Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplement Information File

Combining Multiphoton Excited Photoluminescence and Second Harmonic Generation to investigate TiO2 Nanoparticle Powders.

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1 Polarization Resolved Intensity Plots of SHG and MEPL at 788 nm excitation wavelength

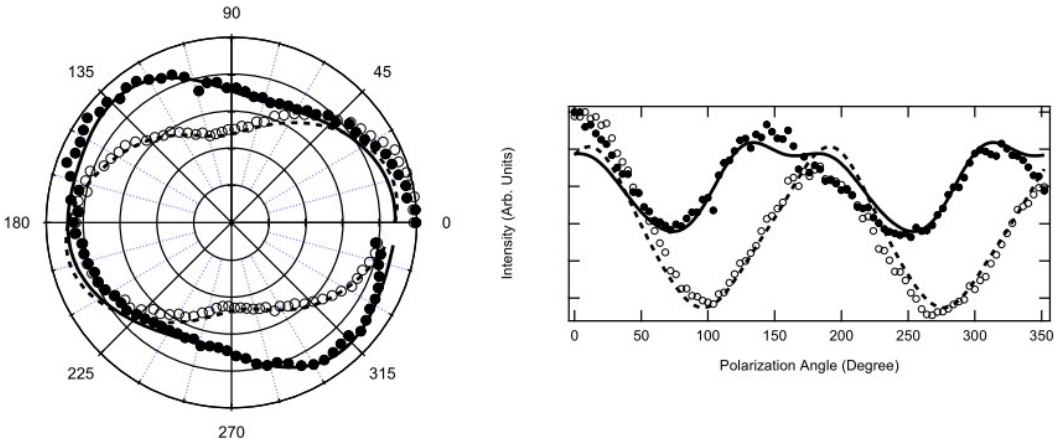

Figure S1a : Polar graphs of the SHG (full circles) band and the MEPL (empty circles) contributions. The SHG and MEPL curve fits are in solid and dashed lines, respectively. The depth position is z = - 0.012 mm

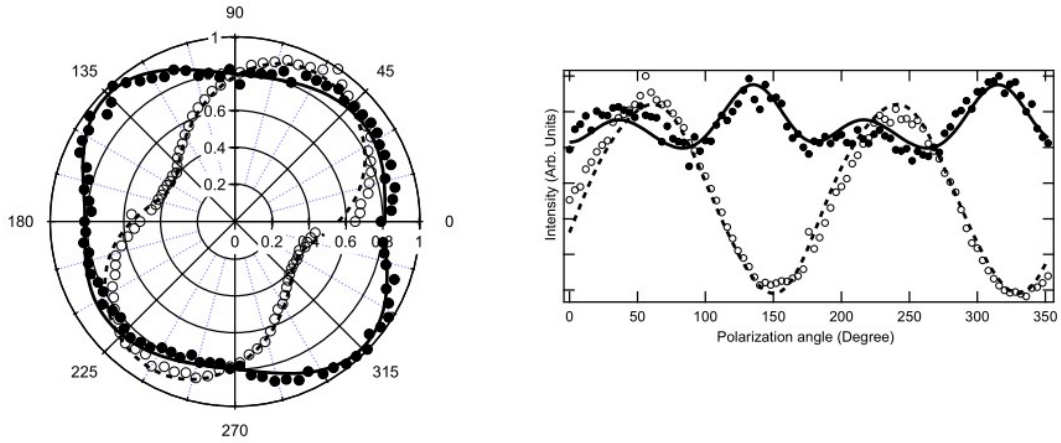

Figure S1b : Polar graphs of the SHG (full circles) band and the MEPL (empty circles) contributions. The SHG and MEPL curve fits are in solid and dashed lines, respectively. The depth position is z = 0.008 mm

