

## **Enhanced plasmonic photocatalytic performance of $C_3N_4/Cu$ by the introduction of reduced graphene oxide interlayer**

Qixiao Gai<sup>a,b</sup>, Shoutian Ren<sup>a\*</sup>, Xiaochun Zheng<sup>a,b</sup>, Wenjun Liu<sup>a\*</sup>

<sup>a</sup> Department of Optoelectronic Science, Harbin Institute of Technology at Weihai, Weihai 264209,  
People's Republic of China

<sup>b</sup> Department of Physics, Harbin Institute of Technology, Harbin 150001, People's Republic of  
China

\*Corresponding author:

E-mail address: [renst77@163.com](mailto:renst77@163.com); [liuwenjun86@163.com](mailto:liuwenjun86@163.com)

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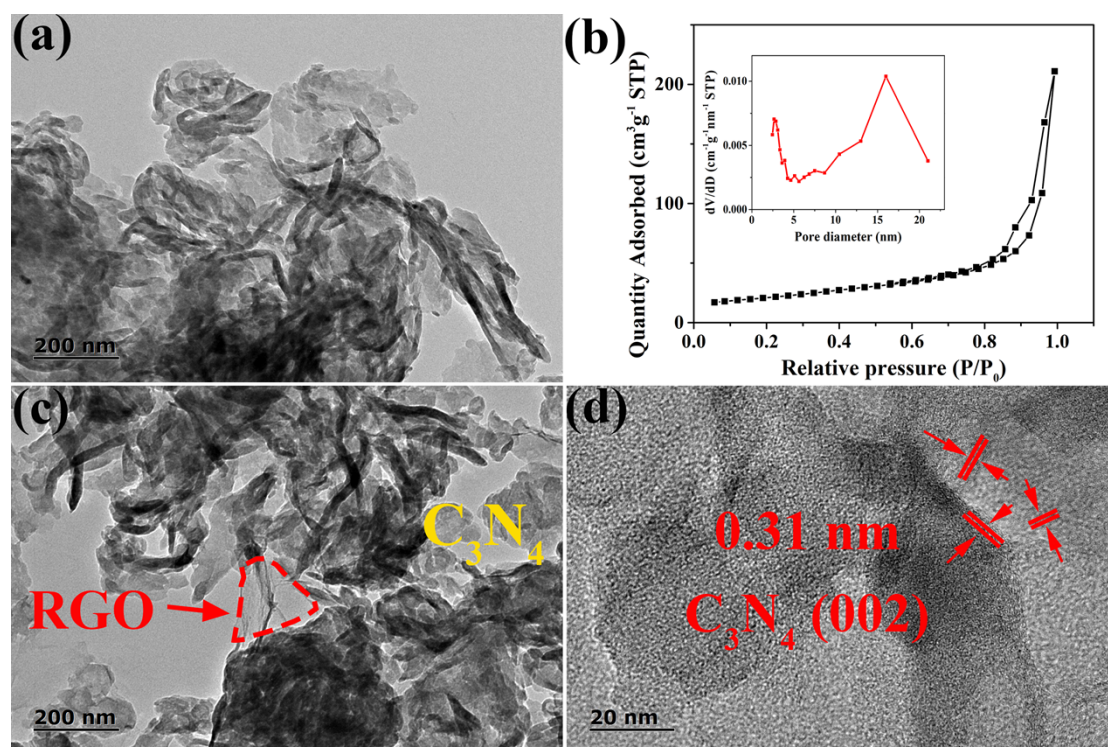


Fig. S1 (a) TEM image and (b) N<sub>2</sub> adsorption-desorption isotherm distribution of PCN, and (c) TEM and (d) HRTEM images of PCN/RGO. The insets in panel (b) correspond to the corresponding pore diameter distribution of PCN.

