Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information for

Facile Synthesis of Brookite TiO_2 Nanoparticles

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Experimental

Materials

Titanium tetra-isopropoxide (TTIP, $Ti[OCH(CH_3)_2]_4$, 97%), titanium tetrachloride ($TiCl_4$), Titanium (IV) butoxide ($Ti(OBu)_4$), titanium (IV) oxysulfate ($TiOSO_4$), isopropanol (C_3H_8O, 99.8 %), glycolic acid ($HOCH_2COOH$, 99 %), ammonium hydroxide (NH_4OH, 28-30 % NH_3), sodium oleate ($C_{18}H_{33}NaO_2$, ≥ 82% fatty acids) and triethanolamine ($C_6H_{15}NO_3$, ≥ 99.0%) were purchased from Sigma-Aldrich and used as received.

Synthesis

A mixture of 5g of titanium source (either TTIP, $TiCl_4$, $Ti(OBu)_4$ or $TiOSO_4$) and 5g of isopropanol was poured into 50 mL of demineralized water under magnetic stirring for 3 hours. The suspension was centrifuged and washed several times with demineralized water to collect the wet amorphous precipitate. The precipitate was then added to 50 ml of 1.05 M aqueous solution of glycolic acid under magnetic stirring for 2 h. The mole ratio of titanium to glycolic acid was 0.34 i.e. $n_{Ti} : n_{GA} = 0.34$. The resulting suspension was transferred to a 175 mL teflon-lined autoclave, which was first heated to 90-100 ˚C and kept at this temperature for 20 hours. Then the autoclave was cooled down to room temperature and the pH was adjusted to 12 by addition of concentrated NH_4OH. Finally, the autoclave was heated to 200 ˚C and kept at this temperature for 20 hours. After cooling to room temperature the product was washed, centrifuged and resuspended with clean water before drying overnight at 60 ˚C.

Characterization

Powder X-ray diffraction (PXRD) data was measured on a SmartLab Rigaku diffractometer equipped with a monochromatized Cu $K\alpha_1$ source, parallel beam optics, and a D/tex Ultra 250 1D detector. The PXRD patterns were analyzed using Rietveld refinement in the Fullprof software suite. A LaB_6 standard was used to correct for instrumental peak broadening.

Raman spectroscopy was carried out using a Renishaw inVia Raman confocal microscope using a 514 nm Ar-ion laser operating at an intensity of ~1 mW and employing a 100x lens. The Raman system was calibrated using a silicon reference. Typically, 200 spectra were acquired using a 1s acquisition time in the streamline HR mode. Renishaw's program wire 4.3 was used for the recording and analysis of the acquired spectra.

Transmission electron microscopy (TEM) and high resolution transmission microscopy (HRTEM) images were obtained on a TALOS F200A with a TWIN lens system, X-FEG electron source, Ceta 16M

Camera and a Super-X EDS Detector. Spatially resolved elemental analysis, with a spatial resolution better than 2 nm, was obtained using the same TALOS microscope in STEM mode. Exposure times of 5 minutes were used to create elemental distribution maps with satisfactory counting statistics, while minimizing potential problems such as beam damage and specimen drift. Scanning transmission electron microscopy (STEM) images were obtained using a High Angle Annular Dark Field detector (HAADF). RG overlays of the STEM EDS elemental maps were made using the FIJI (v.1.49q) software.

Optical diffuse reflectance measurements were performed at room temperature using a Shimadzu UV-3101 PC spectrometer. $BaSO_4$ was the reference sample and the spectra were recorded in the range of 200-700 nm. The band gap was estimated using Tauc plot assuming direct and indirect allowed transitions. This involves plots of $[F(R)\cdot hv]^n$ against hv, where n=2 for direct band gaps and n=1/2 for indirect band gaps. $F(R)$ is the Kubelka-Munk function and hv is incident photon energy.

Specific surface area was measured on a Quantachrome autosorb NOVA 2000 automated gas sorption system using the multipoint Brunauer-Emmett-Teller (BET) nitrogen adsorption technique. The samples were degassed 20 h at 423 K in glass tubes inserted into a vacuum oven before measurements.

