

Colloidal TiO₂ Nanocrystals with Engineered Defectivity and Optical Properties

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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 (TiCl₄, 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 TiO₂ 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. TiO₂ thin film samples were prepared by spin-coating TiO₂ nanoparticle colloidal solution onto glass substrate.

Plasma processing: Oxygen and Helium plasma processing of TiO₂ 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 TiO₂ powder samples by using Siemens D500 x-ray diffractometer. X-ray was created by copper X-ray tube with a wavelength of 1.54 Å.

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 $\lambda = 440$ 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 gr mm⁻¹ holographic grating (0.05 nm resolution) and CCD camera (Princeton Instruments Pixis 400).

Supporting Discussion

Crystalline size calculation¹

p is defined as true crystallite size with following equation:

$$p \equiv \text{cube root of the crystalline volume} \quad (1)$$

When TiO₂ nanoparticles are assumed as fully crystalline:

$$p_{TEM} = \text{cube root of octahedron} = \sqrt[3]{\frac{\sqrt{2}}{3}a^3} \approx 0.7783a \quad (2)$$

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

For XRD spectrum, the true crystalline size is defined as (3)

the following: $\varepsilon = \frac{\lambda}{b \cos\theta}$

$$p_{XRD} = K\varepsilon \quad (4)$$

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 (5)

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

$$\text{get } p_{XRD} = \frac{7.7885}{w} nm$$

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 plot²

Transition type of TiO₂ bandgap was determined by taking the 2nd derivative of TiO₂ 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

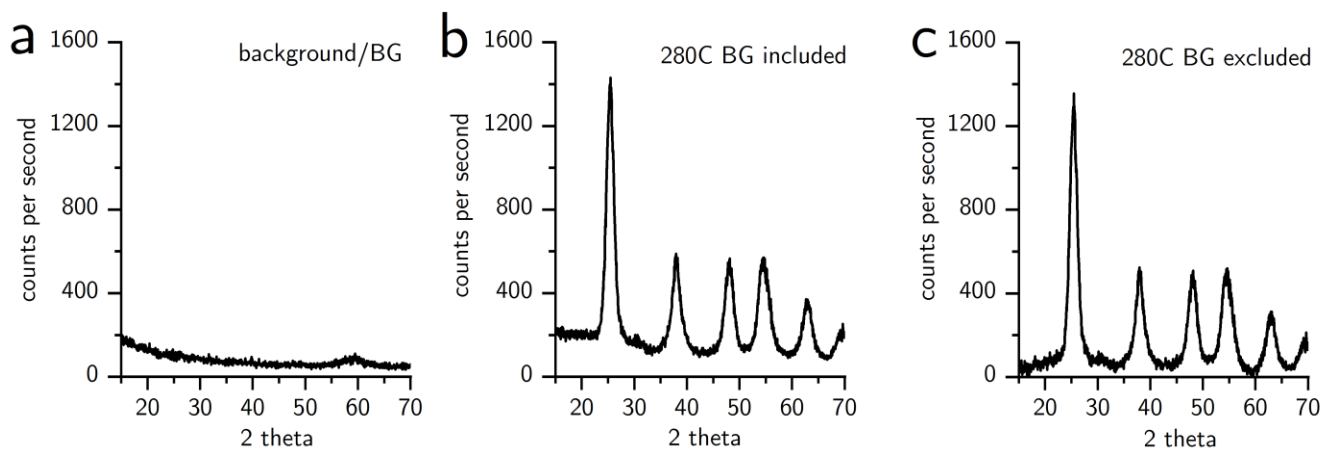


Figure S1. XRD spectrum background subtraction example of TiO_2 powder samples synthesized at 280°C . (a) Background signal from sample holder, (b) Before and (c) after background subtracted.

