Supplementary Information (SI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

Influence of light on ad- and desorption processes on titanium dioxide surfaces towards efficient CO_2 photoreduction

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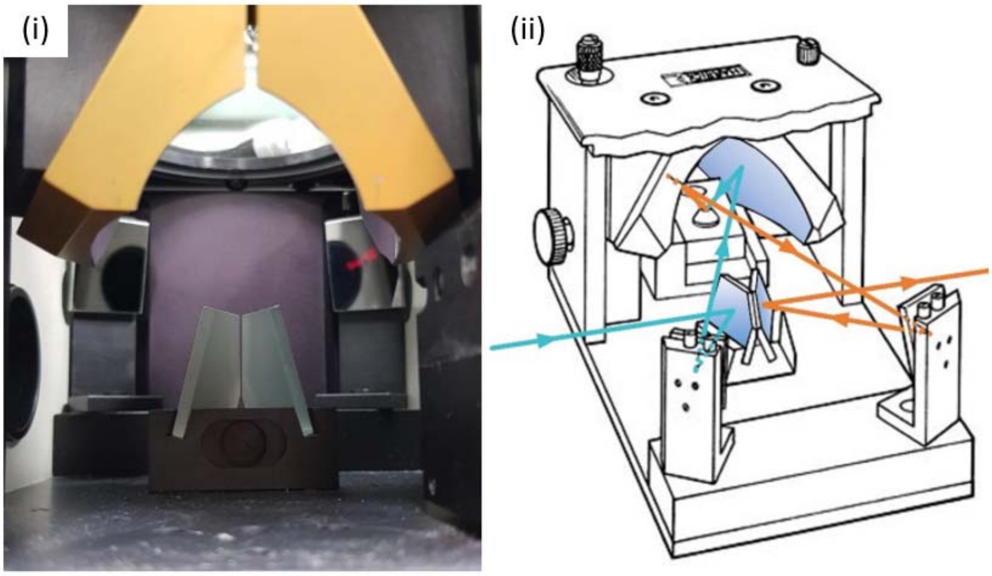

Figure S1.: Praying Mantis Mirror geometry utilized for measurements of DRIFT spectra: (left) photograph, front view; (right) schematic depiction, back view (modified from ''*The Praying Mantis(TM) User's Manual*'', Harrick Scientific Products, INC, 2009), Blue: incident IR beam, orange: cumulated diffuse reflected IR beam after having contact with the sample and carrying the information to the detector.

Comment: The entire macroscopic surface of the powdered sample was irradiated by the light source. However, since the IR light is expected to penetrate deeper into the sample than the UV light, it cannot be prevented that bands of CO_2 adsorbed on the dark surface will always appear in the spectra, too.

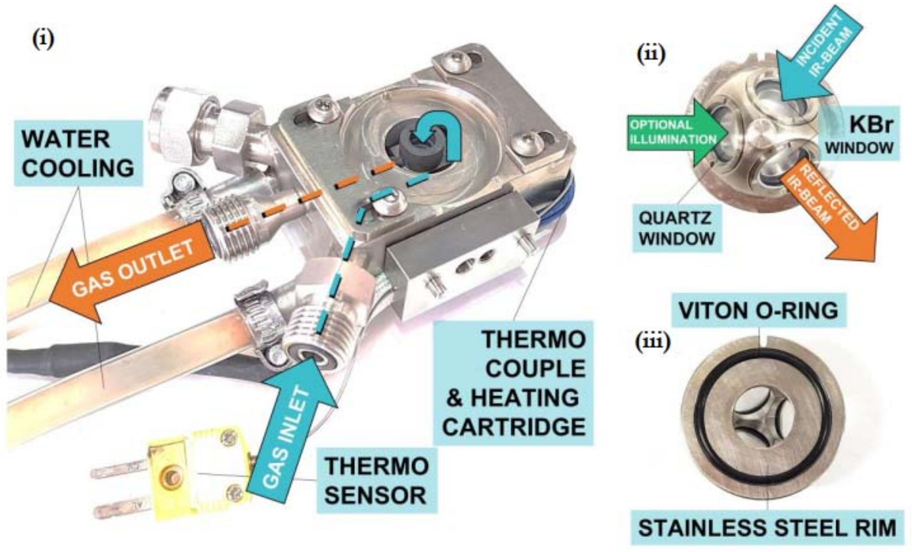

Figure S2: (i) Harrick in-situ high temperature cell, (ii) top view and (iii) bottom view of the hemispherical stainless-steel dome with three windows (2x KBr, 1x SiO_2).

