Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

A combined theoretical and experimental investigation on the photocatalytic hydrogenation of CO_2 on Cu/ZnO polar surface

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Table. S1 Adsorption energies (in eV) for Cu adsorbed on clean polar surfaces of ZnO(0001) and ZnO($000\bar{1}$)

Cu/ZnO	top	bridge	fcc	hcp
(0001)	-2.44	-2.57	-2.86	-2.79
($000\bar{1}$)	-3.85	-4.49	-4.49	-3.86

Table. S2 Adsorption energies (in eV) for CO_2 and H_2 adsorbed on clean surface of ZnO(0001) and ZnO($000\bar{1}$)

Clean ZnO surface	top	bridge	fcc	hcp
(0001)/CO_2	-0.08	-0.04	-0.05	-0.06
(0001)/H_2	-0.05	-0.04	-0.03	-0.02
($000\bar{1}$)/CO_2	-0.05	-0.04	-	-
($000\bar{1}$)/H_2	-3.30	-4.96	-4.96	-0.01

Table. S3 Adsorption energies (in eV) of Cu_9 adsorbed on clean surface of ZnO(0001), CO_2 adsorbed on Cu_9/ZnO(0001) surface, and H_2 adsorbed on Cu_9/ZnO(0001) surface.

	ZnO(0001)	Cu_9 /ZnO(0001)
Cu_9	-7.45	-
CO_2	-	-0.80
H_2	-	-0.27

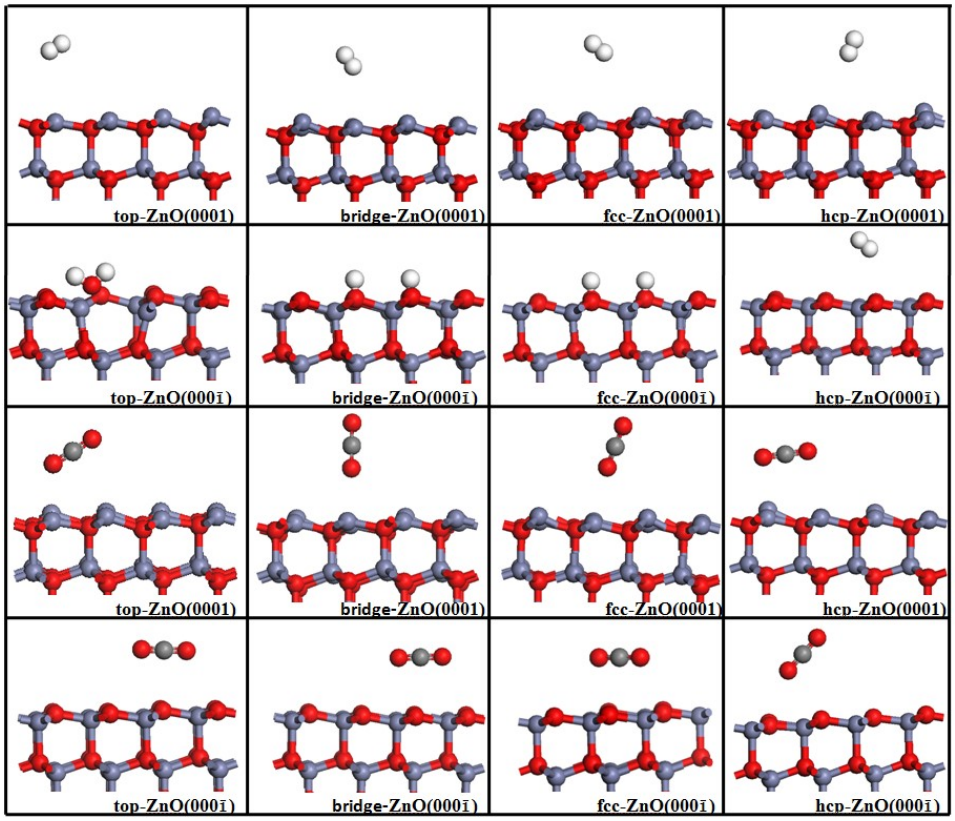

Fig. S1. The geometrical structures of CO_2 and H_2 adsorb on four different sites of clean polar ZnO(0001) and ZnO(000$\bar{1}$) surfaces

