

# Optimized hot electron injection from Cu Nanoparticles to S-doped C<sub>3</sub>N<sub>4</sub> by the formed S-Cu bonds for enhanced photocatalytic performance

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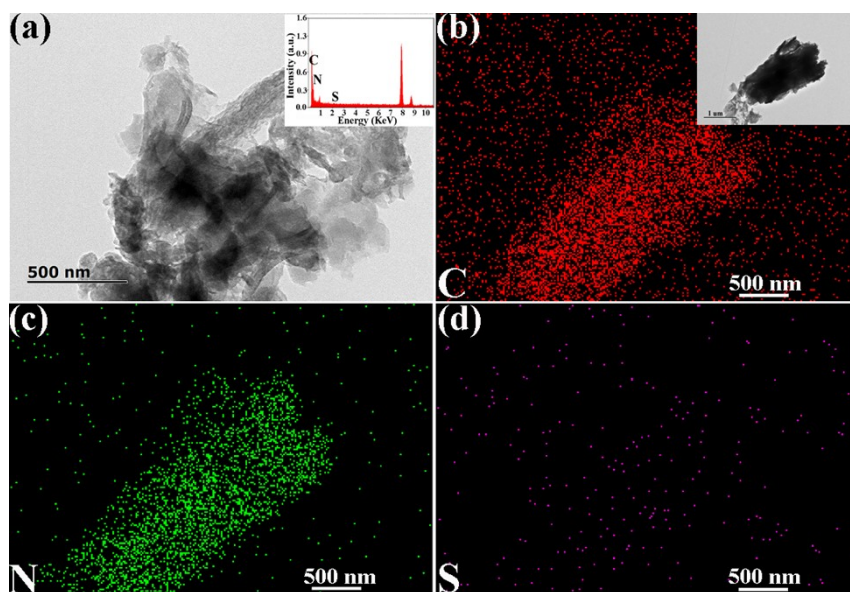


Fig. S1 (a) TEM image and (b-d) element mapping images of SCN. The insets in panel (a) and (b) correspond to its EDX spectrum and selected sample, respectively.

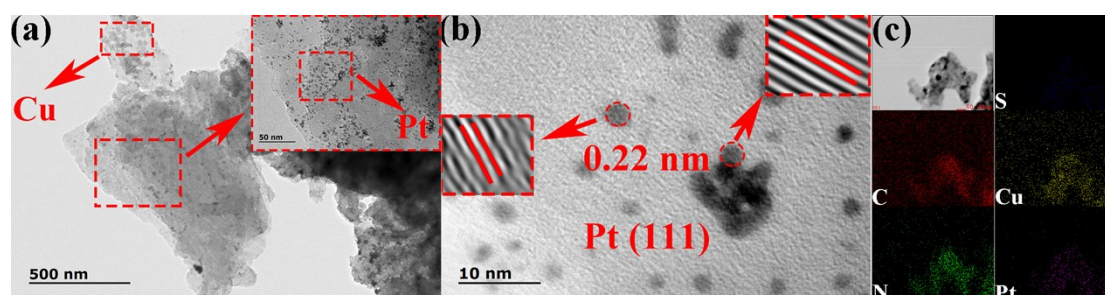


Fig. S2 (a) TEM, (b) HRTEM images and (c) element mapping of SCN-0.3Cu/Pt. Cu and Pt NPs are marked with red boxes in the upper left corner and inset of panel (a), respectively. The insets in panel (b) indicate that the lattice spacing of Pt is 0.22 nm.

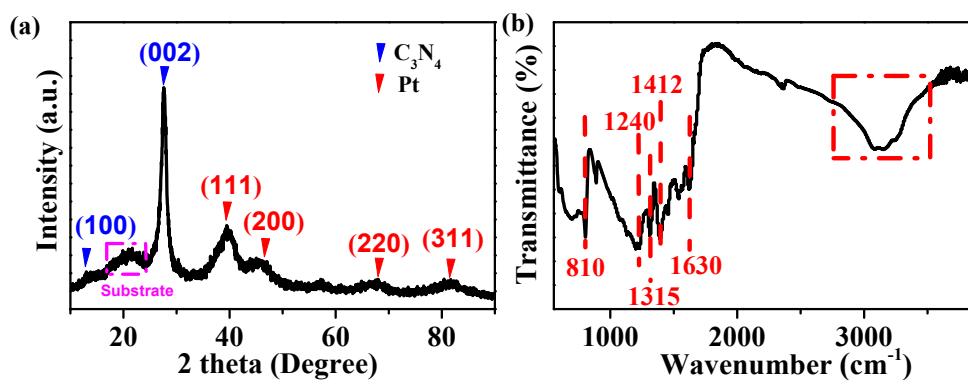


Fig. S3 (a) XRD spectra and (b) FT-IR spectra of SCN-Cu/Pt.