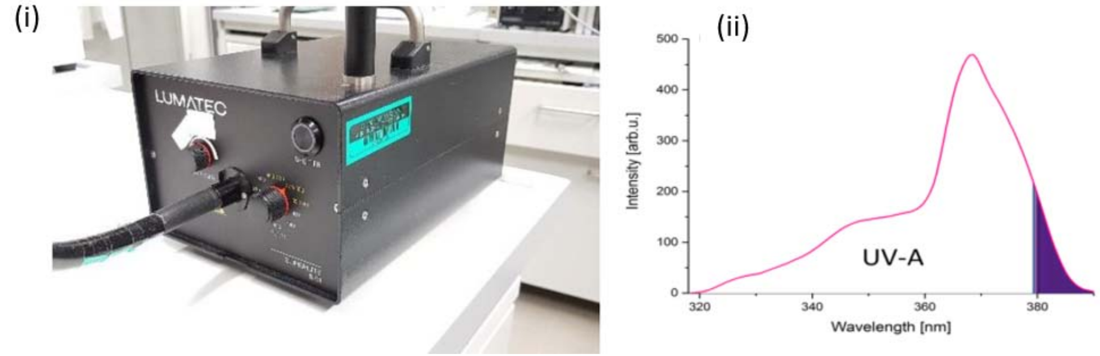

Figure S3: (i) LUMATEC Superlite S04 lamp utilized for the illumination of the sample during CO_2 adsorption, (ii) illumination spectrum of the applied light source.

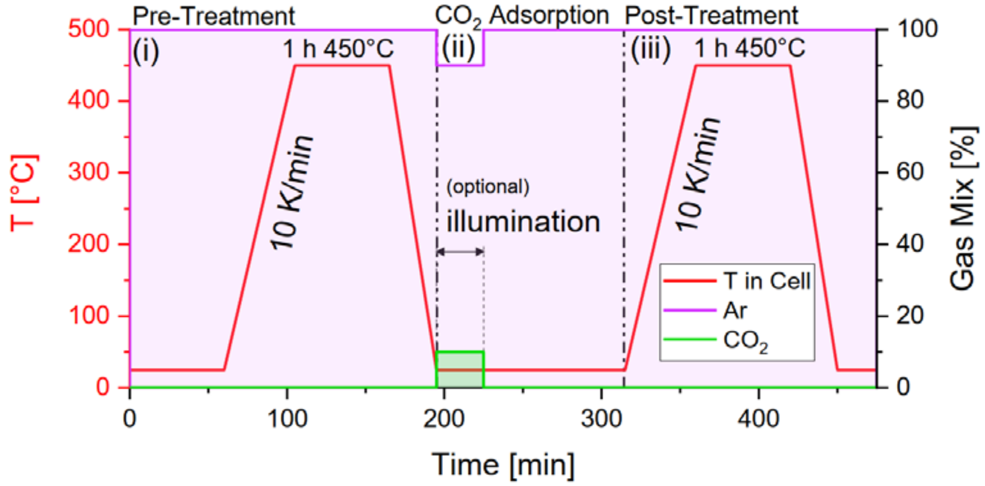

Figure S4: Schematic depiction of the experimental procedure: i) pre-treatment, ii) CO_2 adsorption, iii) post-treatment.

