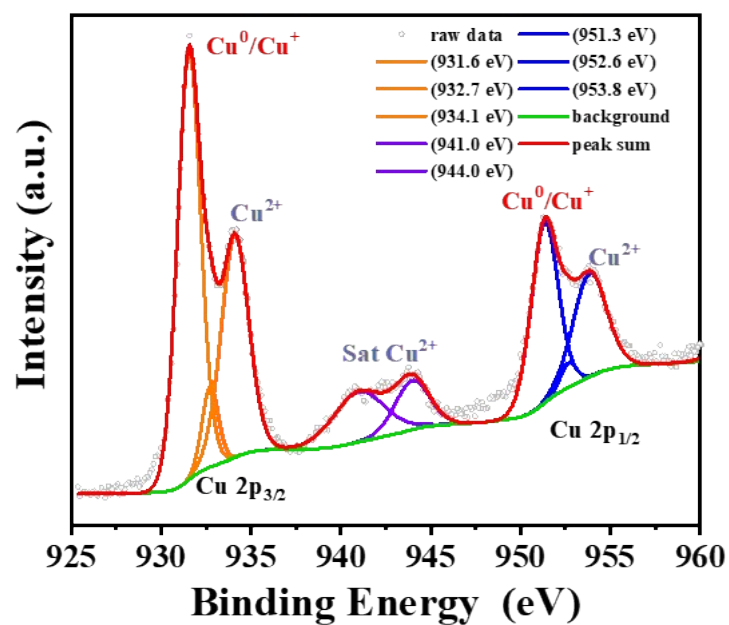
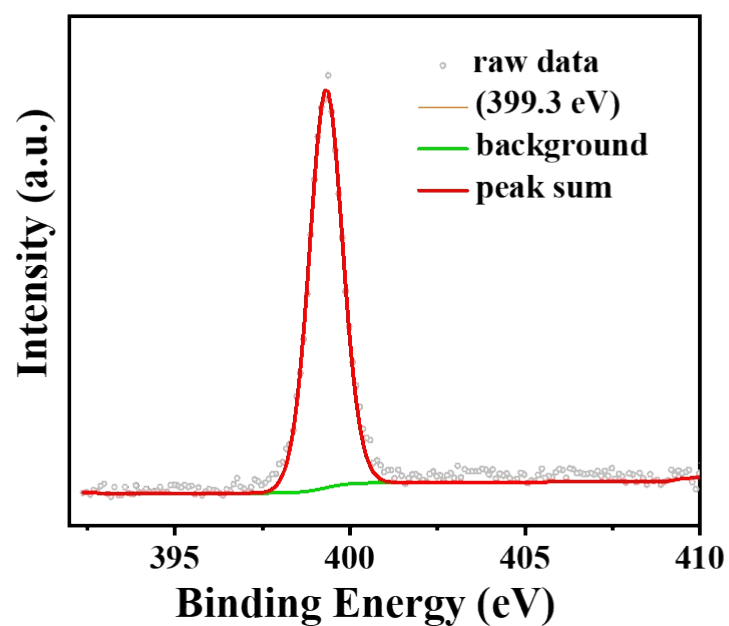Fig. S8 Cu 2p XPS spectra of CuCl-bpy
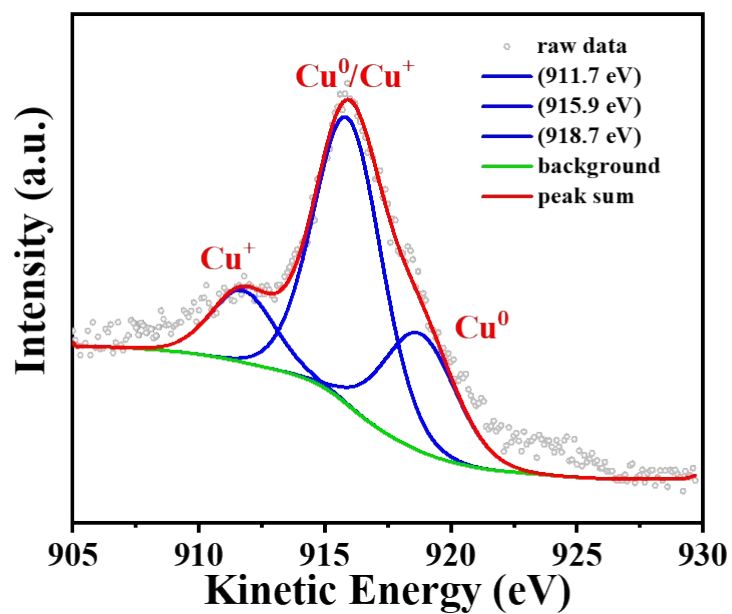

