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Tandem Effect of Atomically Isolated Copper–Nitrogen Sites and Copper
Clusters Enhances CO₂ Electroreduction to Ethylene

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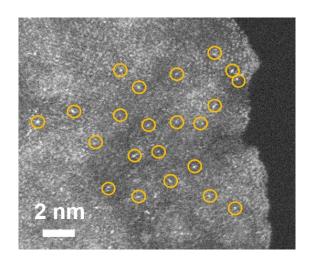


Figure S1. STEM image of PDI-Cu

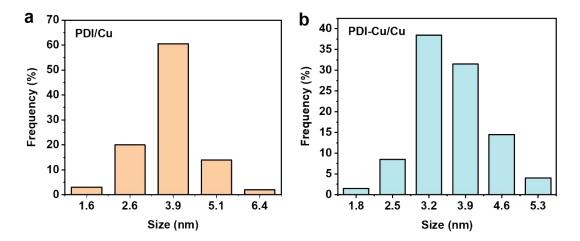


Figure S2. size distribution of Cu clusters on (a) PDI/Cu and (b) PDI-Cu/Cu.

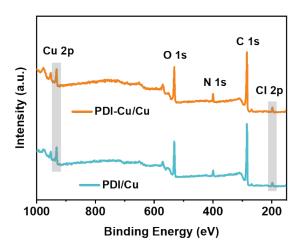


Figure S3. The full XPS survey spectra.

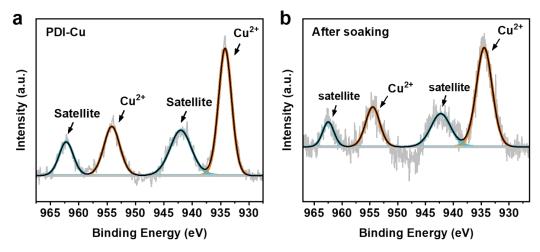


Figure S4. Cu 2p XPS spectra of (a) PDI-Cu and (b) PDI-Cu after soaking L-ascorbic acid.

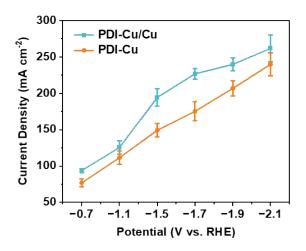


Figure S5. Total current densities of PDI-Cu/Cu and PDI/Cu.

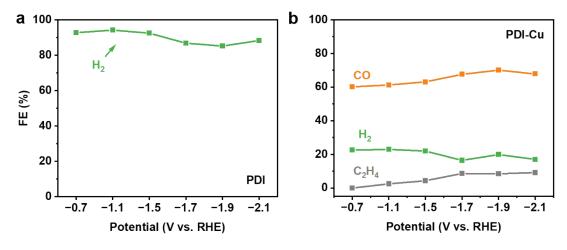


Figure S6. FEs of different products for (a)PDI and (b) PDI-Cu.

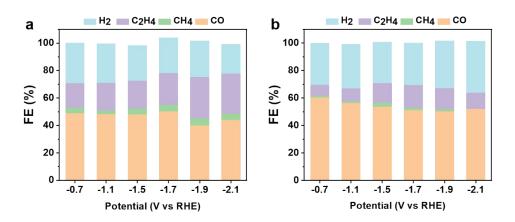


Figure S7. FEs of CO2RR products at different applied potentials (V vs. RHE) catalyzed by (a)PDI-Cu/Cu and (b) PDI/Cu.

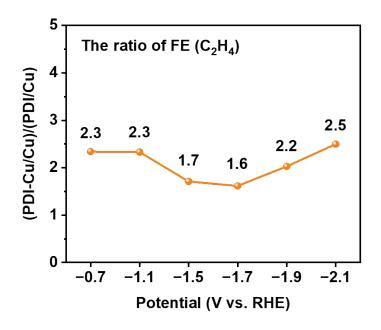


Figure S8. The FE (C₂H₄) ratio of PDI-Cu/Cu to PDI/Cu.

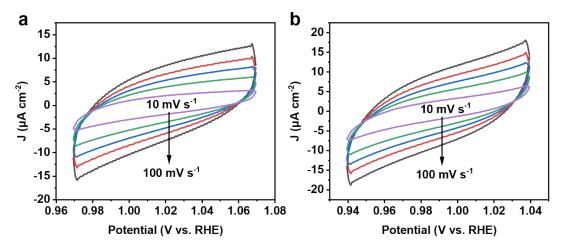


Figure S9. Typical cyclic voltammograms of (a) PDI-Cu/Cu and (b) PDI/Cu at different scan rate.

