Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Plasmon-free SERS detection of environmental CO_2 on TiO_2 surfaces

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SI1: Experimental

a) *Synthesis of T-rex beads and 3D colloidal crystals*

The T-rex beads were synthesized according to the procedure reported in references 23 and 25. Briefly, the SiO_2 (core) beads were prepared by the Stöber method from Tetraethylortosilicate (TEOS, Fluka) precursor. Monodisperse particle batches were obtained through repeated filtering/centrifugation cycles. The mean sizes were 2.06 ±0.05 μm. The a-TiO_2 shell layer was obtained by atomic layer deposition (ALD) at 90°C using tetrakis(dimethylamino)titanium(IV) (TDMAT, Sigma-Aldrich) and ultrapure milliQ water as titanium and oxygen precursors, respectively. The nominal thickness of the shell layer was estimated from x-ray reflectivity (XRR) measurements (*see* ref. 30) Our previous results indicated that the thickness of the anatase layers is very uniform. The conformal coating was checked by secondary-electron microscopy (SEM) (LEO-1521, high resolution instrument equipped with field emission gun).

3D colloidal crystals were achieved in two steps:

1) preliminary formation of close-packed silica sphere crystals, obtained through controlled sedimentation from aqueous suspension of the silica spheres.
2) ALD infiltration of the 3D silica sphere crystals (see the procedure described before) and subsequent annealing to convert amorphous titania into anatase (23,25,30).

b) *Raman spectra of T-rex samples (3D colloidal crystals)*

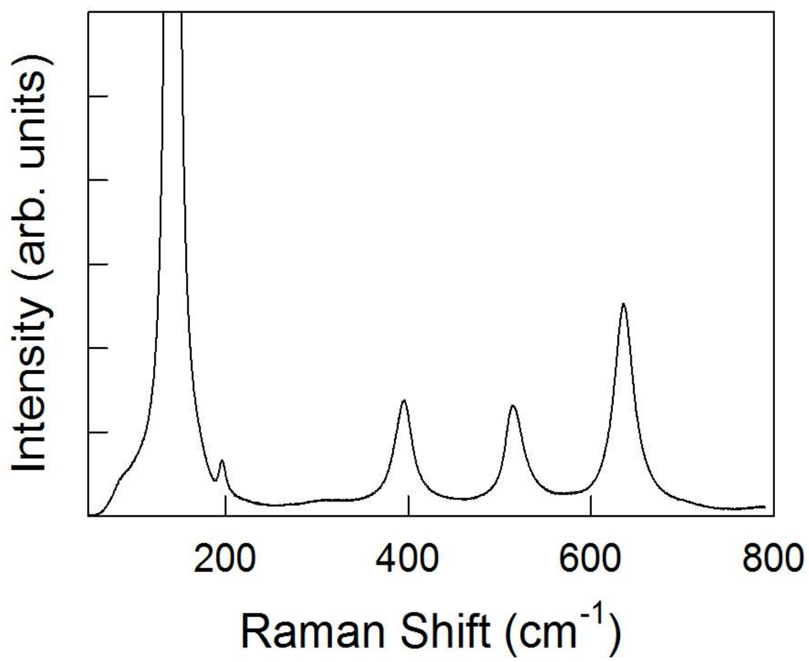

Figure S1b: Raman spectrum of 3D colloidal crystal T-rex100 beads, showing the typical modes of anatase.

c) *Raman detection experiments*

The Raman analyses have been carried out using a Labram HR-800 by Horiba-Jobin Yvon® equipped with an optical microscope (BX41; Olympus Optical Co. Ltd., Objective Numerical Aperture: 0.9 and 0.5), with 632.81 nm HeNe laser and with a CCD (Wright Instruments Ltd.) in backscattering configuration. The nominal laser power on the sample surface is 5mW. Each spectrum was acquired for 240s. The spectral output is the result of an average of 3 different analysis.

