SUPPLEMENTARY INFORMATION

Surface features of TiO_2 nanoparticles: combination modes of adsorbed CO probe the stepping of (101) facets

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Table S1. Relaxation energies of different low-index anatase surfaces (J/m^2).

Surface	**(101)**	**(100)**	**(001)**	**(110)**
a)	0.28	0.36	0.39	0.40
b)	0.49	0.58	0.98	1.15
c)	0.60-0.65	0.75-0.80	1.25-1.30	1.30-1.35

a) Present results; b) from Ref. M. Lazzeri, A. Vittadini, A. Selloni, *Phys. Rev. B*, 2001, **63**, 155409; c) data extracted from Figure 1a in Ref. L. Mino, A.M. Ferrari, V. Lacivita, G. Spoto, S. Bordiga, A. Zecchina; J. *Phys. Chem. C*, 2011, **115**, 7694-7700.

Comment to Table S1:

Surface energies. In table S1 the surface energies of low-index anatase surfaces from literature are reported and compared to the relaxation energies calculated in our work. Here the atoms of bottom TiO_2 layer of the slab models were fixed to the crystallographic positions (see text). The surface relaxation energy was calculated by:

$$E^{(hkl)} = \frac{E(TiO_2)^{bulk} - E(TiO_2)^{(hkl)}}{A(TiO_2)^{(hkl)}}$$

where, E(TiO_2) refers to the total energy per TiO_2 unit for the reference bulk and for the (hkl) slab, respectively. *A* refers to the area per Ti atom on a given surface and is calculated by dividing the slab area by the number of Ti sites in the surface layer. In our calculations, a system containing 36(TiO_2) units was considered as reference bulk, corresponding to a 3×3×1 supercell.

For the (101) surface we considered 6 layers each consisting of 6(TiO_2) units; 6 layers of 6(TiO_2) units for the (100); 6 layers of 9(TiO_2) units for the (001) and 8 layers of 6(TiO_2) units for the (110) surfaces respectively. Exposed areas are 1.1627 nm^2, 1.0803 nm^2, 1.2894 nm^2 and 1.0185 nm^2 for the (101), (100), (001) and (110) surfaces, respectively. All calculations were performed according to the procedure reported in the main text, namely 80Ry cutoff, at Γ point using the PBE approximation. The literature data were obtained by relaxing all atoms in the slabs. Interestingly the surface relative stabilities have the same trends in all cases. Moreover, it is to be stressed that, in all cases, the (001) and the (110) surfaces have very similar energies.

Table S2. Assignment of the IR signals observed in the spectra of 45 mbar CO adsorbed on TiO_2 nanoparticles (ca. 100 K, P_{CO} = 45 mbar, resulting in a full surface coverage, ref. S1.1) considered in the manuscript (TiO_2 P25, TiO_2 HT, TiO_2 HT-HF).

νCO band [cm^{-1}]	**Assignment**	
	Adsorbing site	*References*
2206[a]	α sites (notation as in ref. S1.2), i.e. Ti^{4+} in coordinatively defective position	S1.2, S1.3
2183[a]	Ti^{4+}_{4c} on (110) anatase surface	S1.1
2179[b]	β sites (notation as in ref. S1.2), i.e. Ti^{4+}_{5c} on (101) anatase surface	S1.1
2164[b]	Ti^{4+}_{5c} on (100) or (001) anatase surface*	S1.1
2156[c]	-OH groups	S1.2
2149[a]	rutile surfaces	S1.4
2139	physisorbed CO	S1.2, S1.5
2127[b]	^{13}CO on β sites	S1.1, S1.2, S1.5

Comment to Table S2:

[a] Signal present only for TiO_2 P25

[b] Signal downshifted of 1 cm^{-1} in TiO_2 HT and TiO_2 HT-HF

[c] Signal upshifted of 1 cm^{-1} in TiO_2 HT and TiO_2 HT-HF

* This band is usually assigned to the stretching of CO adsorbed on Ti^{4+} exposed at the (001) anatase surfaces (ref. S1.2). However, our recent theoretical calculations suggested that it should be due to CO on Ti^{4+} exposed at (100) anatase surfaces (ref. S1.1).