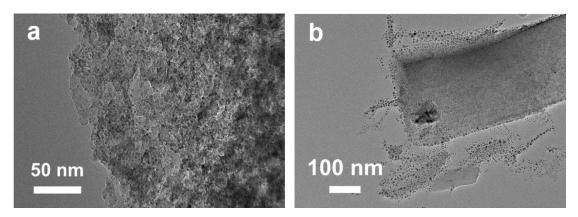


Figure S10. The TEM images of (a) PDI-Cu/Cu and (b) PDI/Cu after the electrochemical CO₂RR.

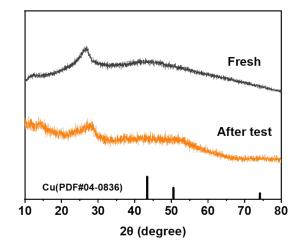


Figure S11. XRD patterns of before and after electrochemical CO₂RR of PDI-Cu.

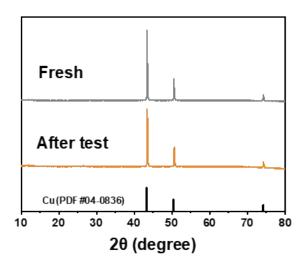


Figure S12. XRD patterns of before and after electrochemical CO₂RR of PDI-Cu/Cu.

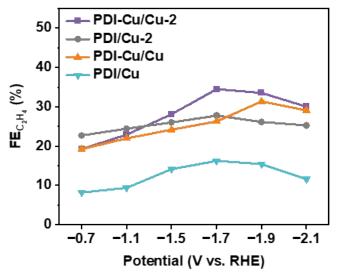


Figure S13. The FEs for C_2H_4 conversion catalyzed by PDI-Cu/Cu, PDI-Cu, PDI-Cu/Cu-2 and PDI/Cu-2.

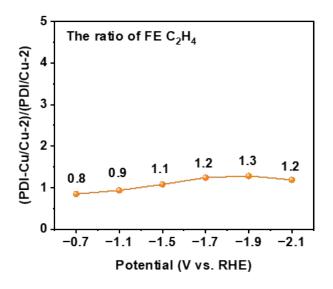


Figure S14. The FE (C₂H₄) ratio of PDI-Cu/Cu-2 to PDI/Cu-2.

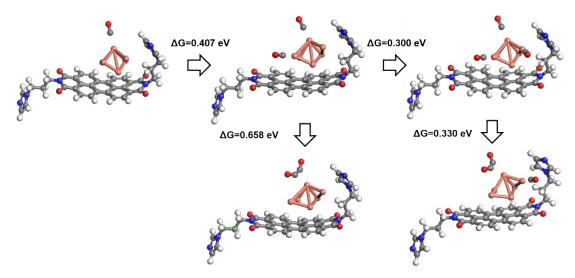


Figure S15. The complete structures of CO adsorption and C-C coupling on Cu clusters.

 Table S1. The ICP results of the PDI-Cu, PDI-Cu/Cu and PDI/Cu samples.

| | PDI-Cu | PDI-Cu/Cu | PDI/Cu |
|---------------------|--------|-----------|--------|
| Content of Cu (wt%) | 7.70 | 46.3 | 40.2 |

Table S2. The EXAFS curve-fitting results of the PDI-Cu samples.

| Sample | Path | CN | R (Å) | $\sigma^2 (10^{-3} \text{ Å}^2)$ |
|--------|-------|----------------|------------------|----------------------------------|
| PDI-Cu | Cu-N | $2.0(\pm 0.2)$ | $1.95(\pm 0.01)$ | $0.7(\pm 0.1)$ |
| | Cu-Cl | $2.0(\pm 0.1)$ | $2.30(\pm0.02)$ | $1.2(\pm 0.1)$ |

 Table S3. The ICP results of the PDI-Cu/Cu-2 and PDI/Cu-2 samples.

| | PDI-Cu/Cu-2 | PDI/Cu-2 |
|---------------------|-------------|----------|
| Content of Cu (wt%) | 74.7 | 84.2 |