The detection of CO_2 with different T-rex beads (Figs. 1-3 in the main text) was carried out under environmental conditions (temperature: 298±1K, initial concentration in air: 396 ppm, ambient pressure). All the experiments of each series were acquired during the same day. Data on daily variation of environmental CO_2 are reported in SI4. The dynamic study of environmental CO_2 as a function of temperature (Fig. 4 in the main text) was carried using an optimized T-rex colloidal crystal (T-rex75) placed in a HFS91 Linkam oven. The temperature, monitored with TP93 Linkam controller, was increased and decreased by 25K steps in the range 298-573 K. A scheme of the temperature ramp is shown below:

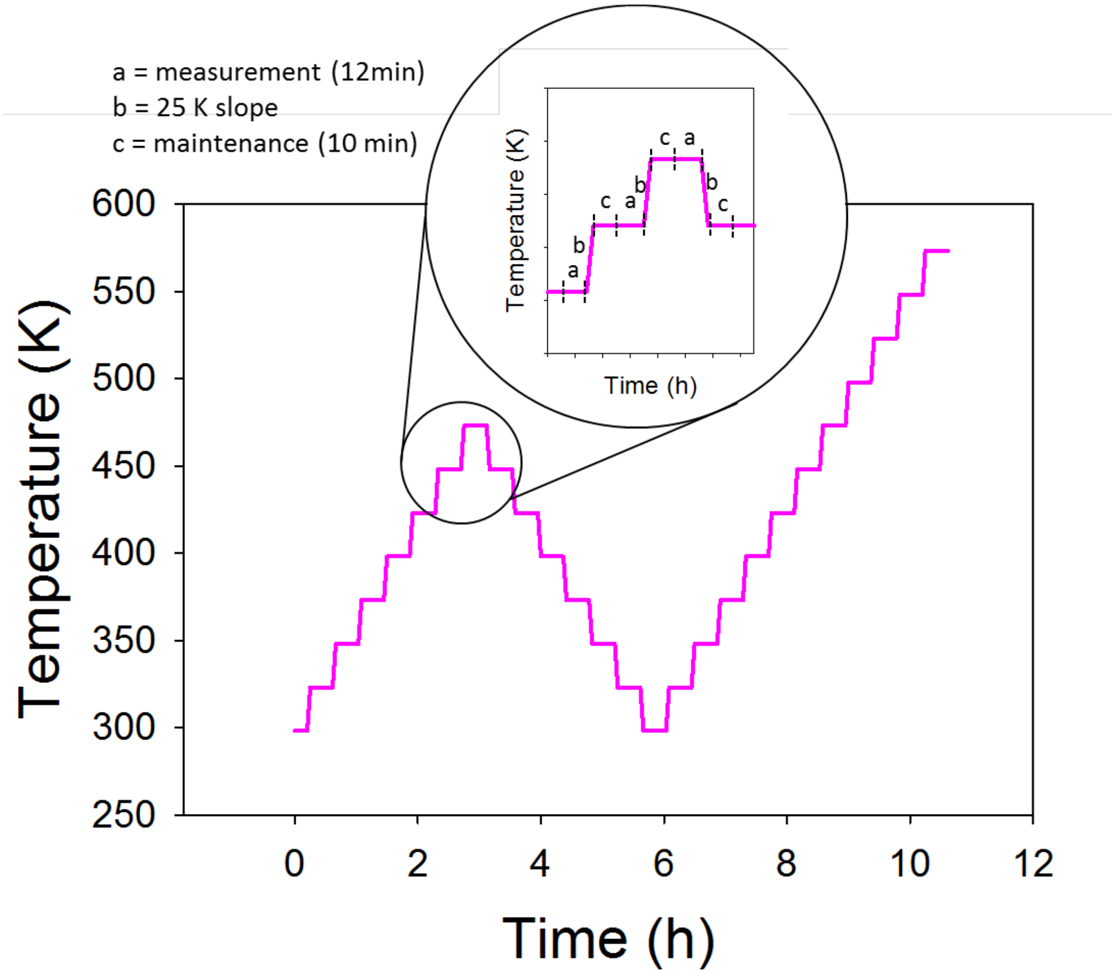

Figure S1c: Scheme of the temperature sweep cycle. The different stages of temperature increase/decrease, equilibration and Raman acquisition are indicated in the inset.