References

S1.1. C. Deiana, M. Minella, G. Tabacchi, V. Maurino, E. Fois and G. Martra, *Physical Chemistry Chemical Physics*, 2013, **15**, 307-315.

S1.2. K. Hadjiivanov, J. Lamotte and J. C. Lavalley, *Langmuir*, 1997, **13**, 3374-3381.

S1.3. C. Deiana, E. Fois, S. Coluccia and G. Martra, *Journal of Physical Chemistry C*, 2010, **114**, 21531-21538.

S1.4. L. Mino, G. Spoto, S. Bordiga and A. Zecchina, *Journal of Physical Chemistry C*, 2012, **116**, 17008-17018.

S1.5. G. Spoto, C. Morterra, L. Marchese, L. Orio and A. Zecchina, *Vacuum*, 1990, **41**, 37-39.

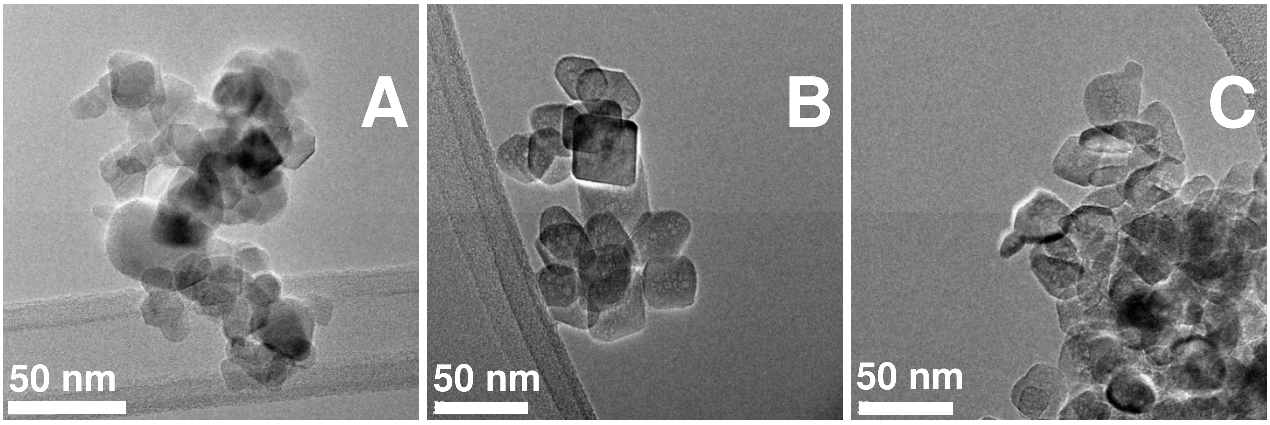

Figure S1. TEM images representative of the overall morphology of: A) TiO_2 P25 (original magnification 120k ×); B) TiO_2 HT (original magnification 100k ×); C) TiO_2 HT-HF (original magnification 100k ×). In panel B, the square-like shape can be due to a truncated bipyramid particle with the (101) type facets parallel to the line-of-sight (corresponding to the direction of the impinging electron beam).

References

S2.1. M. Čaplovičová, P. Billik, L. Čaplovič, V. Brezová, T. Turáni, G. Plesch, P. Fejdi, *Applied Catalysis B: Environmental*, 2012, 117-118, 224-235.

S2.2. C. Deiana, M. Minella, G. Tabacchi, V. Maurino, E. Fois and G. Martra, *Physical Chemistry Chemical Physics*, 2013, **15**, 307-315.