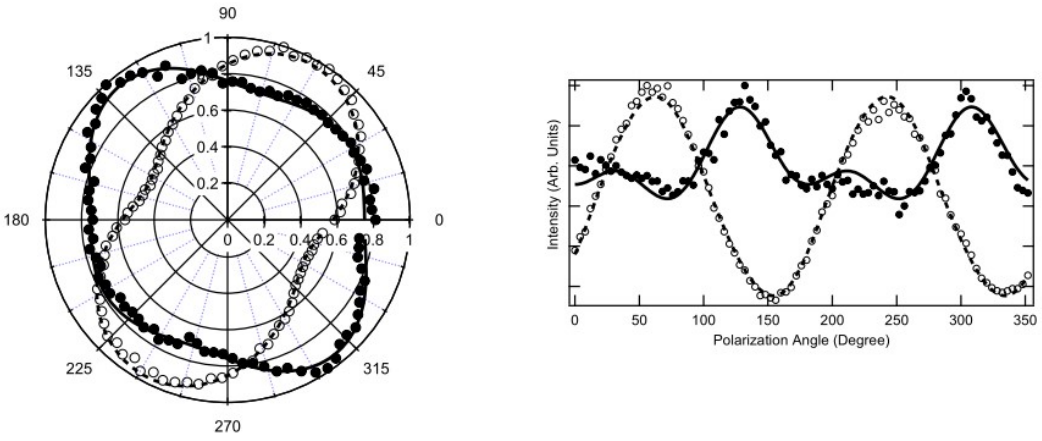

Figure S1c : Polar graphs of the SHG (full circles) band and the MEPL (empty circles) contributions. The SHG and MEPL curve fits are in solid and dashed lines, respectively. The depth position is z = 0.012 mm

2 Depth dependance of the $\alpha(z)$ parameter

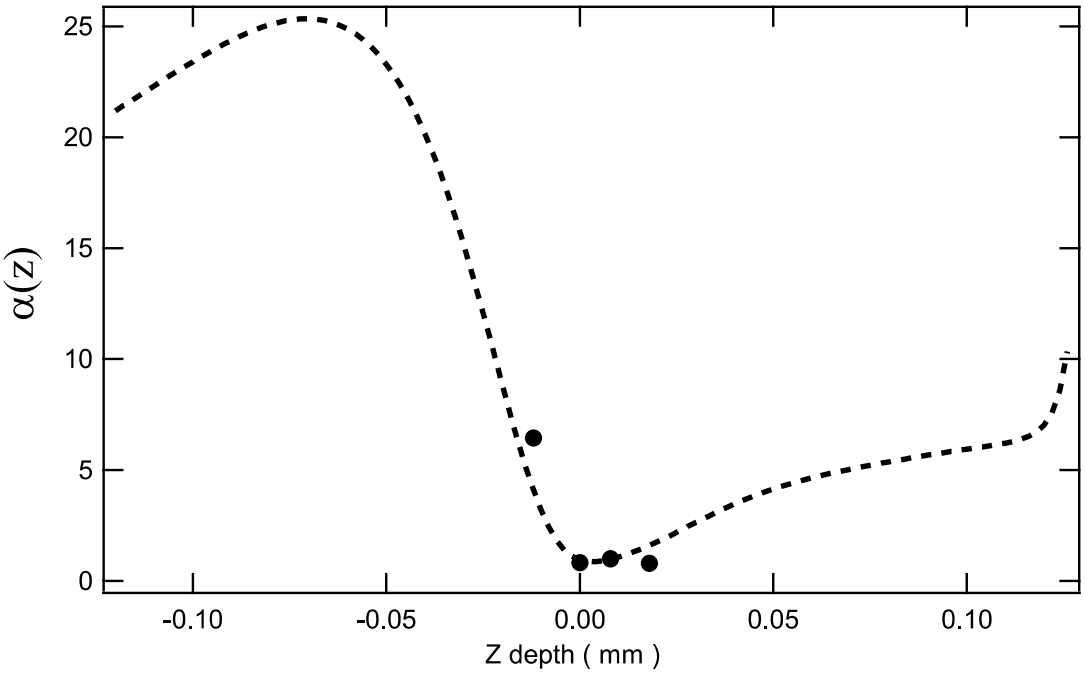

Figure S2 : Depth dependence of the $\alpha(z)$ parameter determined from the polar graphs fitted with Eqs.(1)-(3). Dashed line is an adjustment using Eq.(4).