SI2. CO_2 detection from T-rex beads coated by water droplets

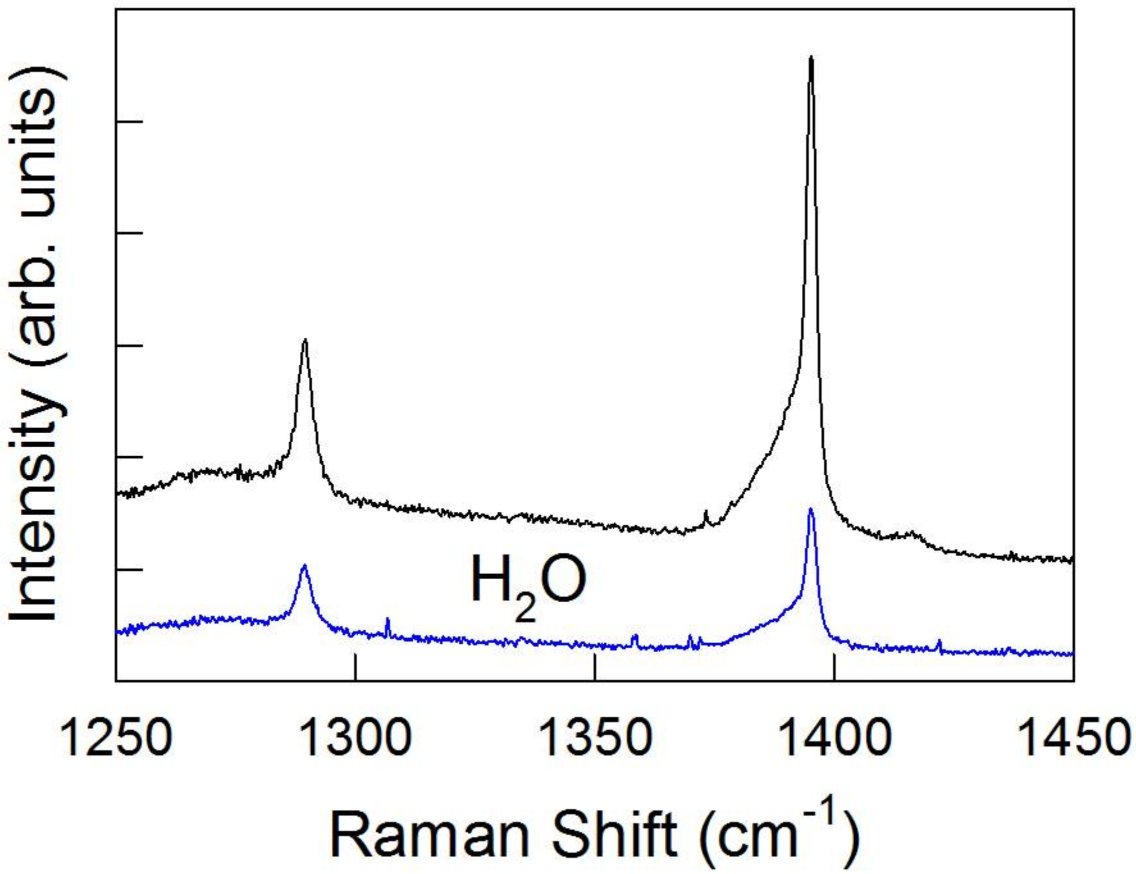

Figure S2. CO_2 detection in the absence (black) and in the presence (blue) of water. It can be noted that water does not significantly interfere with Raman detection, making T-rex-based assays suitable for investigating reactions under real working conditions.