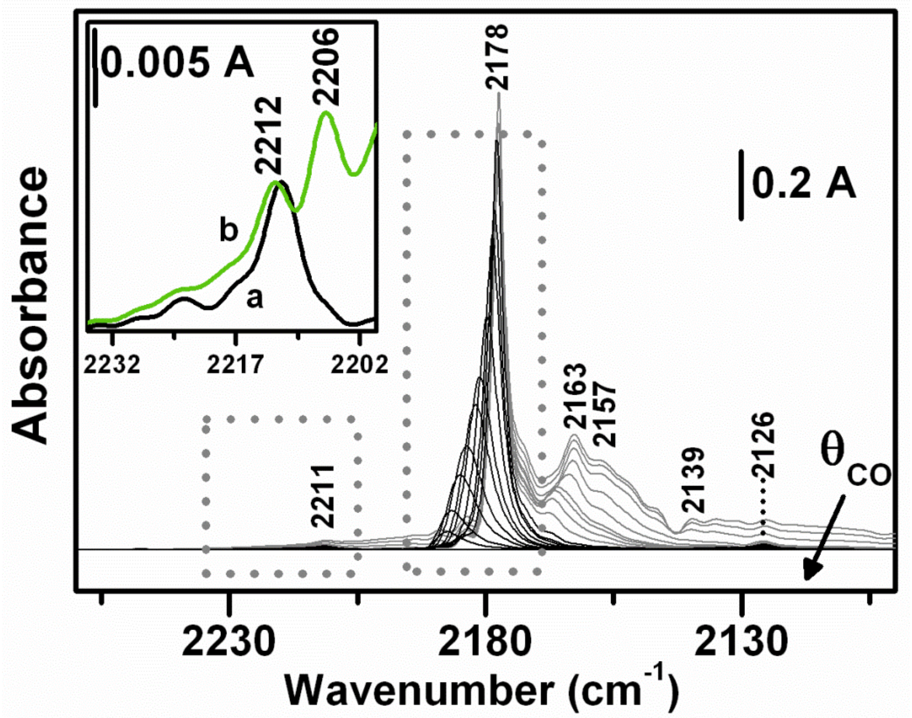

Figure S2. IR spectra of decreasing amount (in the sense of the arrow) of CO adsorbed at ca. 100 K on TiO_2 HT outgassed at 873 K. Spectra collected in conditions ranging from the presence of 45 to 0.1 mbar and from 0.06 mbar to outgassing for 10 minutes at ca. 100 K: grey and black curves, respectively. The dashed frames mark the spectral regions displayed in Figure 3 in the main text. Inset: IR spectra, in the 2235-2200 cm^{-1} range, obtained by admitting 0.06 mbar CO at 100 K on TiO_2 HT-HF (curve a) and 0.1 mbar CO at 100 K on TiO_2 P25 (curve b) outgassed at 873 K. The two curves have been normalized to the maximum of the band at 2212 cm^{-1}.