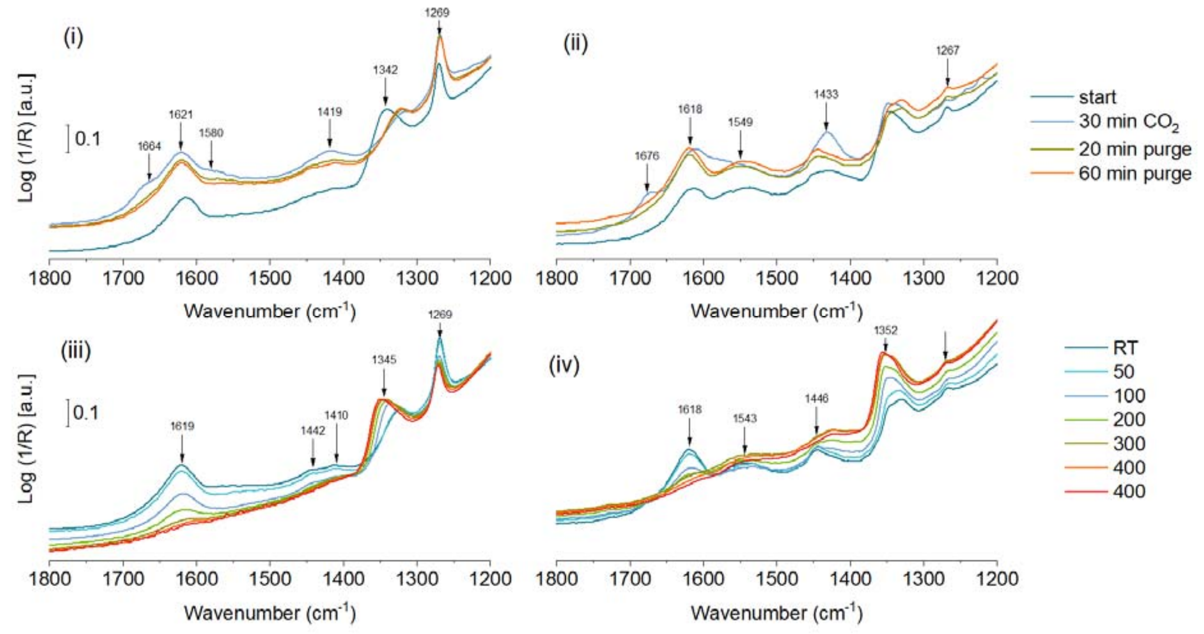

Figure S5: DRIFT spectra of CO_2 adsorption in dark (i) and under illumunation (ii) as well as the subsequent thermal treatment (iii-iv) of the anatase sample. The last spectrum of the the top depictions (red) is the first spectrum of the bottom depictions (dark teal).

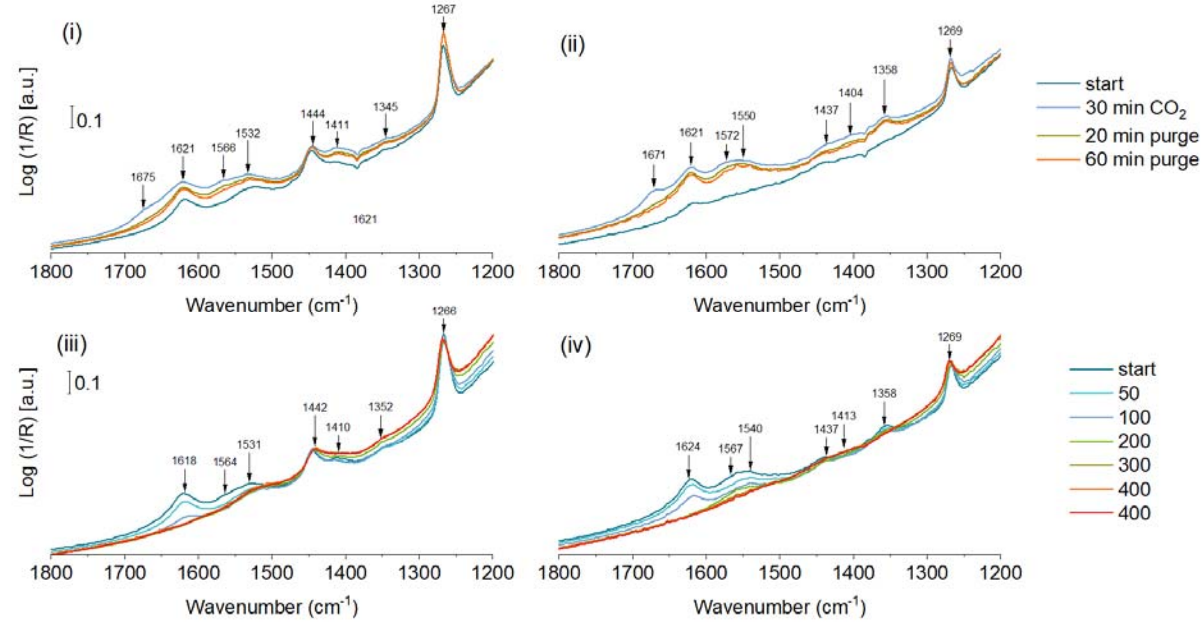

Figure S6: DRIFT spectra of CO_2 adsorption in dark (i) and under illumination (ii) as well as the subsequent thermal treatment (iii-iv) of the P25 sample. The last spectrum of the the top depictions (red) is the first spectrum of the bottom depictions (dark teal).