SI3: CO_2 detection on Si and TiO_2 P25-Aeroxide Degussa references

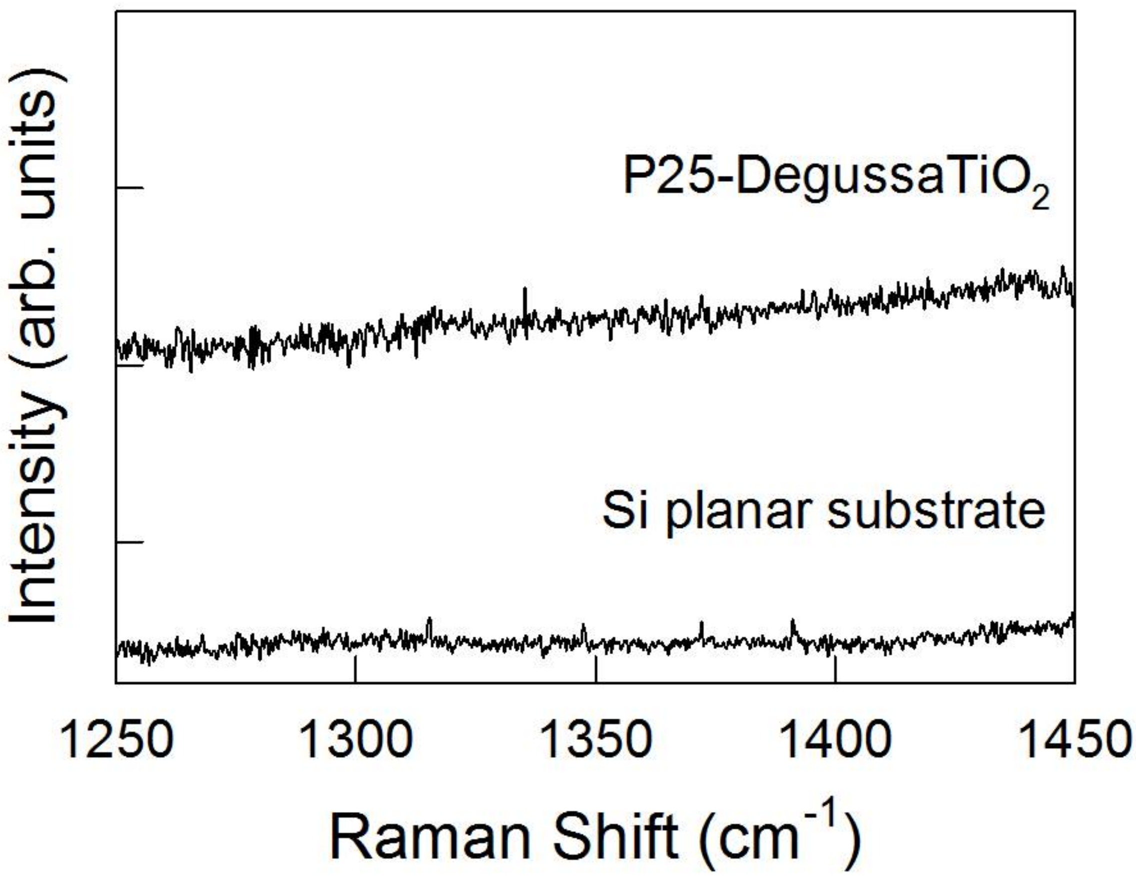

Figure S3. Raman spectra acquired from Si planar substrates and P25-Degussa TiO2 particles (surface area_ 50±15 m^2/g) in the 1250-1450 cm-1 spectral region under the same conditions utilized for CO_2 detection with T-rex samples. No CO_2 bands are detected.

SI4 a) CO_2 detection from single T-rex beads: data before and after surface area normalization

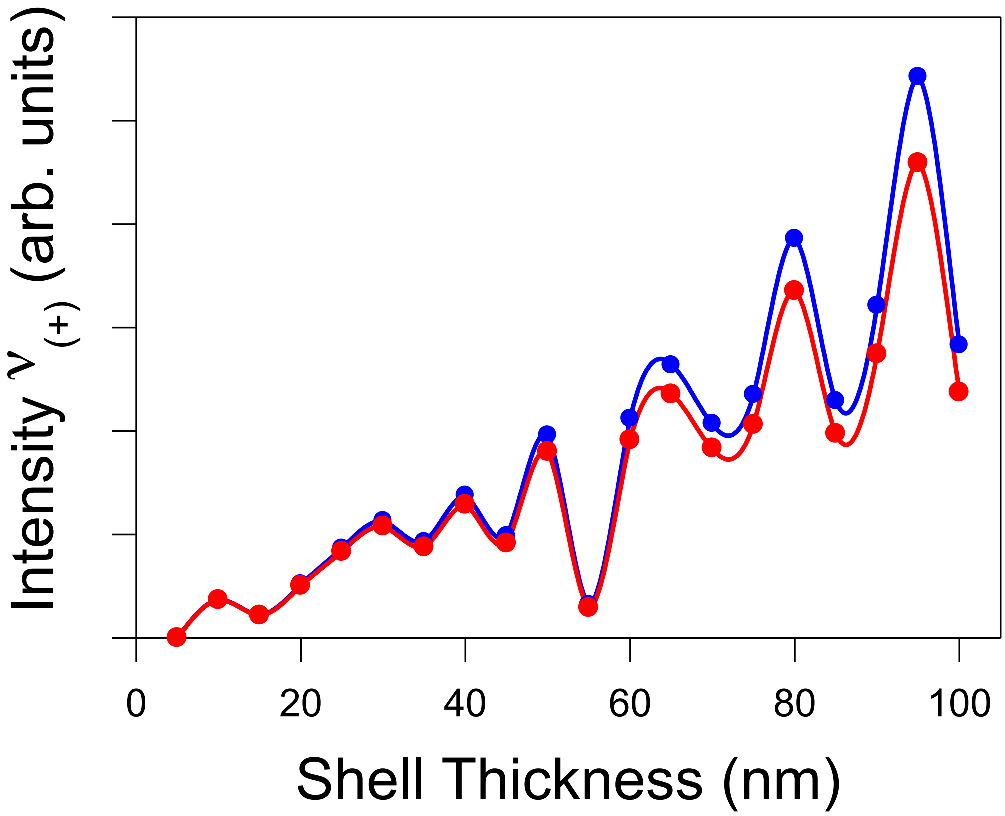

Figure S4a. Intensity of $\nu_{(+)}$Raman band before (blue) and after (red) normalization over surface area as a function of the shell thickness.