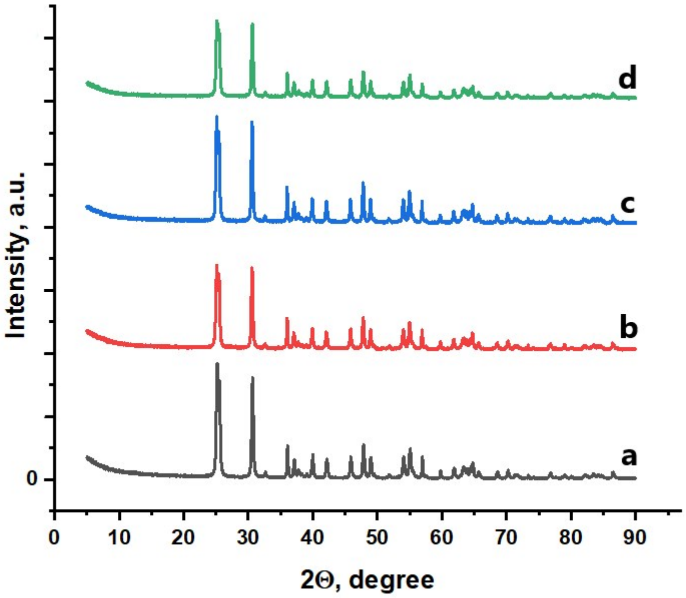

Fig. S1 PXRD of brookite nanoparticles as synthesized from titanium glycolate complex using (a) titanium (IV) isopropoxide, (b) titanium (IV) butoxide, (c) titanium tetrachloride and (d) titanium oxysulfate as starting materials, respectively.

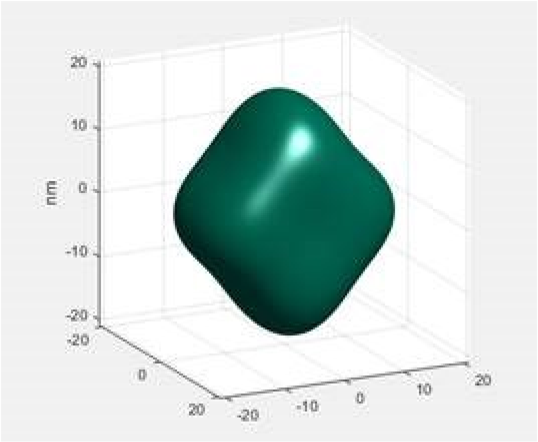

Fig. S2 3D reconstruction of crystallite morphology using spherical harmonics peak shape analysis during Rietveld refinement. The average crystallite size is 19(1), 44(1) and 41(1) nm along the *a*, *b* and *c* axes, respectively.

Table S1. Structural parameters and refinement residuals obtained from Rietveld analysis of PXRD data.

Sample	**Brookite_TTIP**	**Brookite_Ti(OBu)$_4$**	**Brookite_TiCl$_4$**	**Brookite_TiOSO$_4$**
R$_{Bragg}$	3.83	3.98	4.99	5.96
R$_F$	3.98	3.47	4.19	4.79
Unit cell [Å]				
a	9.1795(2)	9.1800(2)	9.1811(2)	9.1801(2)
b	5.45673(9)	5.45526(9)	5.45595(9)	5.4574(1)
c	5.14698(6)	5.14494(6)	5.14531(7)	5.14644(8)
Ti position (x,y,z)				
x	0.1295(1)	0.1295(1)	0.1294(1)	0.1296(1)
y	0.0967(2)	0.0993(3)	0.0985(3)	0.0981(3)
z	0.8615(2)	0.8602(2)	0.8597(3)	0.8605(3)
O1 position (x,y,z)				
x	0.0157(4)	0.0111(4)	0.0142(4)	0.0131(4)
y	0.1502(7)	0.1508(7)	0.1528(8)	0.1493(9)
z	0.1883(5)	0.1910(5)	0.1901(6)	0.1925(6)
O2 position (x,y,z)				
x	0.2279(4)	0.2325(4)	0.2327(4)	0.2314(4)
y	0.116(1)	0.110(1)	0.112(1)	0.113(1)
z	0.5444(4)	0.5401(4)	0.5438(5)	0.5452(5)
Ti occupancy	0.943(4)	0.909(4)	0.914(4)	0.944(5)
Crystallite sizes[nm]				
Along a-axis	13(1)	16(1)	14(1)	13(1)
Along b-axis	20(1)	26(1)	25(1)	21(1)
Along c-axis	36(2)	43(2)	39(2)	34(2)
Coefficients of				

spherical harmonics				
a_{00}	4.67(3)	4.20(3)	4.19(3)	4.66(3)
a_{20}	-1.77(5)	-1.56(5)	-1.53(5)	-1.71(6)
a_{22+}	0.87(6)	0.90(7)	1.03(7)	0.97(8)
a_{40}	-0.08(3)	-0.30(3)	-0.12(4)	-0.02(4)
a_{42+}	-0.52(4)	-0.50(4)	-0.69(4)	-0.75(5)
a_{44+}	0.81(6)	0.24(6)	0.58(7)	0.77(8)