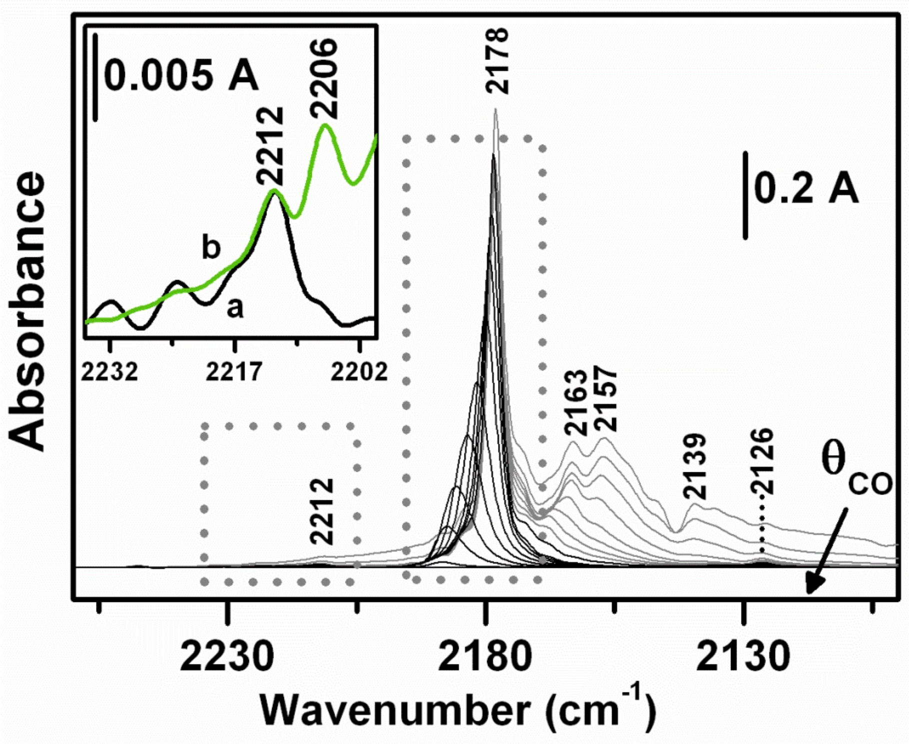

Figure S3. IR spectra of decreasing amount (in the sense of the arrow) of CO adsorbed at ca. 100 K on TiO_2 HT-HF outgassed at 873 K. Spectra collected in conditions ranging from the presence of 45 to 0.1 mbar and from 0.07 mbar to outgassing for 10 minutes at ca. 100 K: grey and black curves, respectively. The dashed frames mark the spectral regions displayed in Figure 4 in the main text. Inset: IR spectra, in the 2235-2200 cm^{-1} range, obtained by admitting 0.07 mbar CO at 100 K on TiO_2 HT-HF (curve a) and 0.1 mbar CO at 100 K on TiO_2 P25 (curve b) outgassed at 873 K. The two curves have been normalized to the maximum of the band at 2212 cm^{-1}.

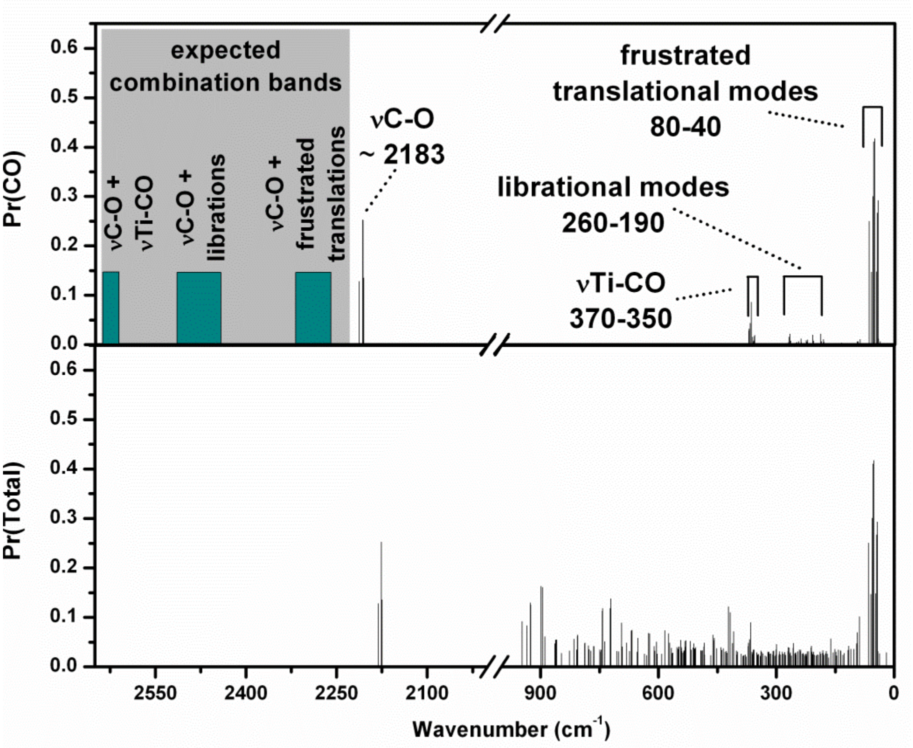

Figure S4. Calculated Participation Ratio (PR) for a θ =1 coverage of CO on (110) TiO_2 anatase slab. Bottom panel: PR obtained by including all the atoms in the system. Top panel: PR obtained by taking into account just the CO atoms.