SI4 b) CO_2 detection from single T-rex beads at different days

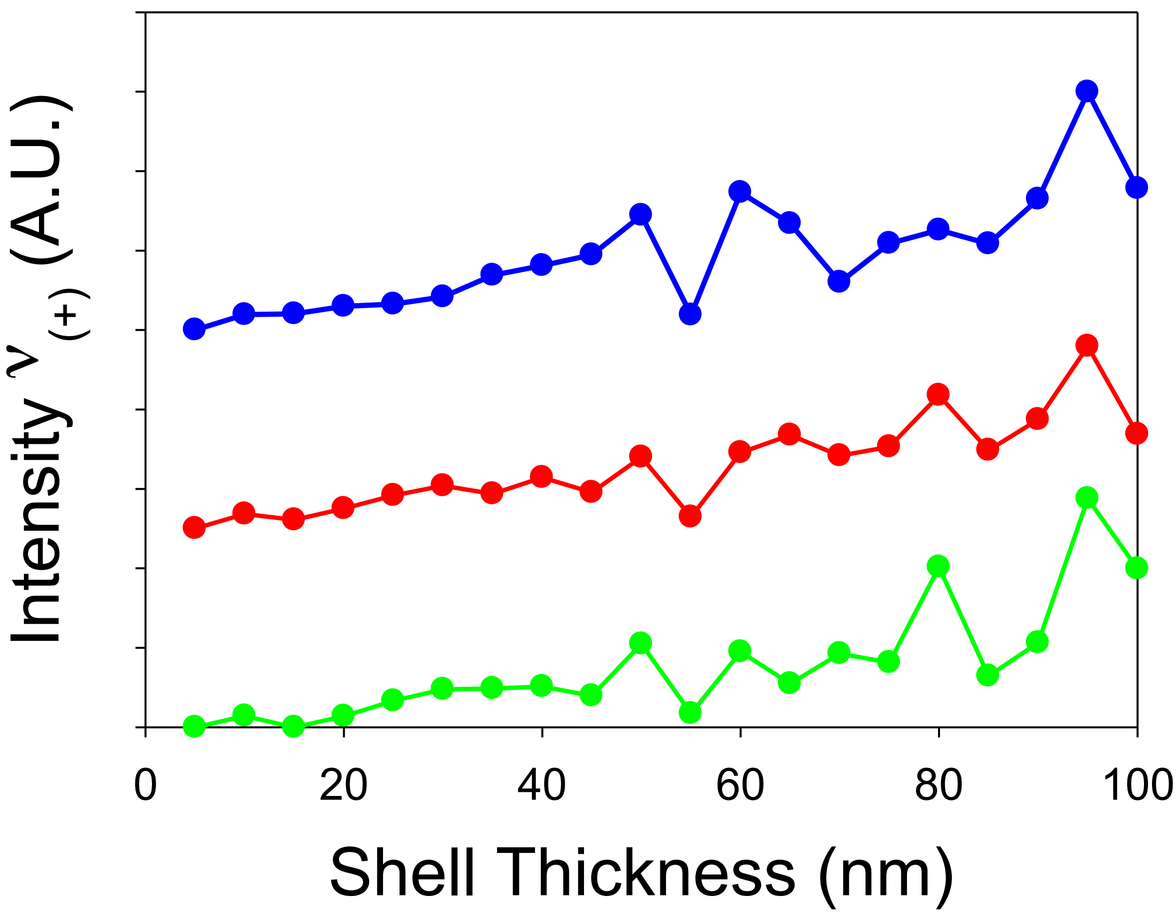

Figure S4b: Intensity of $\nu_{(+)}$ Raman band *vs.* shell thickness acquired at three different days**.**

