Electronic Supplementary Material (ESI) for Nanoscale Horizons.

# Colloidal $TiO_2$ Nanocrystals with Engineered Defectivity and Optical Properties

*Julia J. Chang[1], Bin Yuan[2], Sandro Mignuzzi[3], Riccardo Sapienza[3], Francesco Mezzadri[4]*
*Ludovico Cademartiri[4]**

1 Department of Materials Science & Engineering, Iowa State University of Science and Technology, 2220 Hoover Hall, Ames, IA, 50011

2 Department of Chemical & Biological Engineering, Iowa State University of Science and Technology, Gilman Hall, Ames, IA, 50011

3 The Blackett Laboratory, Department of Physics, Imperial College London, London, SW7 2AZ, UK

4 Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Parma, 43124, Italy

Author to whom correspondence should be addressed: ludovico.cademartiri@unipr.it

## Supporting Information

## Materials and Methods

*Colloidal nanoparticle synthesis:* Colloidal titanium dioxide nanoparticles synthesis was performed with Schlenk line under Argon atmosphere. 25g triocylphosphine oxide (TOPO, 90%, Strem Chemical, Inc.) was heated to 120 °C and degassed for 30 minutes. 1.0 mL titanium (IV) isopropoxide (TTIP, 97%, Sigma-Aldrich) and 0.3 mL titanium (IV) chloride ($TiCl_4$, 99.9%, Sigma-Aldrich) were injected into TOPO. The solution was heated to reacting temperatures and kept there for 2 hours. After the reaction was done, the reaction product was cooled to 80 °C and 25 mL hexane was added into the solution before purification.

*Purification:* Acetone was added to diluted reaction product at the ratio of 1:1, then centrifugation was performed to centrifuge out the precipitated nanoparticles. After centrifugation, supernatant was discarded, and the precipitate was re-dispersed into hexane. This purifying cycle was repeated for 3 times and the final dispersion was centrifuged at 4000rpm for 10min and filtered through 0.2µm nylon filter.

*Sample preparation:* The $TiO_2$ nanoparticle colloidal solution after purification was used as solution sample directly for TEM, PL, photography (10 mg/mL) and UV-vis spectroscopy (0.1 mg/mL). Powder sample was obtained by air-drying colloidal solutions and finely grinded before used for photography, XRD and EPR characterization. $TiO_2$ thin film samples were prepared by spin-coating $TiO_2$ nanoparticle colloidal solution onto glass substrate.

*Plasma processing:* Oxygen and Helium plasma processing of $TiO_2$ film sample were done by using Harrick plasma cleaner with operating power of 30 Watt and chamber pressure of 500 mTorr. The processing time is 48 hours.

*X-ray Powder Diffraction* (XRD): XRD spectra were collected of $TiO_2$ powder samples by using Siemens D500 x-ray diffractometer. X-ray was created by copper X-ray tube with a wavelength of 1.54 A.

*Transmission Electron Microscopy* (TEM): TEM images were obtained with 2007 JEOL 2100 200kV STEM in TEM mode, operating at 200 kV. Samples for the TEM characterization were made by casting a thin layer of a dilute nanoparticle dispersion on a 200 mesh copper grid coated with a carbon film.

*Ultraviolet-visible spectroscopy* (UV-vis): UV-vis spectra was collected by using Agilent 8453 UV-Vis instrument in the wavelength range of 190-1100 nm.

*Electron Paramagnetic Resonance* (EPR): EPR characterization was performed with ELEXSYS E580 FT-EPR instrument with ER 4122 SHQE Resonator at room temperature. Applied frequency is 9.5 GHz as continuous wave in X band, and the characterizing field sweep was from 3160 to 3560 G.

*Photoluminescence spectroscopy* (PL): Samples were optically pumped at room-temperature with a $\lambda = 440\,\mathrm{nm}$ CW laser (PicoQuant LDH-D-C-440). The emission was spectrally analysed using a grating spectrometer (Princeton Instruments Isoplane-320) equipped with a $800\,\mathrm{gr\,mm^{-1}}$ holographic grating (0.05 nm resolution) and CCD camera (Princeton Instruments Pixis 400).

## Supporting Discussion

### *Crystalline size calculation*[1]

p is defined as true crystallite size with following equation:

$$p \equiv cube\,root\,of\,the\,crystalline\,volume \tag{1}$$

When $TiO_2$ nanoparticles are assumed as fully crystalline:

$$p_{TEM} = cube\,root\,of\,octahedron = \sqrt[3]{\frac{\sqrt{2}}{3}a^3} \approx 0.7783a \tag{2}$$

Where a is the side length of octahedron nanoparticles measured from the TEM images.

