## Spontaneous dissociation of $CO_2$ to CO on defective surface of $Cu(I)/TiO_{2-x}$ nanoparticles at room temperature

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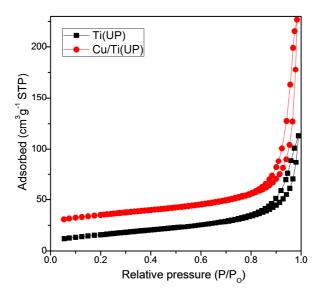


Figure S1. Nitrogen adsorption-desorption isotherms of Ti(UP) and Cu/Ti(UP) samples

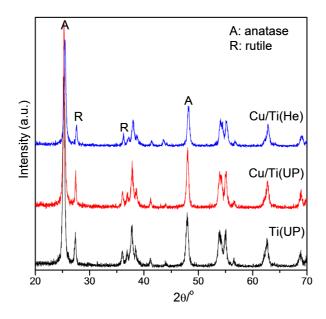


Figure S2. XRD patterns for Ti(UP), Cu/Ti(UP) and Cu/Ti(He) samples

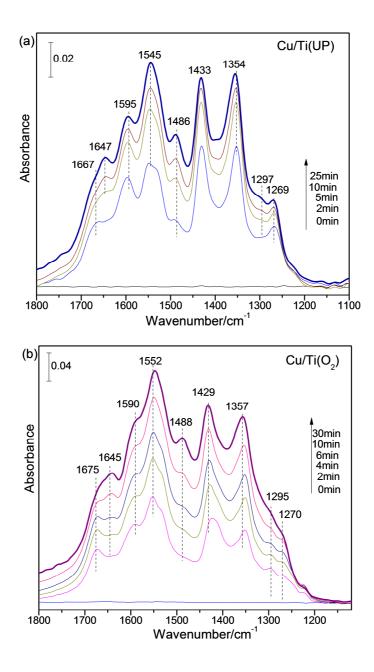
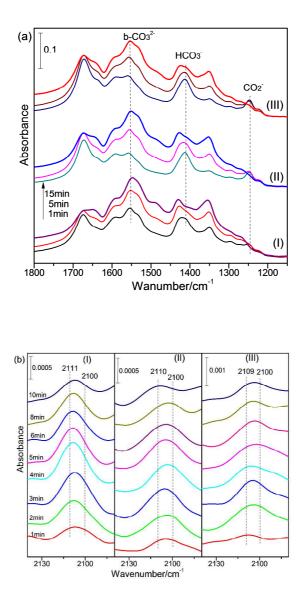
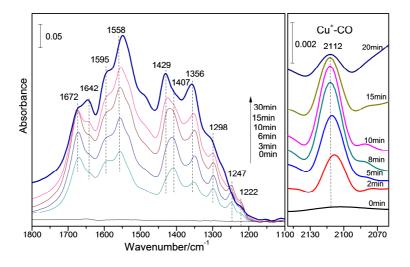


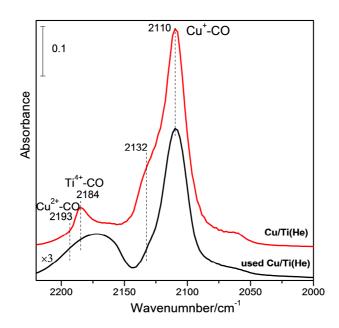
Figure S3. In situ DRIFTS spectra of CO<sub>2</sub> interaction with (a) Cu/Ti(UP) and (b) Cu/Ti(O<sub>2</sub>) at 25  $^{\circ}$ C



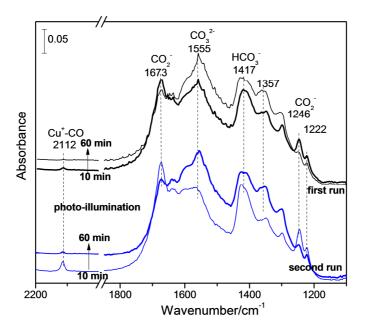
**Figure S4.** In situ DRIFTS spectra for  $CO_2$  interaction with regenerated Cu/Ti(He) that is recycled three times: (a) adsorbed  $CO_2$  species in the range of 1100-1800 cm<sup>-1</sup> and (b) the formed Cu<sup>+</sup>–CO at cycles I, II, and III.



**Figure S5.** *In situ* DRIFTS spectra for adsorbed CO<sub>2</sub> species in the range of 1100-1800 cm<sup>-1</sup> and the formed Cu<sup>+</sup>–CO upon exposing Cu/Ti(He) to CO<sub>2</sub> and photo-illumination (150 W solar simulator) simultaneously.



**Fgiure S6.** *In situ* DRIFTS spectra for CO adsorption on fresh Cu/Ti(He) and used Cu/Ti(He) after CO<sub>2</sub> photoreduction.



Fgiure S7. In situ DRIFTS spectra for  $CO_2$  photoreduction on Cu/Ti(He) (first run) and regenerated

Cu/Ti(He) (second run).