3 Adjustment Parameters of the SHG and MEPL contributions at 772 and 788 nm excitation wavelength

Table S1 : Parameters of the adjustment procedure of the polarization graph given in Figure 3 using Eqs.(1)-(3) and recorded at a fundamental wavelength of 772 nm.

Fit Parameters	$z = 0$
a_0	0.15 ± 0.05
a_1	-0.01 ± 0.01
a_2	-0.25 ± 0.05

a_3	-0.27 ± 0.03
a_4	-0.15 ± 0.05
a_5	0.22 ± 0.08
γ_{SHG}	6.78 ± 0.10
b_0	0.02 ± 0.01
b_1	0.02 ± 0.01
b_2	0.33 ± 0.07
b_3	0.31 ± 0.08
b_4	0.70 ± 0.10
b_5	-0.18 ± 0.02
b_6	0.29 ± 0.01
b_7	0.60 ± 0.10
γ_{MEPL}	-2 .80 ± 0.10

Table S2 : Parameters of the adjustment procedure of the polarization graphs given in Figure 5 and Figure S1 using Eqs.(1)-(3) and recorded at a fundamental wavelength of 788 nm for different z depth positions in mm.

Fit Parameters	$z = -0.012$	$z = 0$	$z = 0.008$	$z = 0.018$

a_0	-0.14 ± 0.06	0.17 ± 0.03	0.03 ± 0.07	0.08 ± 0.02
a_1	-0.09 ± 0.01	0.40 ± 0.10	-0.42 ± 0.08	-0.40 ± 0.10
a_2	-0.26 ± 0.04	0.53 ± 0.07	0.59 ± 0.01	0.64 ± 0.06
a_3	-0.34 ± 0.06	0.50 ± 0.10	-0.86 ± 0.04	-1.32 ± 0.08
a_4	-0.14 ± 0.06	0.18 ± 0.02	0.02 ± 0.08	0.08 ± 0.02
a_5	0.40 ± 0.10	0.62 ± 0.08	0.41 ± 0.09	0.53 ± 0.07
γ_{SHG}	8.32 ± 0.08	2.09 ± 0.01	9.22 ± 0.08	3.74 ± 0.06
b_0	-0.08 ± 0.02	0.42 ± 0.08	0.20 ± 0.10	0.23 ± 0.07
b_1	0.20 ± 0.10	-0.03 ± 0.07	0.48 ± 0.02	0.46 ± 0.04
b_2	0.14 ± 0.06	0.75 ± 0.05	0.42 ± 0.08	0.54 ± 0.06
b_3	0.23 ± 0.07	-0.03 ± 0.07	0.85 ± 0.05	0.81 ± 0.09
b_4	0.57 ± 0.03	0.59 ± 0.01	0.07 ± 0.03	0.29 ± 0.01
b_5	0.30 ± 0.10	0.04 ± 0.06	0.55 ± 0.05	0.46 ± 0.04
b_6	0.28 ± 0.02	0.14 ± 0.06	0.01 ± 0.09	0.02 ± 0.01
b_7	0.57 ± 0.03	0.64 ± 0.06	0.57 ± 0.03	0.59 ± 0.01
γ_{MEPL}	-6 .25 ± 0.05	-0.78 ± 0.02	2.07 ± 0.03	4.20 ± 0.10

4 Numerical values for the depth dependance of the $\alpha(z)$ parameter

Table S3 : $\alpha(z)$ parameter value provided for $\gamma = 0$ and at for the different depth.

Z depth in mm	-0.012	0	0.008	0.018
$\alpha(z)$	6.44 ± 0.60	0.82 ± 0.08	1.00 ± 0.10	0.79 ± 0.08

5 Anatase TiO_2 powder

Scanning Electron micrograph (SEM) picture of the TiO2 nanoparticle powder sample.