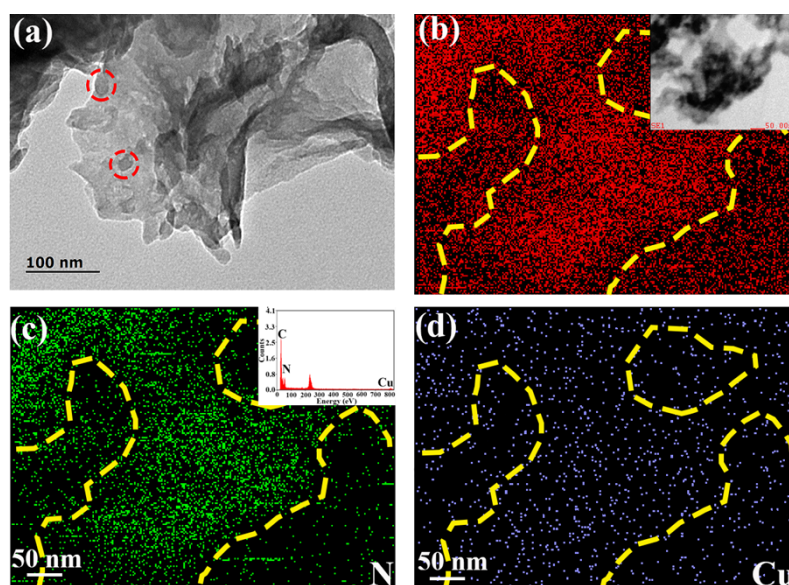


Fig. S2 TEM image (a) and element mapping distribution (b-d) of PCN/23Cu. Cu NPs are marked with red circles in panel (a), and the insets in panel (b) and (c) correspond to the detected sample and EDS result, respectively.

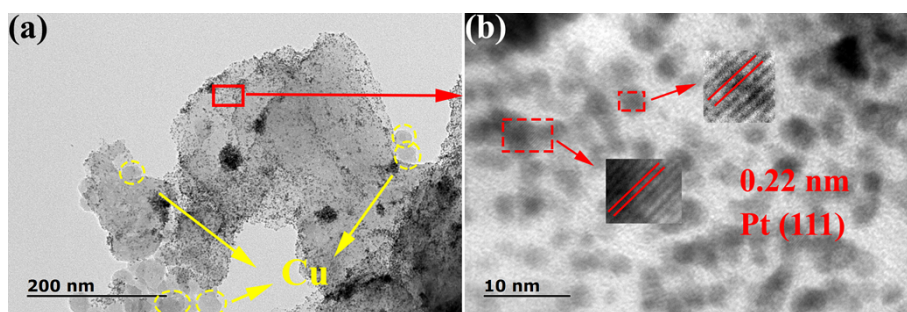


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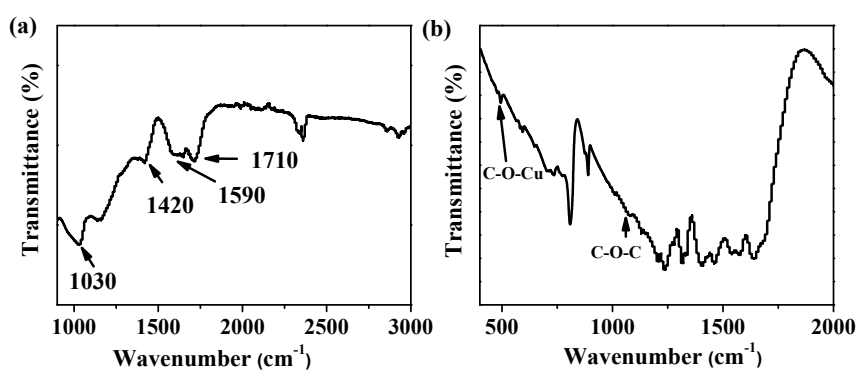


Fig. S4 FT-IR spectra of (a) GO and (b) PCN/RGO/25Cu.

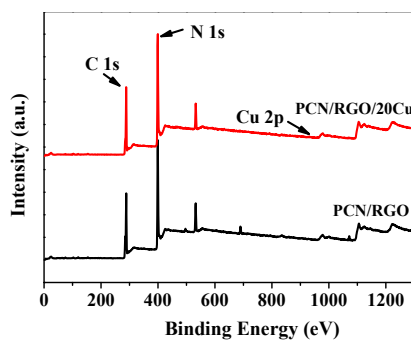


Fig. S5 Survey-level scan XPS spectra of PCN/RGO and PCN/RGO/20Cu.