SI4 c) CO_2 detection from 3D colloidal crystal T-rex beads at different days

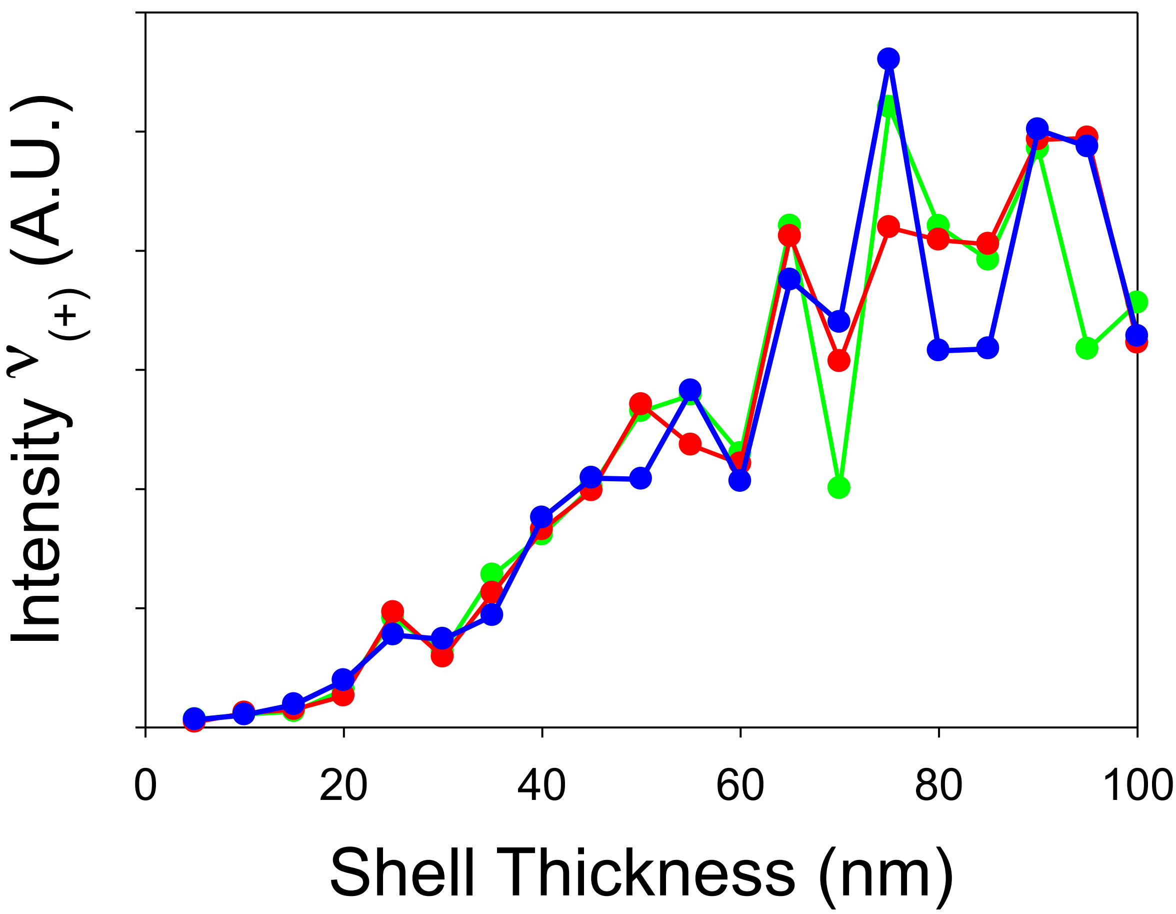

Figure S4c: Intensity of ν+ band vs. shell thickness acquired in three different days.