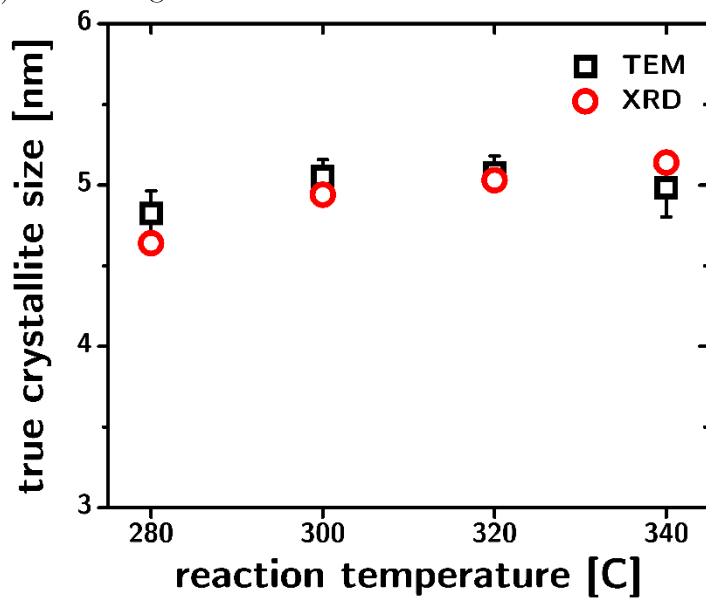


Figure S2. True crystallite size calculated from TEM images and XRD spectrum.

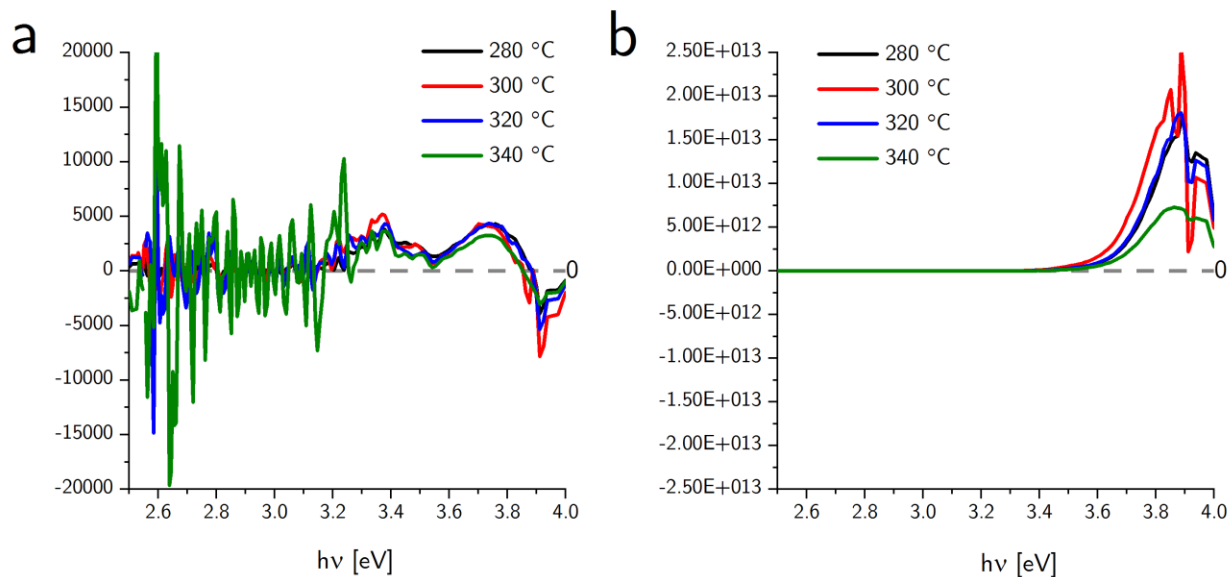


Figure S3. Determination of transition gap type by applying 2nd derivative operation to TiO₂ nanoparticle solution sample UV-vis absorption spectrum. (a) $(\alpha \cdot hv)^{\frac{1}{2}}$ versus hv and (b) $(\alpha \cdot hv)^2$ versus hv .

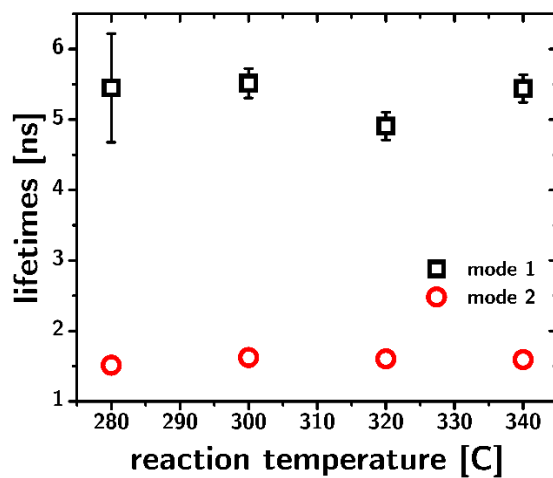


Figure S4. Photoluminescence lifetime of TiO₂ solution samples synthesized at different temperatures by using mode 1 and 2.

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.