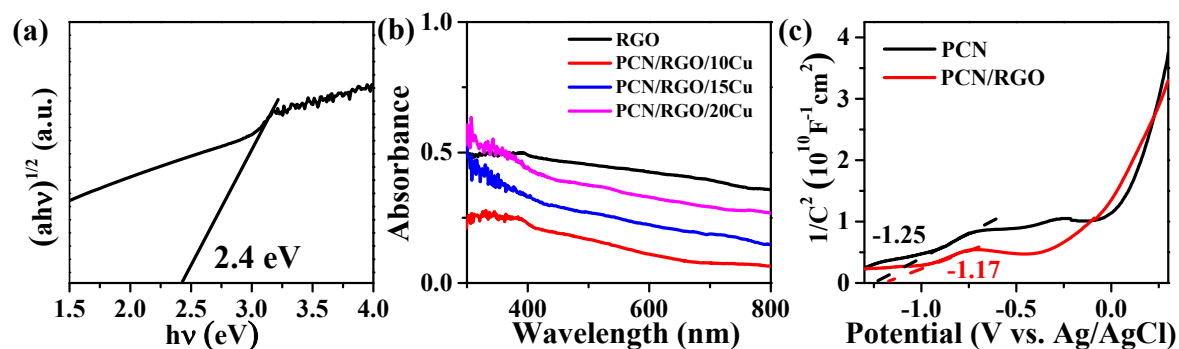


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Table S1 Zeta potential values of PCN, GO and PCN/RGO.

| Potential value (mV)<br>Number | Catalyst |        |         |
|--------------------------------|----------|--------|---------|
|                                | PCN      | GO     | PCN/RGO |
| 1                              | 6.17     | -39.60 | -0.93   |
| 2                              | 7.49     | -43.70 | -0.67   |
| 3                              | 9.81     | -38.70 | -1.60   |
| Average                        | 7.82     | -40.67 | -1.07   |

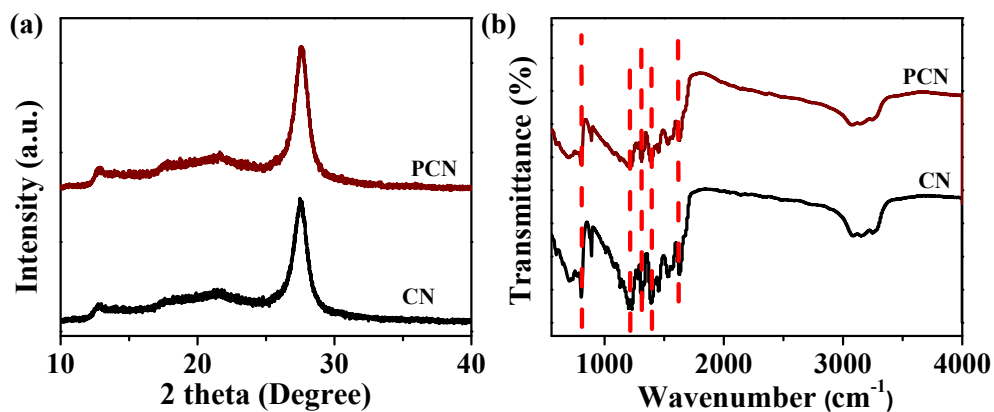


Fig. S7 (a) XRD and (b) FT-IR spectra of CN and PCN.

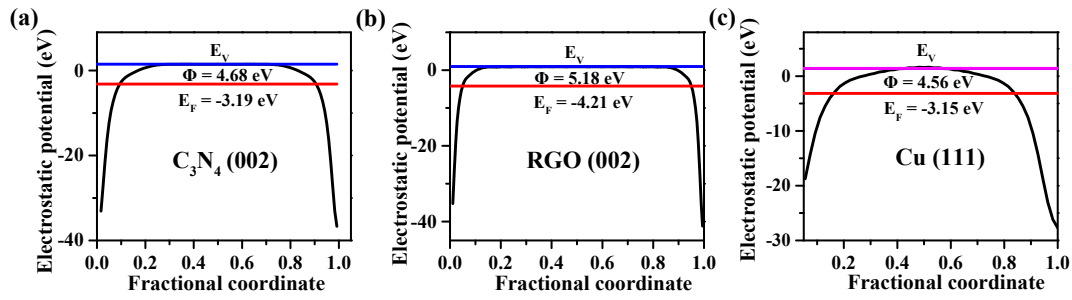


Fig. S8 Calculated Fermi levels of (a)  $C_3N_4$  (002), (b) RGO (002) and (c) Cu (111).