Table S1 The element mass percentage in SCN, SCN-0.3Cu and CN-0.35Cu.

Catalyst Elements	SCN	SCN-0.3Cu	CN-0.35Cu
C	35.95%	38.66%	38.42%
N	61.45%	54.86%	55.86%
S	0.33%	0.36%	-
O	2.27%	5.59%	5.24%
Cu	-	0.53%	0.48%

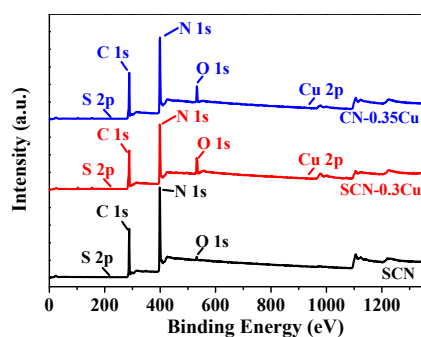


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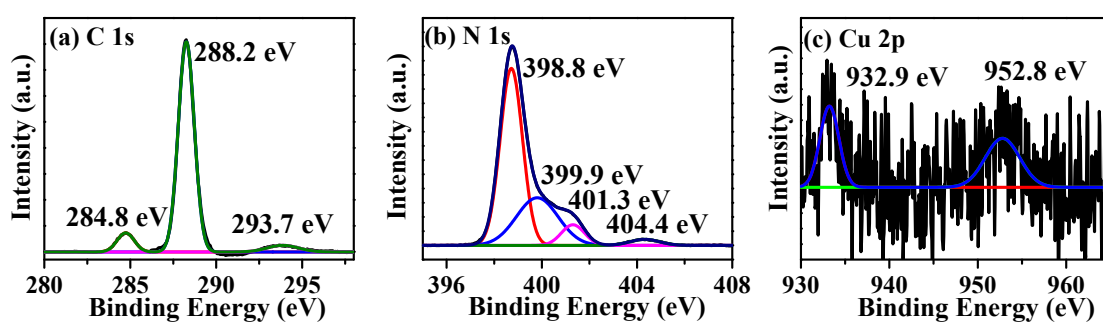


Fig. S5 High-resolution XPS spectra of (a) C 1s, (b) N 1s and (c) Cu 2p of CN-0.35Cu.

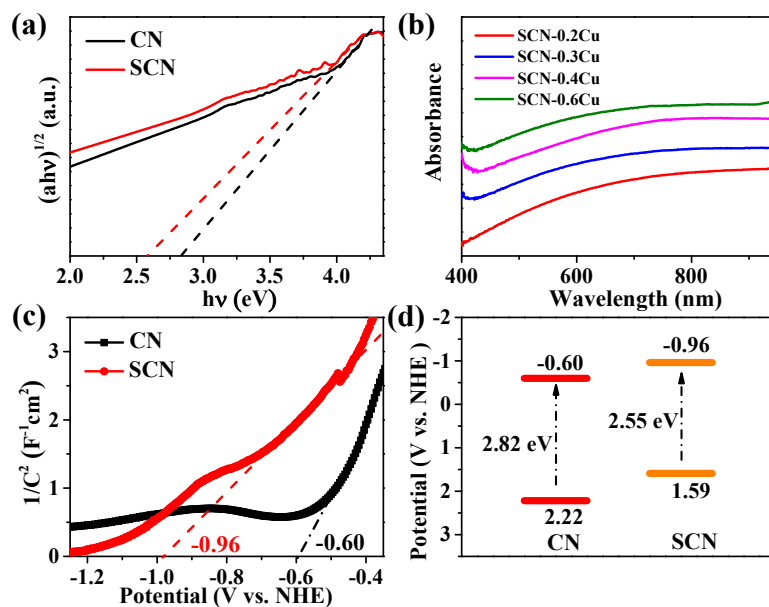


Fig. S6 (a) Tauc plots of CN and SCN, (b) the SPR absorption spectra of Cu NPs extracted by the absorption difference between SCN-xCu and SCN, (c) M-S plots and (d) bandgap structures of CN and SCN.