Comment: Slight shifts in the baseline, and particularly a tilting with a higher absorbance towards lower wavenumbers is indicative of an accumulation of conduction band electrons under irradiation, as has been observed by Lüken et al. [1].

Table S1: Vibrational modes extracted from literature references.

Species	Bands [cm^{-1}]*	Reference(s)
Monodentate Carbonate	1510, 1392, 1076	[2]
	1502, 1453, 1360	[3]
	1502, 1424	[3]
	1432	[4]
	1379, 1367, 1344, 1262	[5]
Bidentate Carbonate	1566, 1355	[2]
	1675, 1244	[3]
	1580, 1320	[4]
	1688, 1573, 1364, 1277, 1250	[5]
Bridged Carbonate	1725, 1291	[3]
Monodentate Bicarbonate	1367, 1262	[5]
	1674, 1245	[6]
Bicarbonate	1623, 1423, 1222	[2]
	1616, 1202	[3]
	1402 (1390), 1202	[3]
	1608, 1225	[3]
	1402, 1222	[4]
	1553, 1424, 1226	[5]
	1409, 1228, 1202	[5]
	1673, 1434, 1222	[6]
	1673, 1430, 1224	[7]
Carboxyl(ate)	1670, 1251	[2]
	1700, 1565	[3]
	1697, 1570	[3]
	1670, 1248	[4]
	1686, 1180	[5]
	1587	[7]
Formate	1558, 1359	[7]
	1590, 1385, 1365	[8]
	1560, 1360	[9]
Bidentate formate	1550, 1370	[10]

*On various types of TiO_2; only bands in the range 1800 to 1100 cm^{-1} are listed.

Key conclusions from this literature overview as used in the main article:

(i) The highest vibrational band (possibly $\nu_{as,COO}$) observed for the carboxyl/carboxylate species (COO or COOH) is usually observed at higher wavenumbers (~1670 cm^{-1}) than the highest vibrational band for a bicarbonate (~1600 to 1670 cm^{-1}, often ~1620 cm^{-1}).

(ii) The assignment of bicarbonate species requires the observation of a band near ~1425 cm^{-1}, whereas the carboxyl(ate) does not feature this band.

(iii) $\nu_{as,COO}$ of carbonates is mostly observed (with a few exceptions) at considerably smaller wavenumbers (~1560 cm-1) than either bicarbonate or carboxyl(ate) species.

In addition, it needs to be noted that bidentate carbonates and formate bands are difficult to distinguish based on their bands in the 1800-1100 cm^{-1} region alone, but formate species feature an additional C-H vibration, that is mostly reported to be located between ~2960 and 2880 cm^{-1} [7-9]

Comments on the use of the term “Carboxylate”:

The proper use of the term “carboxylate” would include any kind of species containing a deprotonated carboxylic acid function, for example formate or acetate species. Yet, Baltrusaitis, for example, used this term to describe a COO- species,[2] previously also termed as “bent CO_2”.[11] Other researchers, for example, Tumuluri et al.[3] or Bando et al.[7] use this term without assigning a structure or chemical composition at all. In spite of this uncertainty with respect to the exact nature of this species, the band assignment was rather consistent across several research articles,[2,3,11,12] with one band at high wavenumbers (~1670 to 1650 cm^{-1}) for a structure with suspected COO group, and another one at very low wavenumbers (~1250 cm^{-1}), possibly accompanied by another band at around 1570 cm^{-1}. In most articles, the nature of the vibration is not described, but it would be conceivable that the band at highest wavenumbers might either be a C=O (double bond) stretch or an asymmetric OCO stretch. It is unusually high for an asymmetric OCO stretch, yet very low for a C=O stretch, which is usually found above 1700 cm^{-1}, often even above 1750 cm^{-1}. Similarly, the band at ~1250 cm-1 is very low for a symmetric OCO stretch (as assigned, e.g., by Baltrusaitis et al.), but too high for a C-O-H deformation vibration, which is usually found closer to 1220 cm^{-1}.