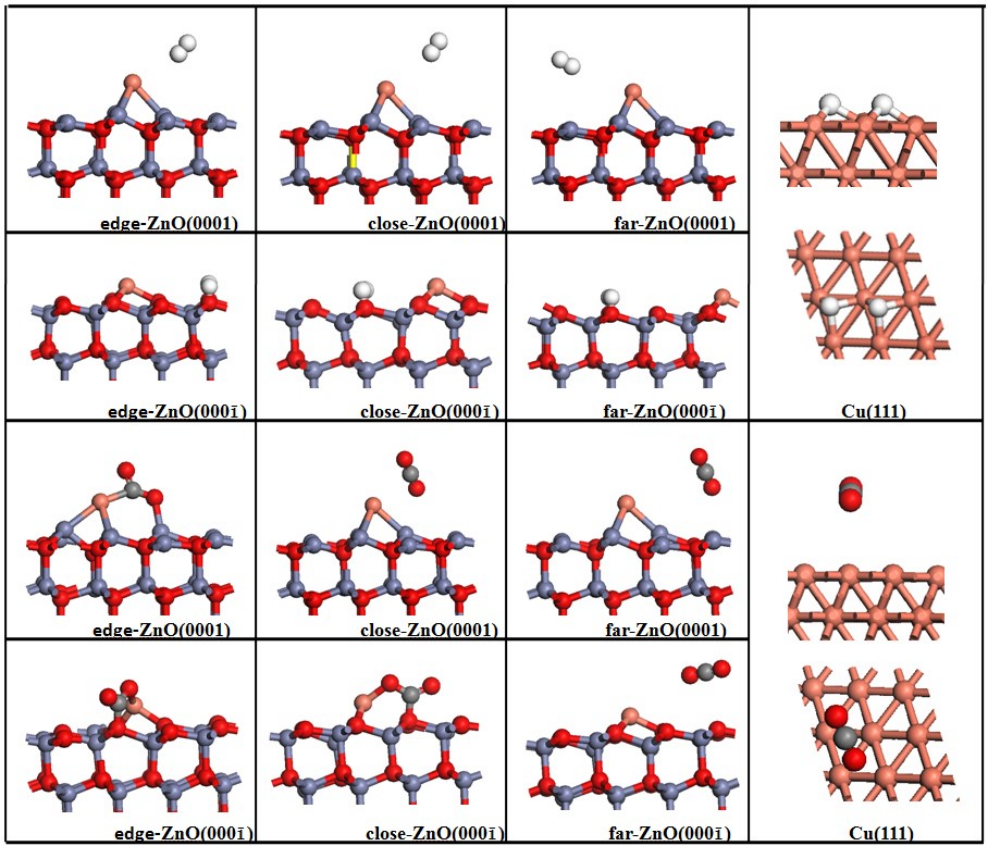

Fig. S2. The geometrical structures of CO_2 and H_2 adsorb on three different sites of polar Cu/ZnO(0001) and Cu/ZnO ($000\bar{1}$) surfaces, including the CO_2 and H_2 adsorb on metallic site on Cu(111) surface.

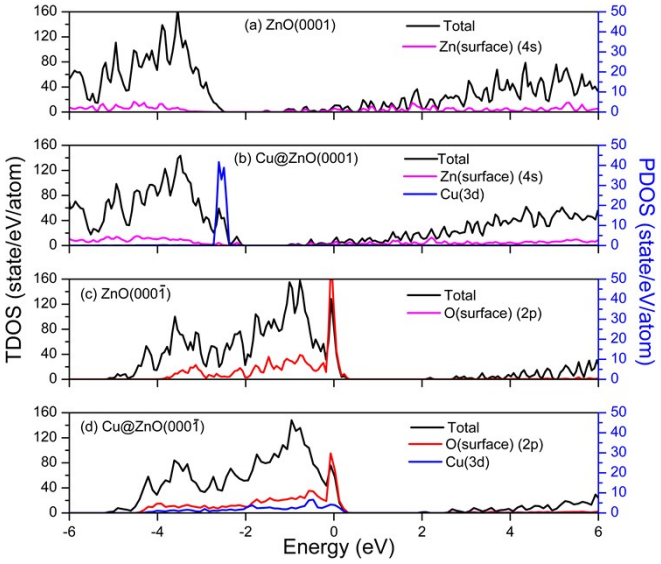

Fig. S3 Partial density of states (PDOS) for (a) clean polar surface of ZnO(0001) , (b) Cu deposited on fcc-site of ZnO(0001), (c) clean polar surface of ZnO(000$\bar{1}$), (d) Cu deposited on fcc-site of ZnO(000$\bar{1}$)