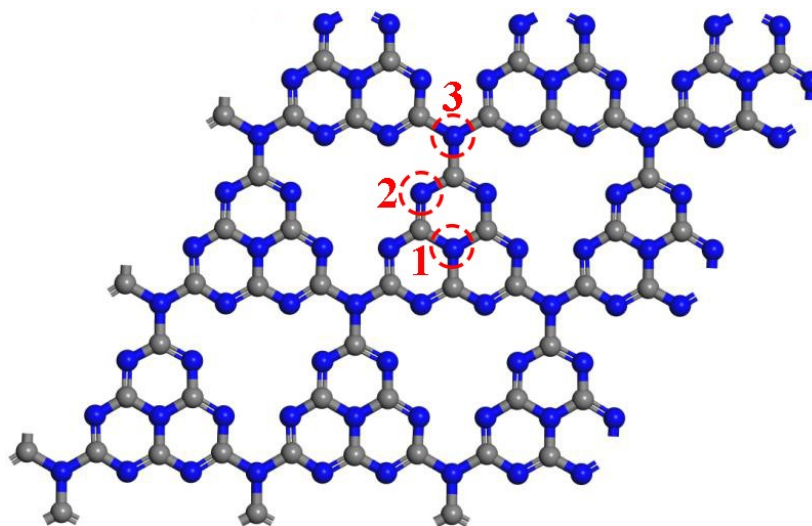


Fig. S7 Schematic diagram of various nitrogen atoms on  $C_3N_4$  in top view.

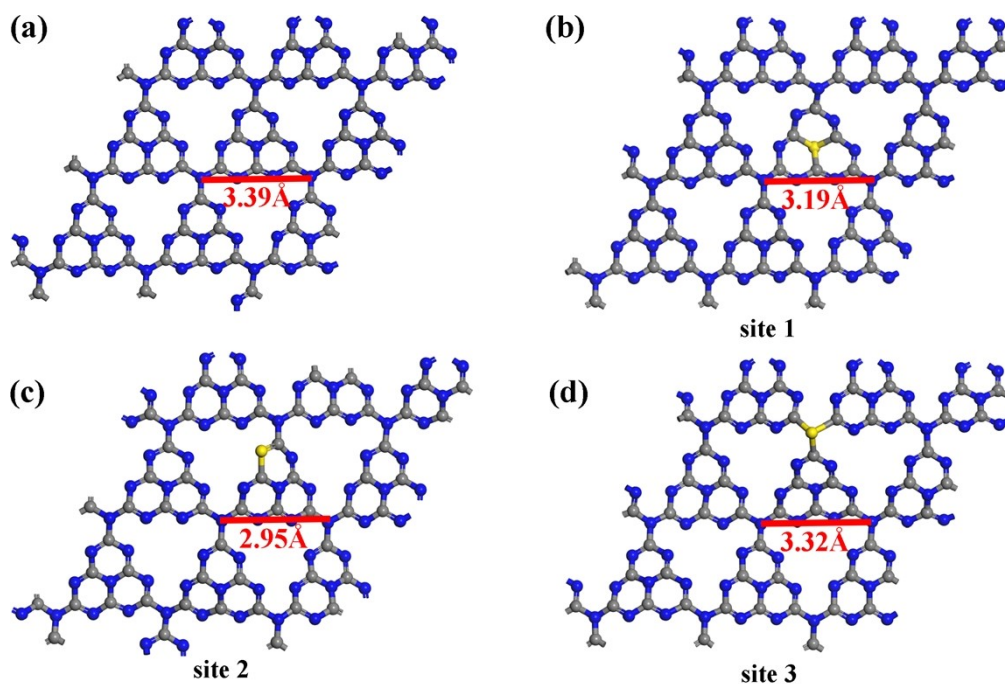


Fig. S8 Final relaxed structures of (a) CN and (b-d) three SCN compounds in which the S atom has been replaced by one of the N atoms.