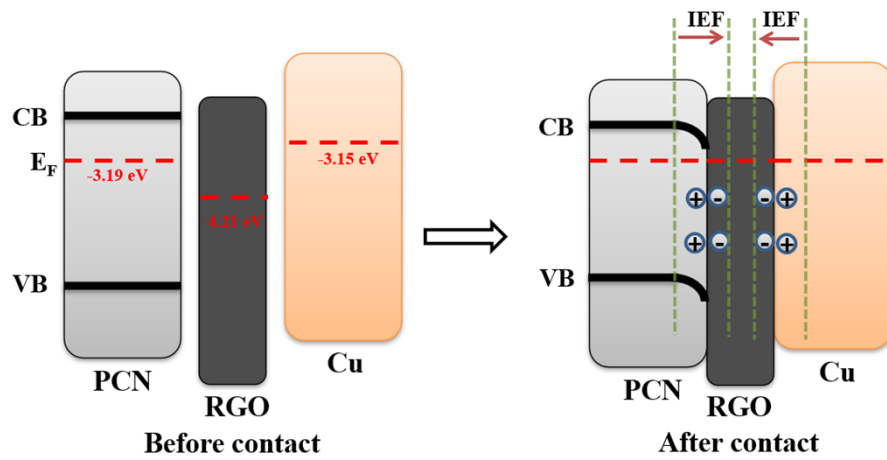


Fig. S9 Schematic diagrams of PCN/RGO/Cu heterojunction: IEF induced charge transfer and separation.

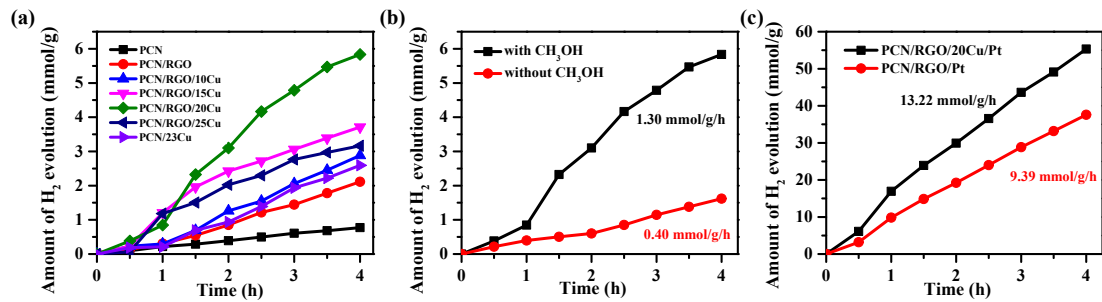


Fig. S10 Time courses of photocatalytic hydrogen production of (a) PCN, PCN/RGO, PCN/23Cu, different PCN/RGO/Cu and (b) PCN/RGO/20Cu with  $CH_3OH$  and without  $CH_3OH$  and (c) PCN/RGO/20Cu/Pt and PCN/RGO/Pt.