Any kind of COO^- or COOH (intact carboxylic acid function), requires electron donation from the surface to be bound via the carbon atom. Baltrusaitis et al. argue here that electron-rich Ti^{3+} sites at the surface are the binding sites for such a carboxylate. It is certainly expected that our commercial TiO_2 sample contains electron-rich sites such as oxygen vacancies and Ti^{3+} cations. Not only is TiO_2 an n-type semiconductor with native oxygen vacancies, but also, we see a slight bending of the baseline under irradiation, which is an indication for an accumulation of conduction band electrons.

Although we admit that we cannot assign a definite structure and binding site to the “carboxylate” species, it appears most likely that it might be a bent CO_2 species interacting with a proton, for example of a surface hydroxyl group, to yield a structure resembling a COOH, a carboxylic acid function. A schematic drawing is provided below. The interaction with the proton would break the symmetry of a bent CO_2 species, reducing the bond order in the C-O bond near the proton, and increasing the bond order in the other C-O bond. Yet, a full COOH structure is not obtained, so the bands do not correspond to a typical carboxylic acid. Given that all hypothesized structures require the surface to be able to donate electrons, the binding site (here symbolized by the blue bar) should be a defect such as a Ti^{3+} site or an oxygen vacancy.

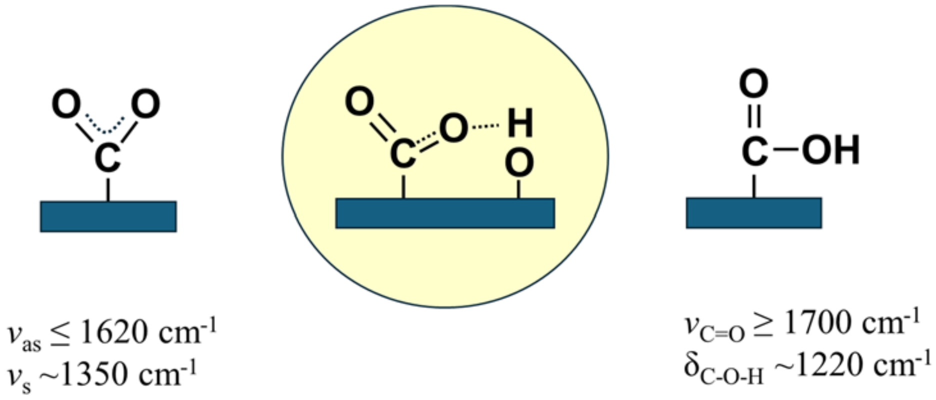

Figure S7: Hypothetical structure of the “carboxylate” species with vibrational bands at ~1670 and ~1250 cm-1 (middle), in comparison with previous suggestions of the “bent CO_2” structure (left) and a true carboxylic acid function (right); Please note: The structures are hypothetical and have not been evidenced, e.g., by surface science or DFT calculations.

Table S2: Vibrational modes and identified species formed during the adsorption of CO_2 on anatase. Corresponding wavenumbers are given in [cm^{-1}]; “n.o.” = not observed.

Dark			
Vibrational mode	**(Monodentate) Carbonate**	**Monodentate bicarbonate**	**Bidentate bicarbonate**
ν(OCO)	1586	1670	1623*
	n.o.	1424	1444*
δ(COH)	-	1221	1218
Light			
ν_a(CO)	1590	1675	1625^{s} | 1613^{c}
	1378 | 1351	1430	1444^{s} | 1501^{c}
δ(COH)	-	1223	1218

* not clearly observed; might be hidden.

^{s} stable bidentate bicarbonate

^{c} chelating bidentate bicarbonate

Table S3: Vibrational modes and identified species formed during the adsorption of CO_2 on P25. Corresponding wavenumbers are given in [cm^{-1}]; “n.o.” = not observed.

Dark				
Vibrational mode	**Carboxylate**	**Formate**	**Monodentate Carbonate**	**Bicarbonate**
ν(OCO)	1670	-	1568	-
			~1400	-
δ(COH)	1252*	-	-	-
Light				
ν_a(CH)	-	2966	-	-
		2869		
		2844		
ν(OCO)	1670	1584 | 1550	1575	n.o. / hidden
		1360	1378	1432
δ(COH)	1248*	1400**	-	1219

*not a δ(COH) vibration, assignment to particular vibrational mode unclear.

** δ(CH) vibration.

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