Fig. S9 N 1s XPS spectra of the CuCl-bpy
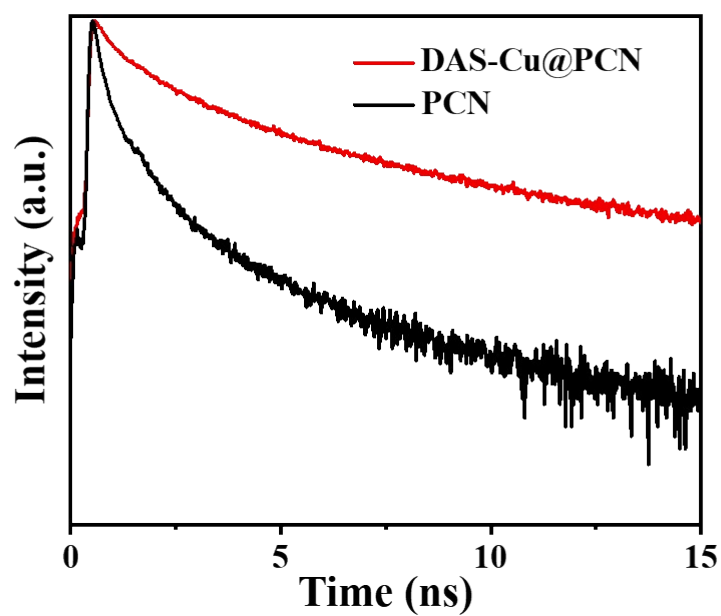
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Fig. S10 Auger spectra of the CuCl-bpy