SI5: CO_2 detection from 3D colloidal crystal T-rex beads vs shell thickness

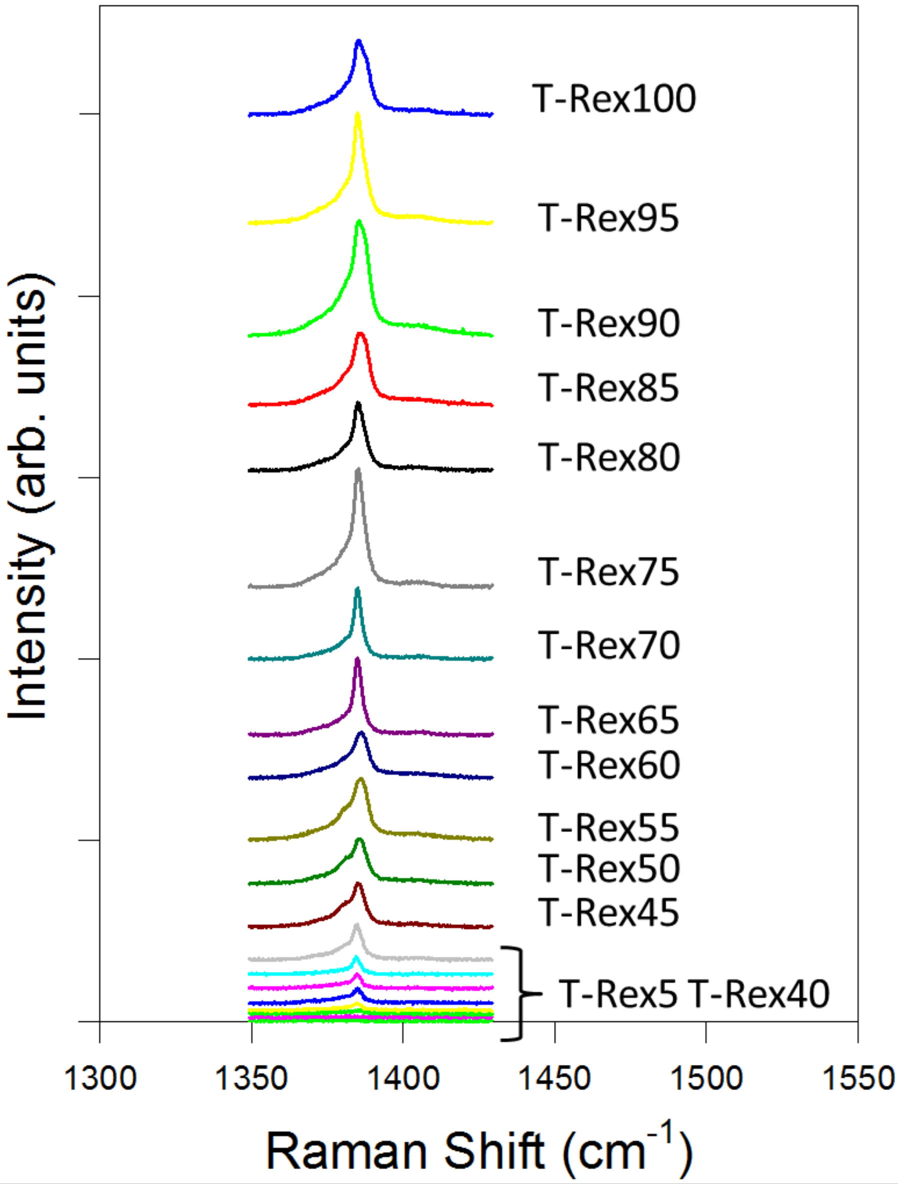

Figure S5: Intensity of $\nu_{(+)}$ Raman band *vs.* shell thickness acquired from T-rex colloidal crystals under the same conditions.

SI6: CO_2 variation: dispersion over a single day

The daily CO_2 oscillation was evaluated by multiple spectral measurements from T-rex80 beads selected from 3D colloidal crystals. The Raman spectra variations were monitored during the same day over each selected region from 10:00 a.m. to 7:30 p.m. with steps of 30 minutes each. The standard deviation is within 4% of the averaged intensity value.

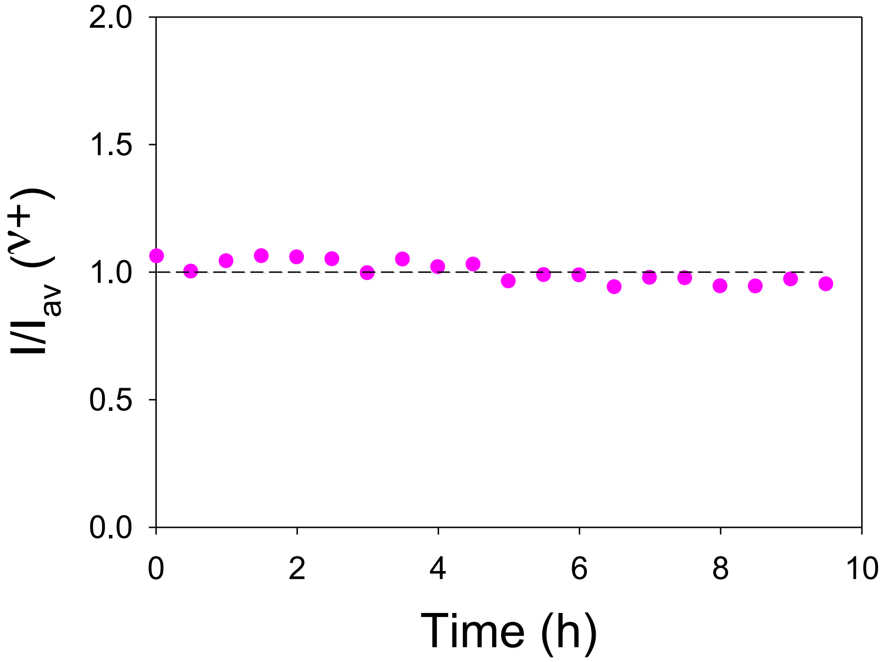

Figure S6: Intensity of $\nu_{(+)}$ Raman band normalized on the averaged intensity *vs.* time.