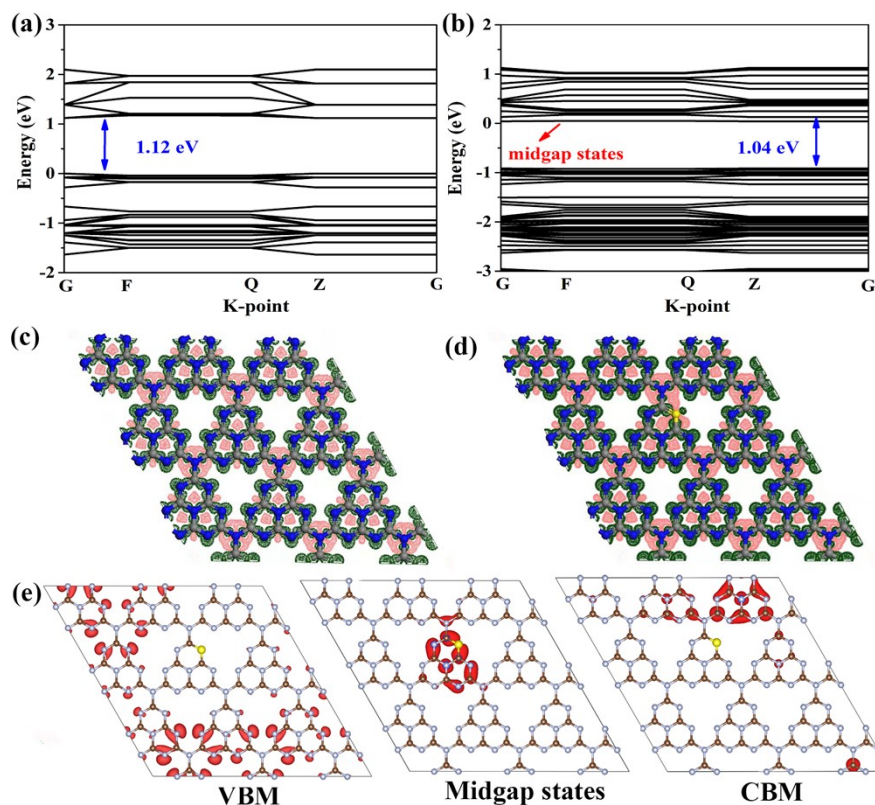


Fig. S9 Calculated band structures of (a) CN and (b) SCN in which N atoms at site 2 are replaced by S atom, and charge density difference of (c) CN and (d) SCN (the pink and green colors indicate charge accumulation and loss), and (e) VBM, midgap states and CBM of SCN in the isosurface value of  $0.002 \text{ e}\text{\AA}^{-3}$ .

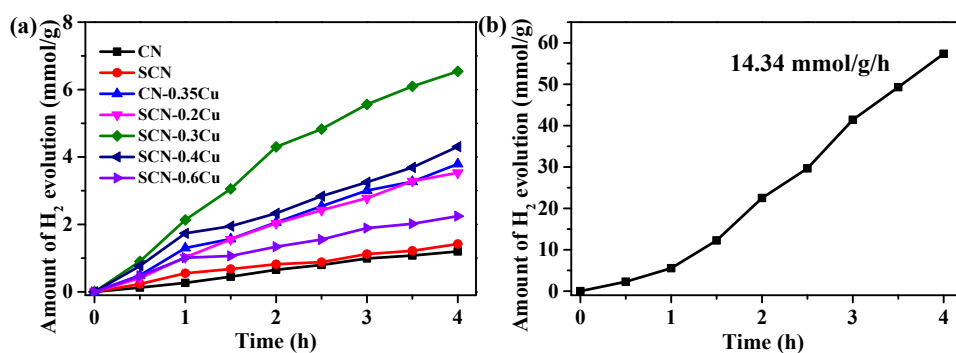


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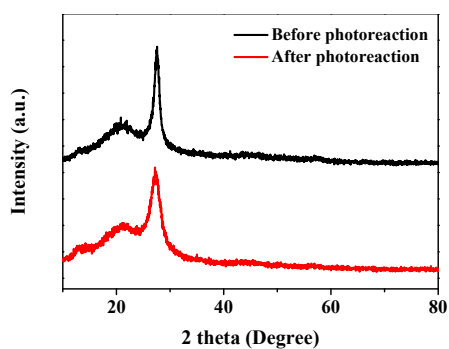


Fig. S11 XRD patterns of SCN-0.3Cu before and after photoreaction.

Table S2 Entries in the table are fitted from EIS results (Fig. 6a).

Samples	CN	SCN	CN-Cu	SCN-Cu
Rs ( $\Omega$ )	0.29	0.38	0.25	0.26
Rct ( $\Omega$ )	2871.0	1871.0	966.9	400.0

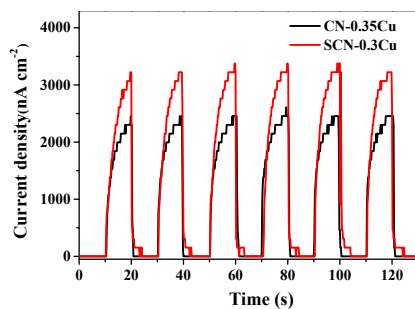


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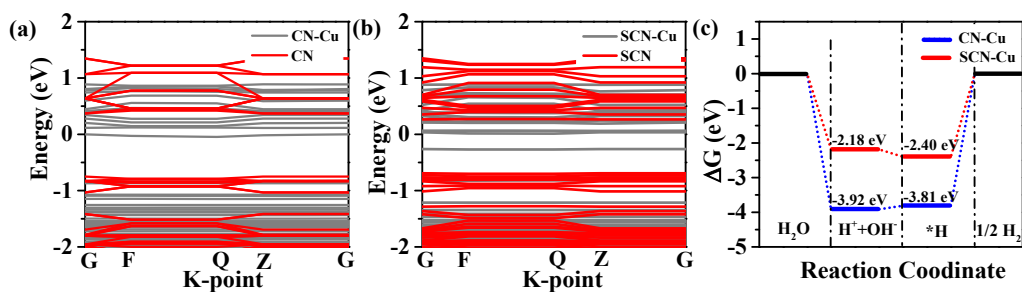


Fig. S13 Band structure of (a) CN-Cu and (b) SCN-Cu, and (c) their Gibbs free energy diagram for HER.