Electronic Supplementary Material (ESI) for Nanoscale.

CO_2 Reduction on Phosphorene and Cu-doped Phosphorene: A first-principles study

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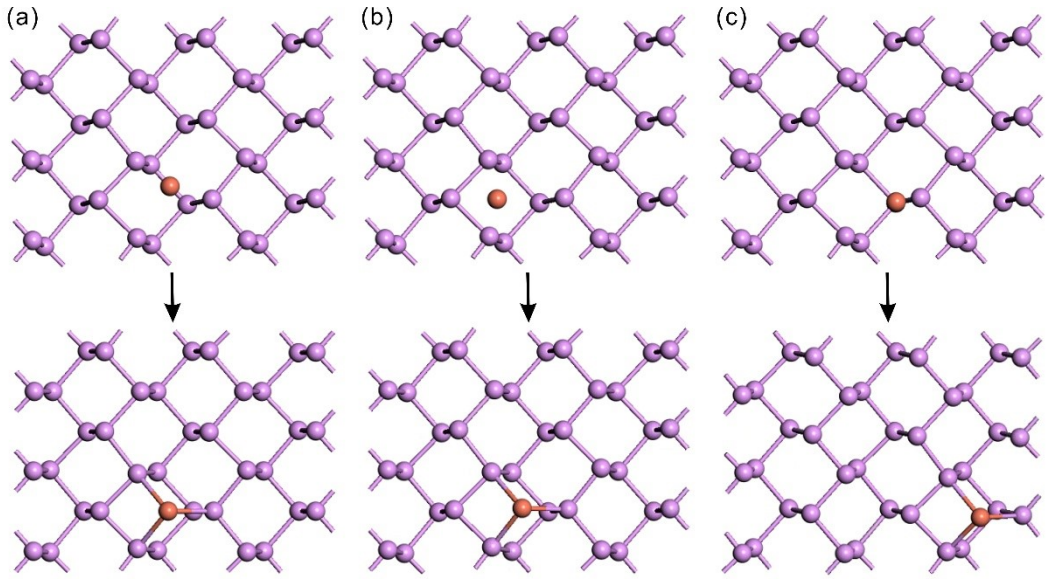


Figure S1. The initial and optimized configurations of different Cu doped phosphorenes: (a) the bridging site, (b) the hollow site and (c) the on-top site. (Colors: purple, phosphorous atom; rust red, Cu atom)

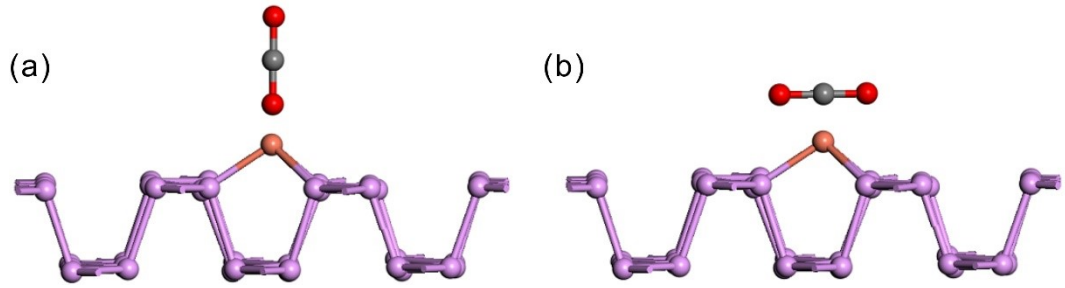


Figure S2. Two different interaction modes of CO_2 on Cu-doped phosphorene: (a) with one O atom pointing to the dopant, (b) CO_2 paralleling to the Cu-doped phosphorene.

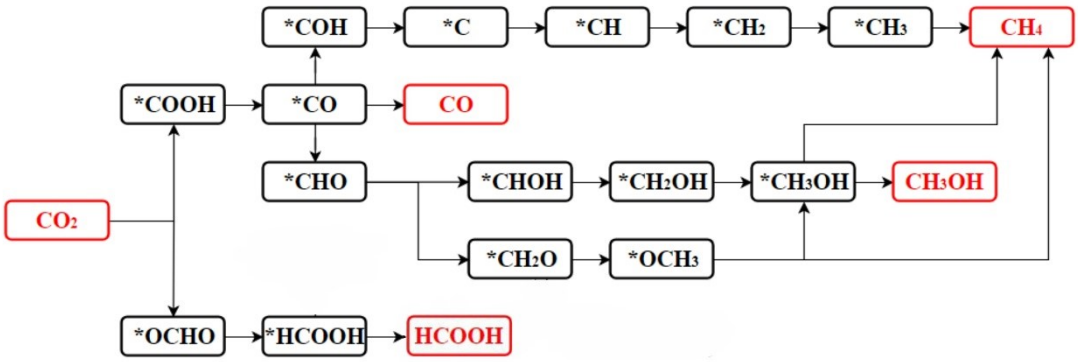


Figure S3. Possible reaction intermediates and pathways of CRR for producing HCOOH, CH_4, CH_3OH and CO.

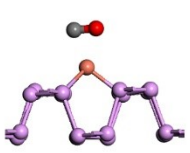
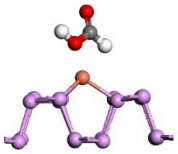
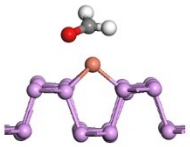
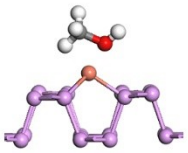
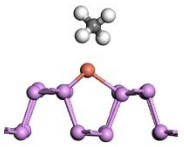
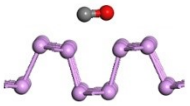
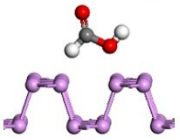
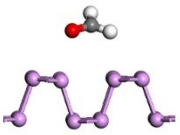
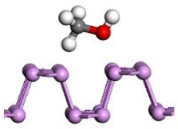
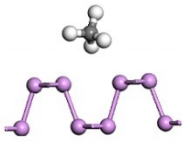
	*CO	*HCOOH	*CH_2O	*CH_3OH	*CH_4
Cu doped	 E_{ads}=-0.95 eV	 E_{ads}=-0.44 eV	 E_{ads}=-0.92 eV	 E_{ads}=-0.49 eV	 E_{ads}=0.01 eV
pristine	 E_{ads}= 0.14 eV	 E_{ads}=-0.07 eV	 E_{ads}=-0.48 eV	 E_{ads}=0.11 eV	 E_{ads}=0.21 eV

Figure S4. Summary of the adsorption energy (E_{ads}) and configurations of possible reaction intermediates on pristine and Cu-doped phosphorene explored by this study.

Table S1. The adsorption energy (E_{ads}) of Cu atom on phosphorene with different initial adsorbed site (See Figure S1).

	hollow	bridge	top
E_{ads}/eV	-2.77	-2.77	-1.75
Distance/Å	0.03	0.03	0.03