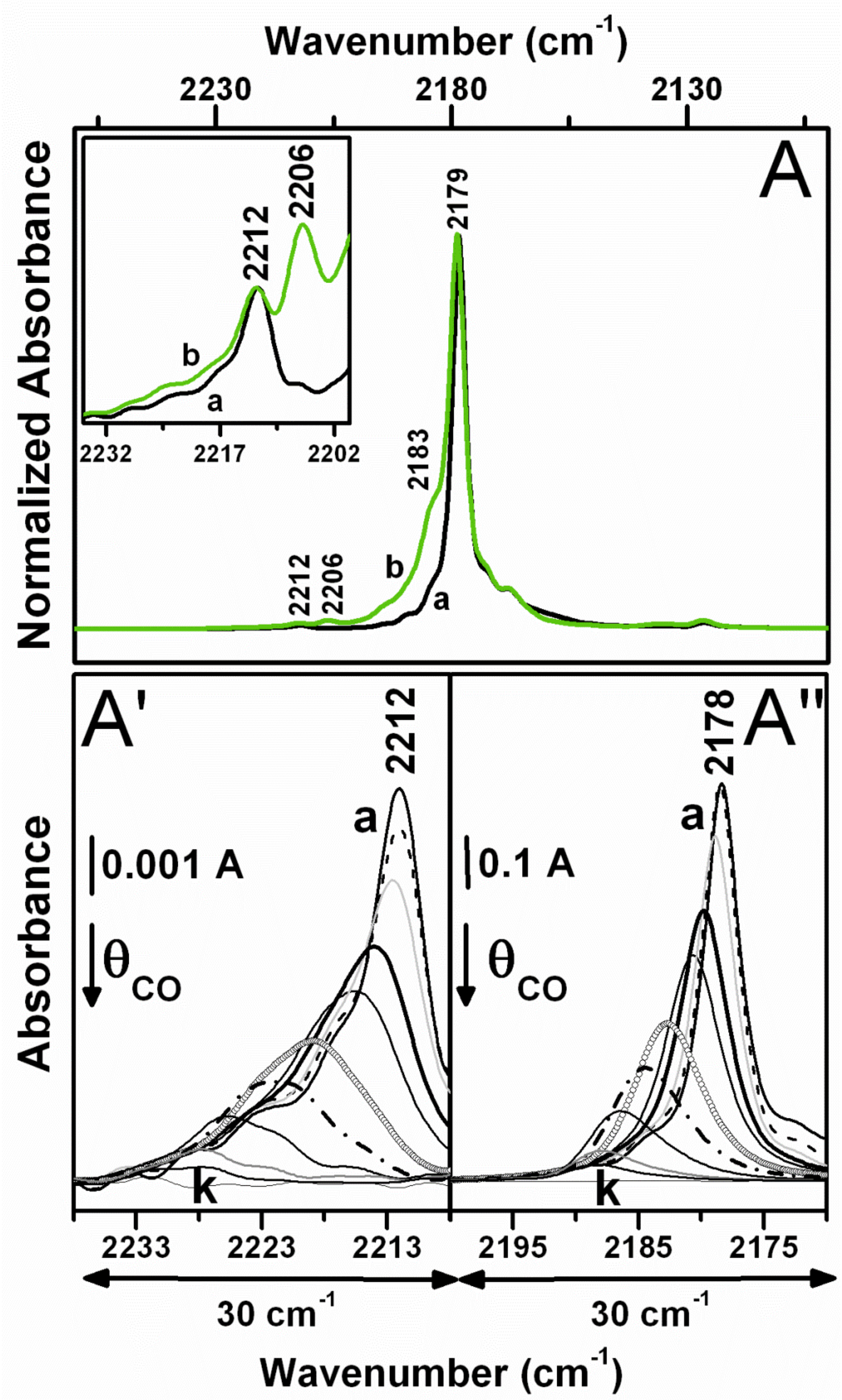

Figure S5. Panel A (2260-2100 cm^{-1} range): IR spectra (normalized to the maximum of the peak at 2179 cm^{-1}) obtained by admitting 0.1 mbar CO at 100 K on TiO_2 P25 outgassed at 573 (curve a) and 873 K (curve b); inset: zoomed view of the 2235-2200 cm^{-1}. Panels A' and A": IR spectra in the 2238-2008 cm^{-1} and 2200-2170 cm^{-1} range, respectively, of decreasing amount of CO adsorbed at ca. 100 K on TiO_2 P25 outgassed at 573 K. Spectra collected in conditions ranging from the presence of 0.1 mbar to outgassing for 10 minutes at ca. 100 K. Decreasing CO coverages are in the sense of lettering.