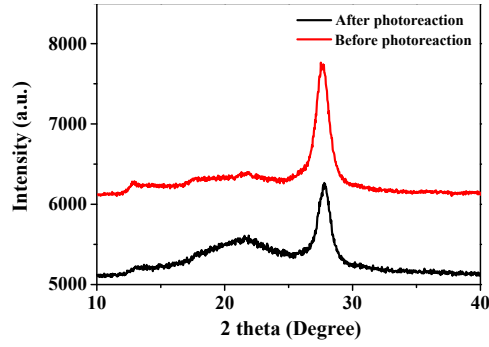


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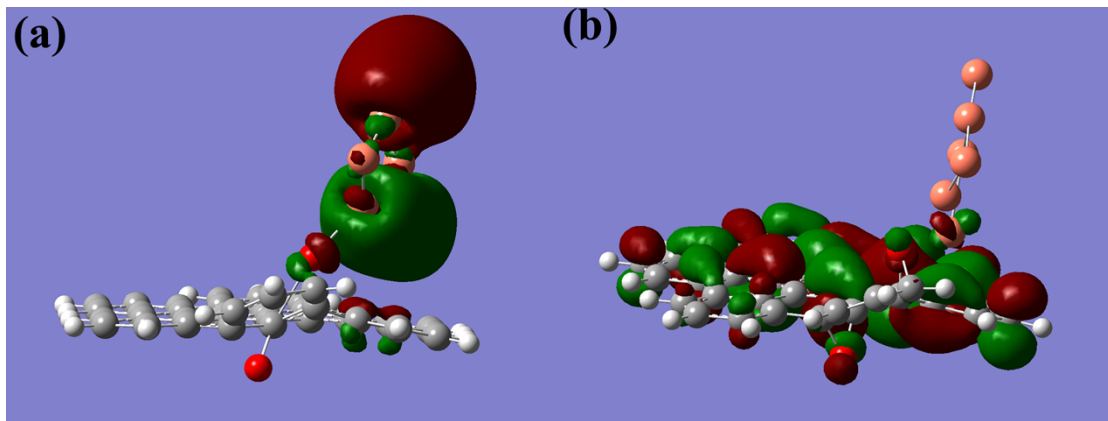


Fig. S12 Orbital distribution of RGO/Cu composites in the highest oscillator strength transition state (a) before and (b) after excitation, respective. The green and red parts are orbital wave functions

Table S2 Entries in the table fitted from EIS results (Fig.7a).

| Samples               | PCN    | PCN/RGO | PCN/23Cu | PCN/RGO/20Cu |
|-----------------------|--------|---------|----------|--------------|
| $R_s$ ( $\Omega$ )    | 0.25   | 0.28    | 0.31     | 0.26         |
| $R_{ct}$ ( $\Omega$ ) | 1213.0 | 946.5   | 659.4    | 209.1        |

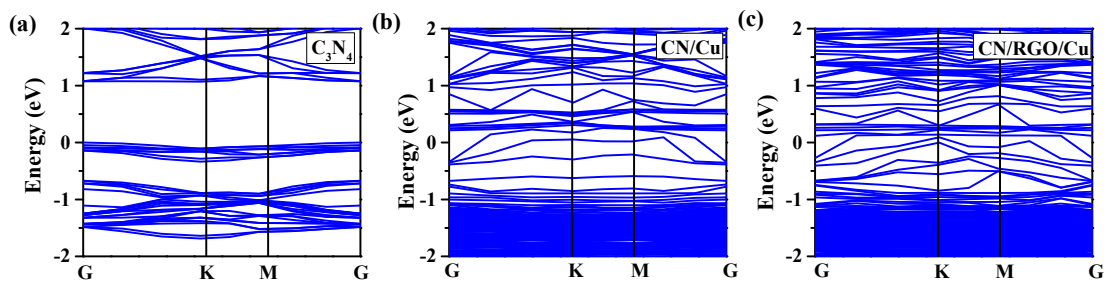


Fig. S13 The band structures of (a)  $C_3N_4$ , (b) CN/Cu and (c) CN/RGO/Cu

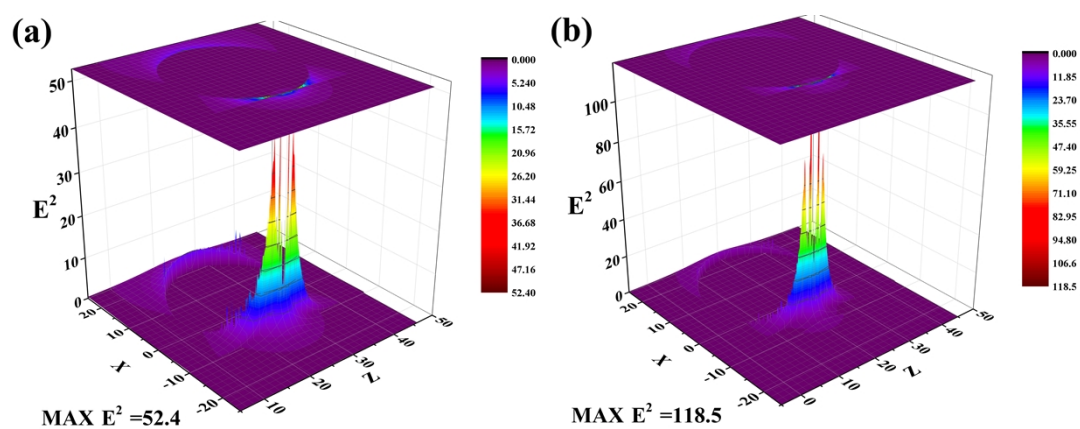


Fig. S14 Colormap surface with projection of the electromagnetic field distributions of (a) PCN/Cu and (b) PCN/RGO/Cu under linear plane wave illumination.