For XRD spectrum, the true crystalline size is defined as the following: $\varepsilon = \frac{\lambda}{b\,cos\theta}$ (3)

$$p_{XRD} = K\varepsilon \tag{4}$$

Where:

ε: apparent crystallite size

λ: wavelength of radiation

b: broadening in radian

ϑ: Bragg angle

K: Scherrer constant.

For calculating ε, λ was 1.54 Angstrom. b was considered for (101) diffraction peak. 2θ equals to 25.281° for (101) diffraction peak. For octahedron crystal shape, Scherrer constant of (101) plane is 0.8613. Taking in all the parameters and we get $p_{XRD} = \frac{7.7885}{w} nm$ (5)

Where w is the (101) peak full width of half maximum from Gaussian fitting in degrees after background subtraction. (Figure 1, SI)

The results of true crystallite size p obtained from TEM images and XRD spectrum are plotted in Figure 2, SI.

### *Tauc plot*[2]

Transition type of $TiO_2$ bandgap was determined by taking the 2nd derivative of $TiO_2$ solution UV-vis absorption spectrum. The intercept point of the 2nd derivative with 0 line represents for the most linear relation between $\alpha\cdot h\nu^{1/2}$ and $h\nu$. Data points lie in the range of (intercept-0.1, intercept+0.1) were fitted into linear functions for each sample. The intercept of the fitted line with x axis is the corresponding bandgap energy.

## Supporting Figures

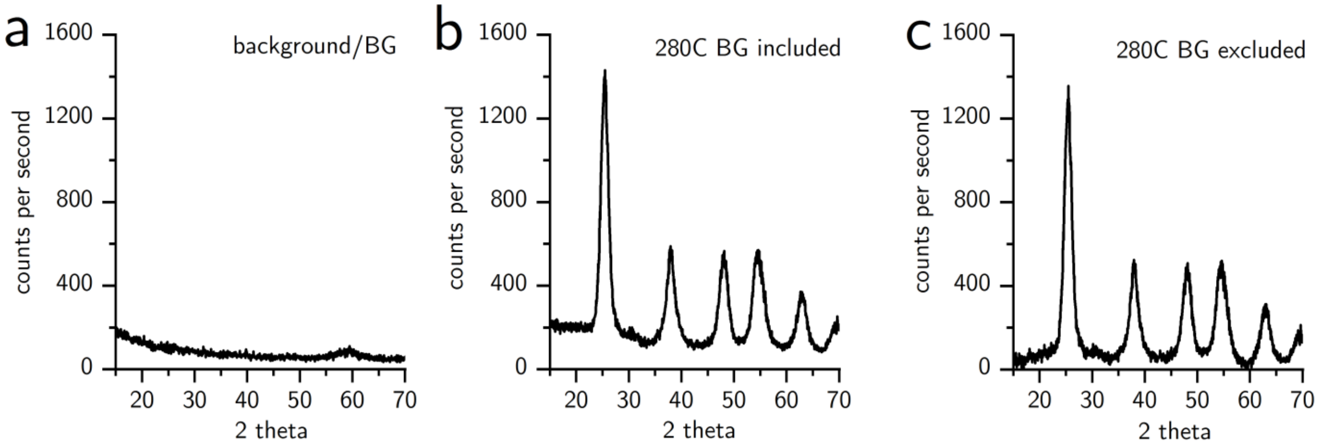

**Figure S1.** XRD spectrum background subtraction example of $TiO_2$ powder samples synthesized at 280°C. (a) Background signal from sample holder, (b) Before and (c) after background subtracted.