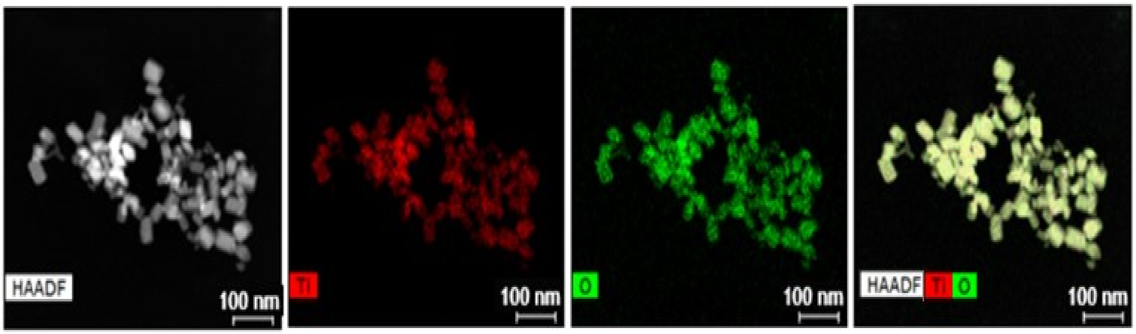

Fig. S3 (a) High-angle annular dark-field (HAADF) image of brookite nanoparticles synthesized from titanium isopropoxide precursor. Elemental mapping of (b) Ti, (c) O, and (d) overlay of Ti and O.

Energy-dispersive X-ray spectroscopy (EDS) elemental mapping results for the brookite nanoparticles synthesized from titanium isopropoxide precursor are shown in Fig. S3. The Ti and O elemental distributions are quite uniform, which implies high homogenity. The composition quantification yields a molar ratio of Ti to O very close to 1 to 2, i.e. TiO_2. This shows that the synthesis product is largely free of defects.

The brookite nanoparticles obtained from titanium (IV) isopropoxide precursor have a BET surface area of 30.7 m^2/g with an average Barretl-Joyner-Halenda (BJH) pore diameter of 4.04 nm and a pore volume of 0.093 cm^3/g. The isotherm is characteristic of a type IV with a type H_2 disordered pores (pore blocking, percolation phenomena).

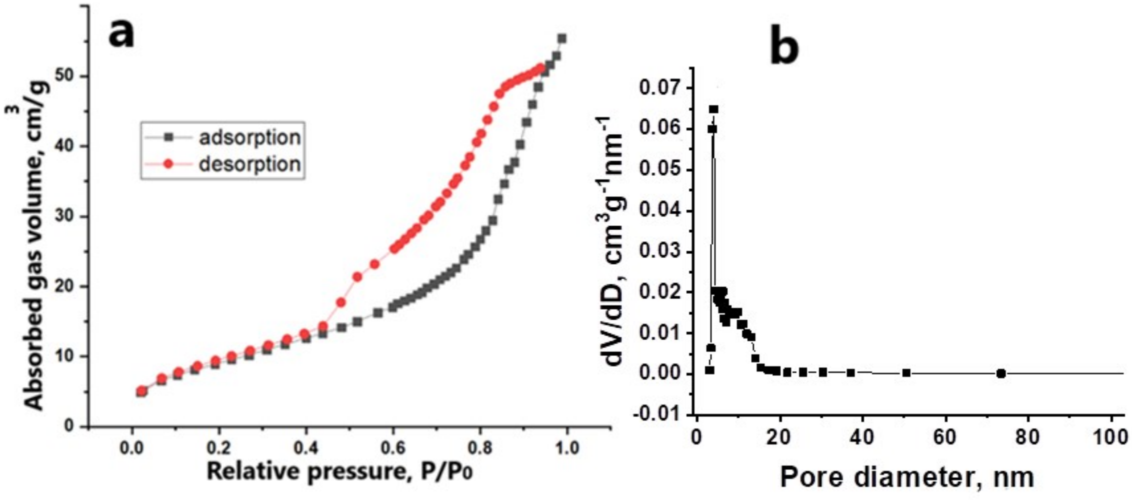

Fig. S4 Nitrogen adsorption and desorption full isotherm at 77 K (a) with corresponding pore-size distribution calculated by BJH method from desorption branch (b).