SI7: Finding optimal T-rex colloidal crystals: numerical simulations *vs* experimental data

Finite-element-method simulations are used to estimate the SERS enhancement for T-Rex colloidal crystal. The simulated structure is depicted in **Figure S7(a)**. The colloidal crystal structure is replaced by a dielectric layer of constant permittivity on which is sitting one single bead. The calculated SERS enhancement for thicknesses ranging from 45nm up to 100nm is reported in **Figure S7(b)** and shows a good agreement with the experimental results. In particular the maximum SERS factor that is obtained through numerical simulation is achieved for the same shell thickness for which the measured SERS signal was maximum.

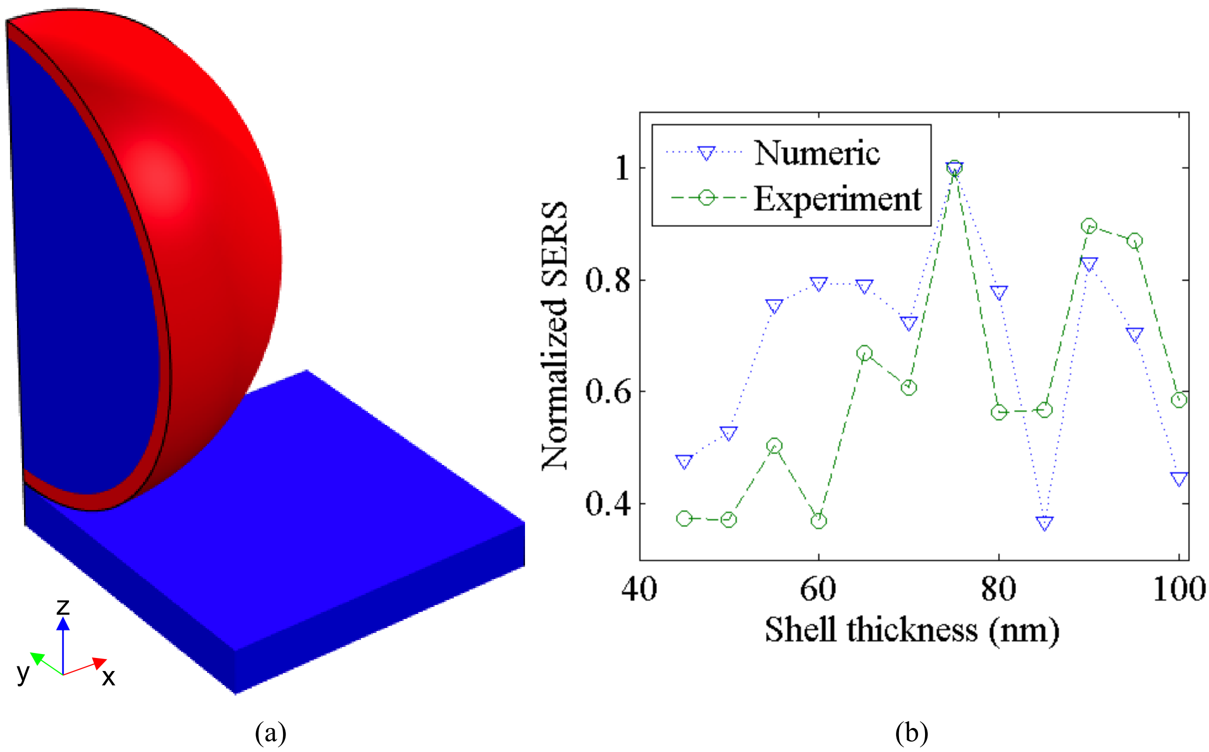

Figure S7: (a) FEM simulation structure. Different colours correspond to different materials: blue = SiO_2, red = TiO_2, air is transparent. The T-rex bead is placed on top of a SiO_2 substrate. Incident field is a x-axis linearly polarized plane wave travelling towards –z direction. (b) Normalized SERS factor as a function of shell thickness estimated from numerical FEM simulations (downward blue triangles) and observed in Raman experiments (green circles).