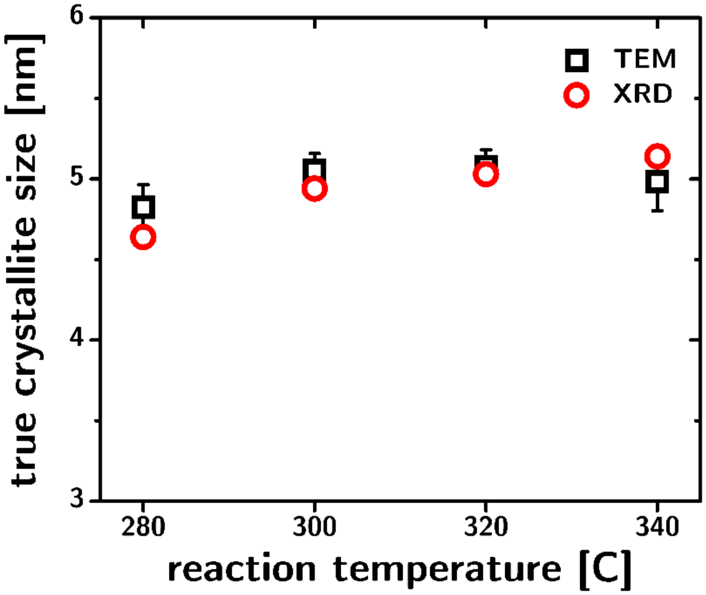

**Figure S2.** True crystallite size calculated from TEM images and XRD spectrum.

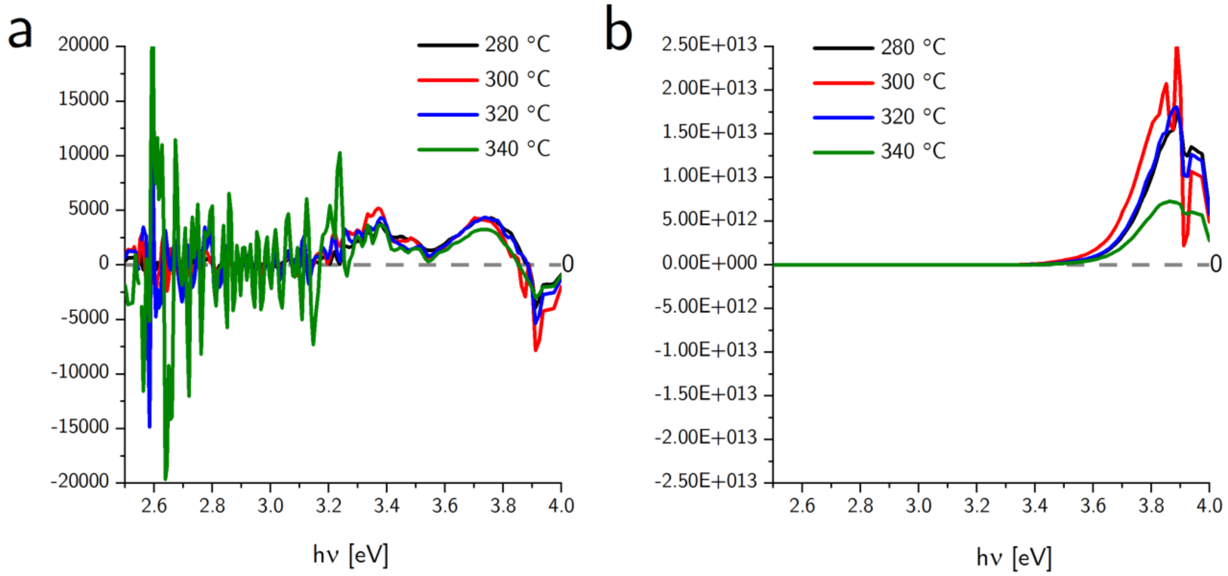

**Figure S3.** Determination of transition gap type by applying 2nd derivative operation to $TiO_2$ nanoparticle solution sample UV-vis absorption spectrum. (a) $(\alpha \cdot h\nu)^{\frac{1}{2}}$ *versus* hν and (b) $(\alpha \cdot h\nu)^{2}$ *versus* hν.

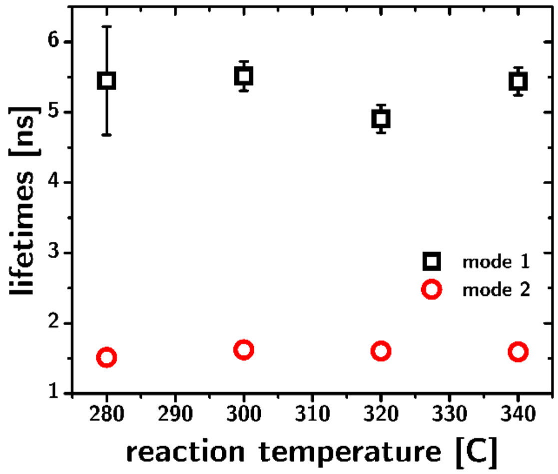

**Figure S4.** Photoluminescence lifetime of $TiO_2$ solution samples synthesized at different temperatures by using mode 1 and 2.

## References

1. J. I. Langford and A. Wilson, *Journal of applied crystallography*, 1978, **11**, 102-113.
2. N. Serpone, D. Lawless and R. Khairutdinov, *The journal of Physical Chemistry*, 1995, **99**, 16646-16654.