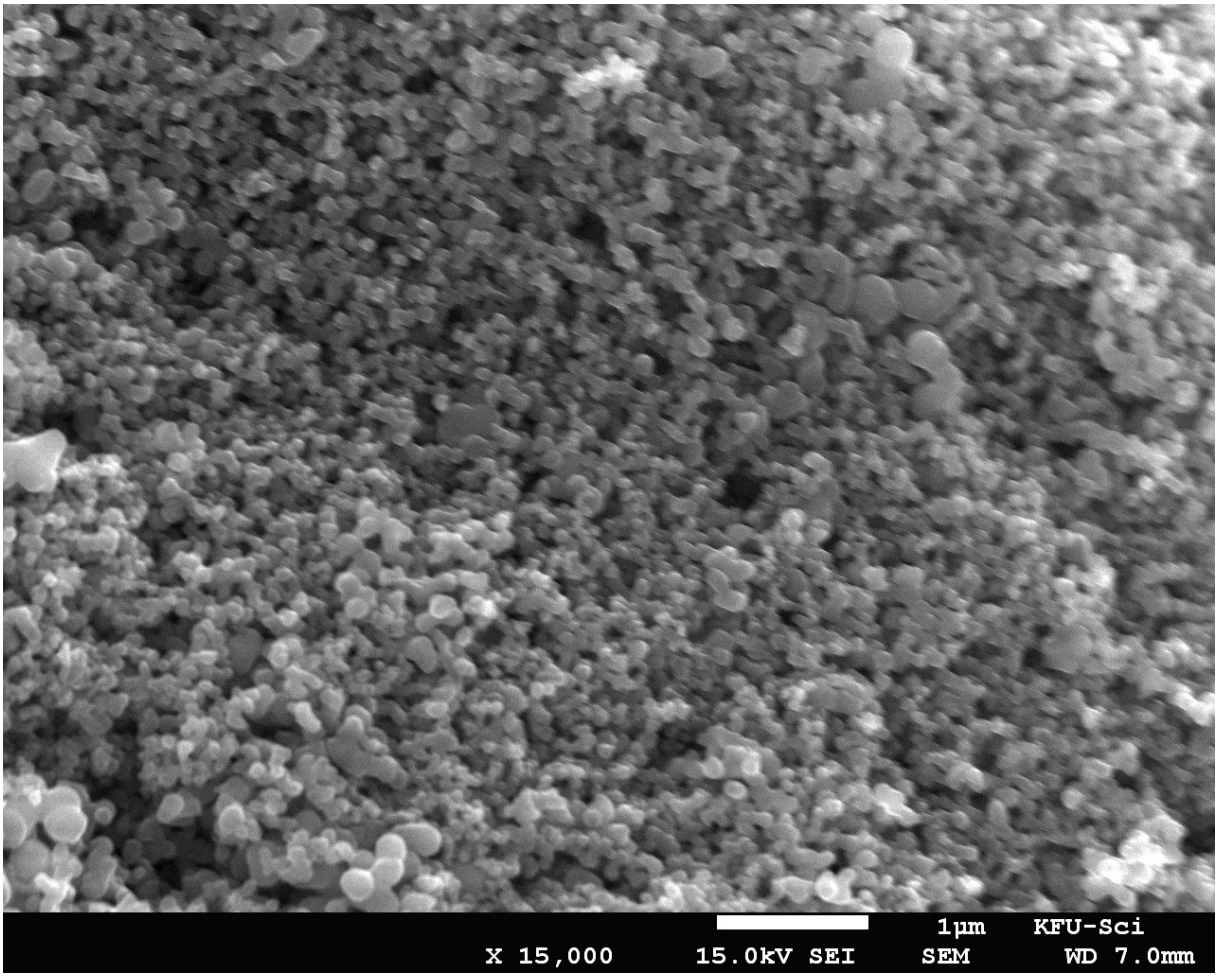

Figure S3 : Scanning Electron Micrograph (SEM) image of the anatase TiO_2 powder sample.