Fig. S11 Tr-PL spectra of different samples obtained at 375 nm excitation and probed at 450 nm.
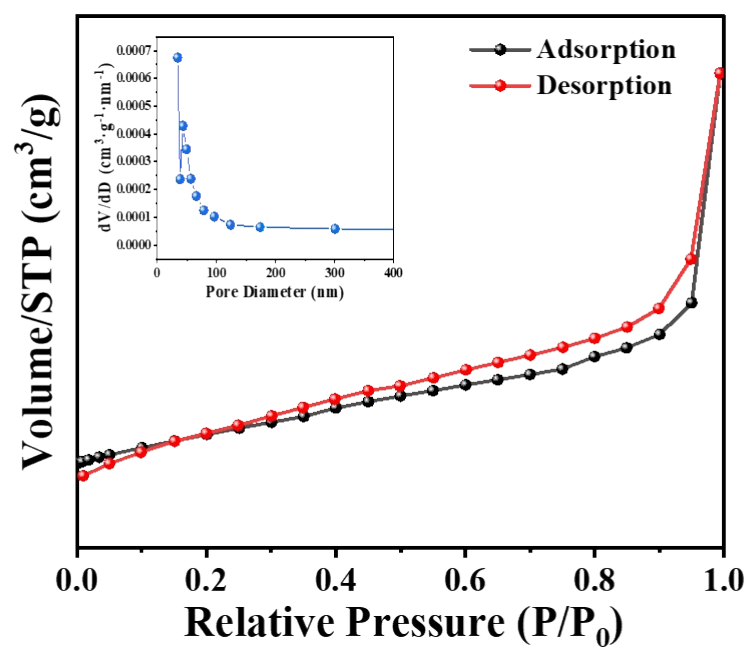
Fig. S12 Nitrogen adsorption and desorption isotherms of DAS-Cu@PCN and BJH pore size distribution curve (illustration)
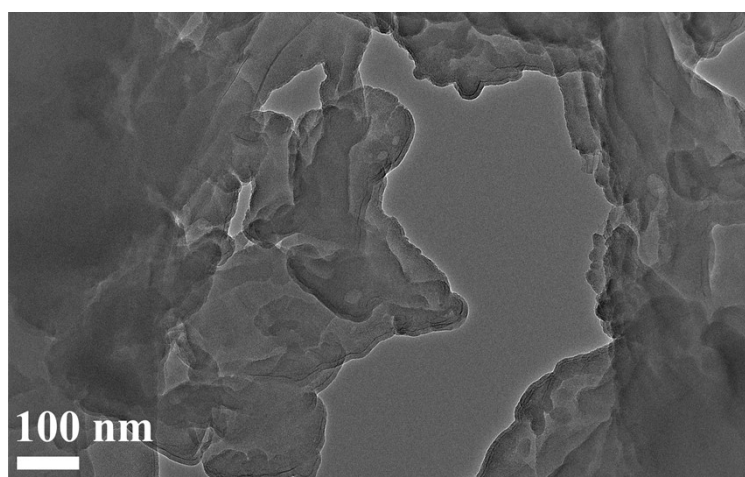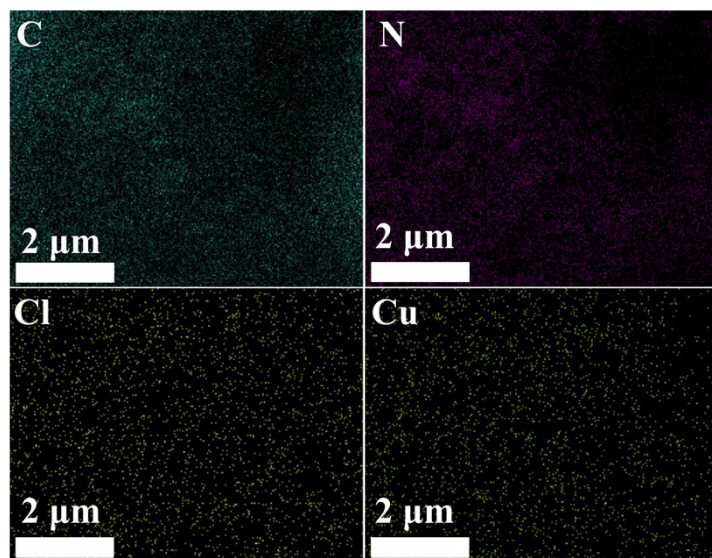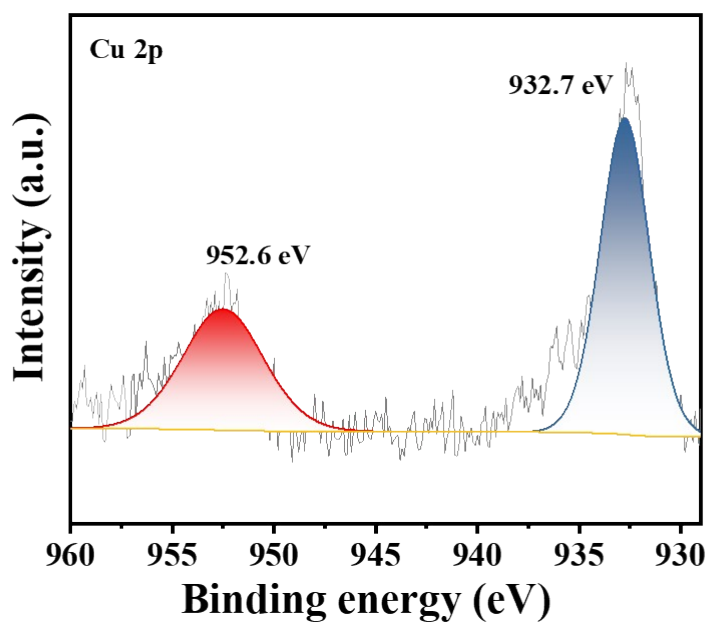

Fig. S13 TEM images of SA-Cu@PCN.

Fig. S14 Elemental mapping of SA-Cu@PCN.

Fig. S15 XPS of Cu 2p in SA-Cu@PCN.