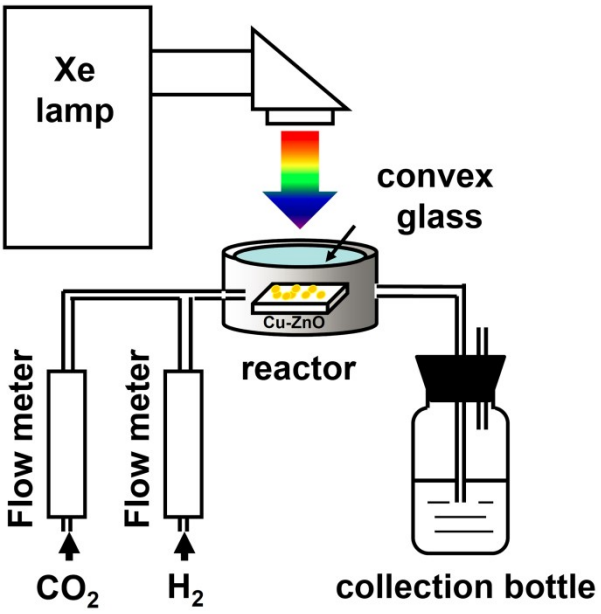

Fig. S4. Schematic illustration of the apparatus for photocatalyticexperiments.

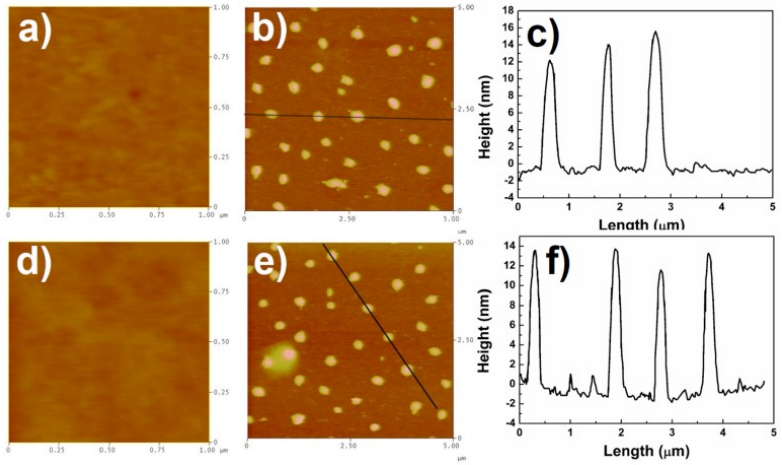

Fig. S5. (a)The morphologies of polished ZnO (0001) facet, (b) Cu nanoislands and (c) height analysis of Cu nanoislands in Cu/ZnO (0001) sample using AFM. (d) The morphologies of polished ZnO ($000\bar{1}$) facet, (e) Cu nanoislands and (f) height analysis of Cu nanoislands in Cu/ZnO($000\bar{1}$) sample using AFM.

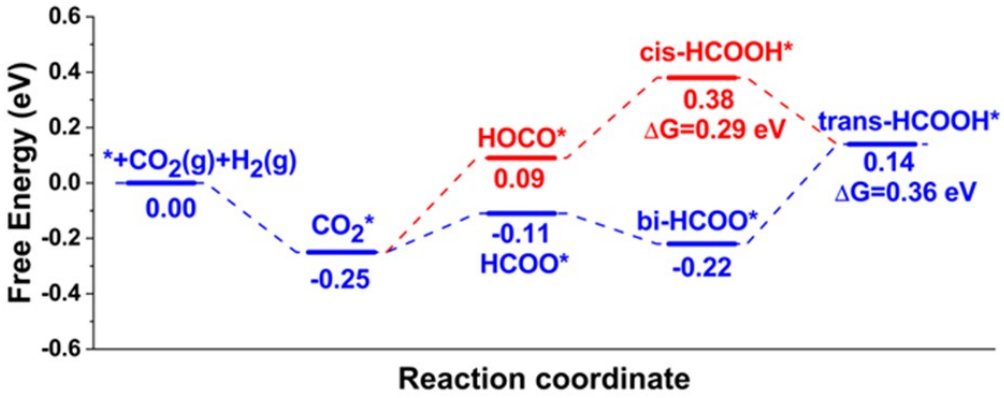

Fig. S6. The Gibbs free energy diagrams of CO_2 reduction calculated by PBE level without using U parameter.