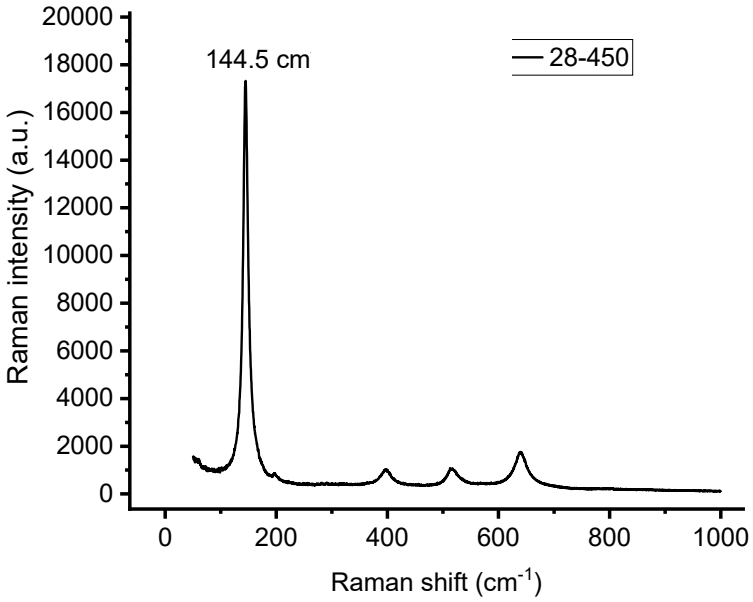

Figure S4 : Raman spectra of pure TiO_2 nanoparticles. An intense Raman peak at 145 cm^{-1} is observed, which can be assigned to the Eg optical Raman mode of anatase TiO_2. The other Raman peaks at 196 cm^{-1},394 cm^{-1}, 512 cm^{-1}, and 636 cm^{-1} were assigned to E_g, B_{1g}, A_{1g}, and E_g Raman modes of anatase TiO_2, respectively.

6 Schematics of the experimental setup

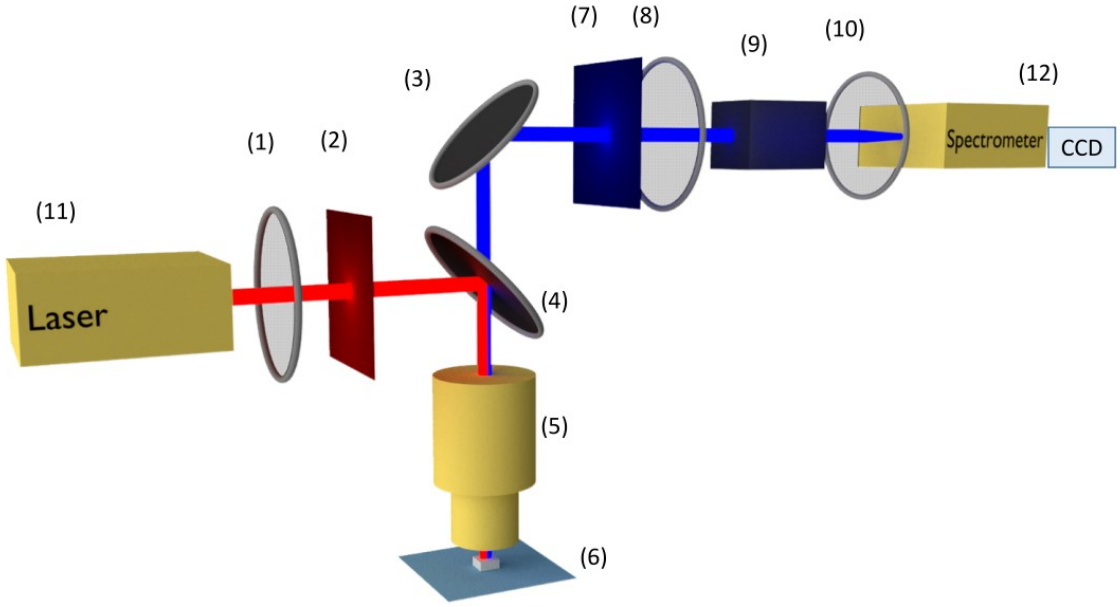

Figure S5 : Schematics of the Experimental setup : (1) Half waveplate (2) Low pass filter (3) mirror (4) Dichroic Mirror (5)Microscope Objective (6) sample (7) High pass filter (8) Half waveplate (9) polarizing Cube (10) Lense (11) Ti:Sa femtosecond laser (12) Detection system.