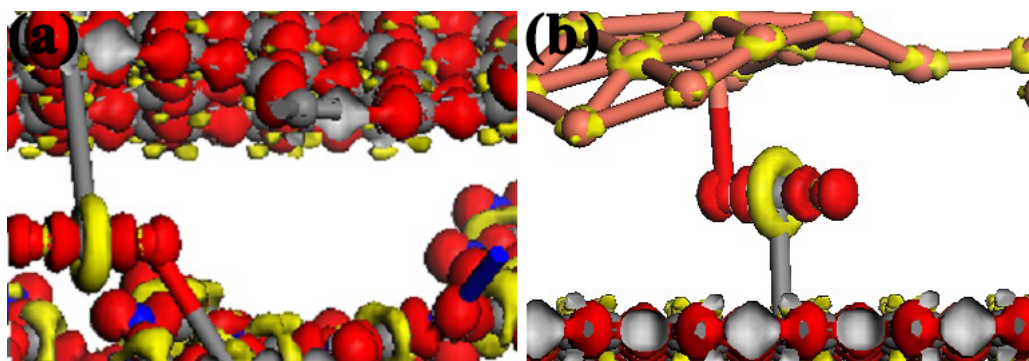


Fig. S15 Charge difference density of PCN/RGO and RGO/Cu. The red and yellow regions represent electron enrichment and depletion regions, respectively.



Table S3 Total Mulliken charge populations of PCN/RGO, WPCN/RGO, RGO/Cu and WRGO/Cu.

|          | SUM PCN (e) | SUM RGO (e) | SUM Cu (e) |
|----------|-------------|-------------|------------|
| PCN/RGO  | -0.46       | 0.44        |            |
| WPCN/RGO | -0.03       | 0.06        |            |
| RGO/Cu   |             | -0.33       | 0.38       |
| WRGO/Cu  |             | -0.25       | 0.31       |

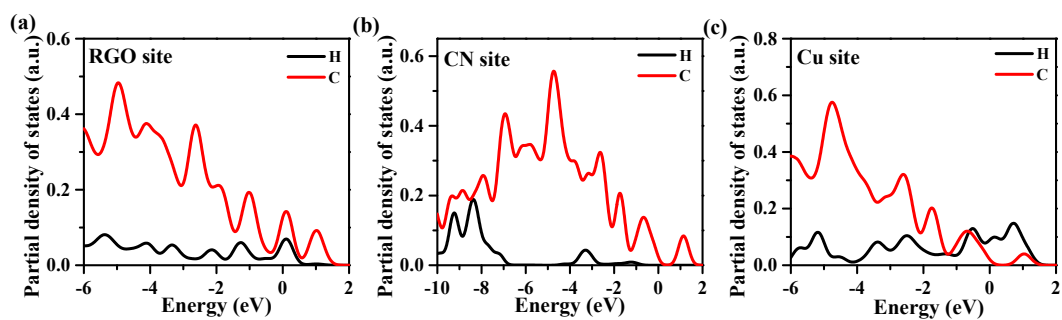


Fig. S16 The partial density of states of different sites.

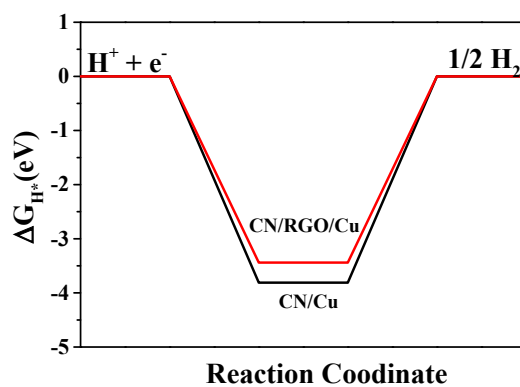


Fig. S17 Gibbs free energy for hydrogen adsorption on CN/RGO/Cu and CN/Cu.