Supporting Information for:

# Hyperbranched Potassium Lanthanum Titanate Perovskite Photocatalysts for Hydrogen Generation

Tobias Grewe,<sup>a</sup> Ting Yang,<sup>b</sup> Harun Tüysüz,<sup>a\*</sup> and Candace K. Chan<sup>b\*\*</sup>

<sup>a</sup>Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm Platz 1, 45470 Mülheim an der Ruhr, Germany. \*tueysuez@kofo.mpg.de

<sup>b</sup>Materials Science and Engineering, School for Engineering of Matter, Transport and Energy, Arizona State University, 501 E Tyler Mall, ECG 301, Tempe, AZ 85287, U.S.A. \*\*candace.chan@asu.edu

# 1. Experimental

A. *Materials:* Potassium hydroxide (KOH, GPR RECTAPUR, min. 85%) was purchased from VWR Chemicals, lanthanum nitrate hexahydrate (La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, puriss. p.a. > 99.0%) was obtained from Fluka, titanium(IV) ethoxide (Ti(OEt)<sub>4</sub>; tetraisopropyl ortho-titanate; impurities  $\leq$  3%) and potassium tetrachloroplatinate(II) (K<sub>2</sub>PtCl<sub>4</sub>,  $\geq$  99.9 % trace metal basis) were purchased from Sigma Aldrich. P25 TiO<sub>2</sub> was obtained from Degussa.

# B. Synthesis of KLTO:

*KLTO hyperbranched structures:* 13.6 g of KOH (0.21 mol) was dissolved in 48 mL of distilled water. The solution was transferred into a 50 mL autoclave inlet made of Teflon. 560 mg of  $La(NO_3)_3 \cdot 6H_2O$  (1.29 mmol) was added to the solution, followed by 420 µL of Ti(OEt)<sub>4</sub> (457 mg, 2.0 mmol). The Teflon inlet was placed in a steel autoclave with a total volume of 100 mL, equipped with a pressure and temperature sensor. The autoclave was heated at a temperature of 200 °C for 12 h and the pressure was 5 bar. Afterwards, the sample was collected and treated using acid etching with 0.1 M HCl solution.

*KLTO nanoparticles:* The procedures from reference S1 were reproduced using P25 as the  $TiO_2$  source and scaling up the reagents 4-fold. During the reaction, the pressure was approximately 1.5 bar. All other reagent quantities and volumes are the same as for the hyperbranched structures above.

# C. Acid etching

To remove  $La(OH)_3$  that formed as a side product during the KLTO synthesis, the sample was collected and washed with 0.1 M HCl. Two etching procedures were studied. The KLTO was either: 1) exposed to acid for a short duration (10 min) with mild stirring; or 2) etched five times, 20 min each time, in the acid using a shaker. In the second method, the sample was recovered

using centrifugation after each etching step and re-suspended in fresh acid. In both cases, after the final etching step, the sample was washed with water, recovered using centrifugation, and dried at 50  $^{\circ}$ C.

#### D. 1 wt% Pt loading by impregnation and thermal decomposition:

120 mg of KLTO were dispersed in 3 mL aqueous solution of  $K_2PtCl_4$  (2.6 mg, 1 wt% loading of Pt) and stirred for 1 hour in a 5 mL sample vial. After 1 h, the magnetic stirrer was removed and the sample was dried at 50 °C. Subsequently, the sample was transferred into a crucible and then treated at 300 °C in a muffle furnace in air for 2 h (ramping rate: 5 K/min). After cooling down to room temperature, the light orange sample was collected.

# E. 1 wt% Pt loading by photodeposition:

The photodeposition of Pt onto KLTO was performed in-situ immediately prior to the photocatalytic H<sub>2</sub> generation test without removing the KLTO from the reactor.  $K_2PtCl_4$  (2.2 mg, 1 wt% loading of Pt) was dissolved in 10 mL of a 10 vol% methanol/water mixture and 100 mg KLTO was added. The mixture was shaken for 1 min and poured into the photoreactor. 190 mL of the 10 vol% methanol/water mixture was added into the reactor as well in order to have 200 mL of solution total. Photodeposition was conducted using a 150 W middle pressure mercury lamp (TQ 150) from Peschl Ultraviolet, which was also used for the photocatalytic hydrogen production.

# F. Photocatalytic hydrogen production:

Photocatalytic H<sub>2</sub> production was performed in an in-house built inner irradiation photoreactor cell with a total volume of 260 mL. The reactor was filled with 200 ml solution (10 vol% methanol in distilled water) and 100 mg of catalyst. The catalyst was dispersed in 10 mL reactor solution by shaking for 1 min and then transferred into the reactor that was filled with the rest of the solution. Inside the photoreactor the catalyst solution was stirred for 20 min before the lamp was switched on. A 150 W middle pressure mercury lamp (TQ 150) from Peschl Ultraviolet was used as light source that was irradiating the catalyst for 16 h. Afterwards, the lamp was switched off and the reactor was purged for 30 min. Then the lamp was switched on again for 4 h. An Ar flow of 50 mL/min is connected to the reactor and purges through the solution, carrying the evolved gases out of the reactor via another connection into a gas analyser (X-STREAM Enhanced XEGP Gas Analyzer from Emerson).

# 2. Materials Characterization:

Ultraviolet and visible light spectroscopy (UV-Vis) was conducted in diffuse reflectance mode on a Varian Cary 5G with praying mantis set-up using MgO as white standard. Transmission electron microscopy (TEM) images were obtained either with a Hitachi H-7100 at 100 kV, or with a JEOL 2010F at 200 kV. The samples were prepared onto lacey carbon film covered copper grid. Energy dispersive X-ray spectroscopy (EDS) was performed on the JEOL 2010 F using an EDAX detector for determining the composition of individual KLTO nanostructures. Scanning electron microscopy (SEM) was performed using an FEI XL-30 FESEM. The sample powders were dispersed in isopropanol and then deposited onto a silicon wafer substrate. For some samples, a very thin layer of gold (< 10 nm) was sputtered to improve conductivity and reduce charging during imaging. SEM-EDS was conducted on samples without gold coatings using a Hitachi S-3500N instrument to monitor the average K and La content after photocatalytic testing. The microscope was equipped with a Si(Li) Pentafet Plus detector from Texas Instruments. An area of about 1 mm<sup>2</sup> of sample is analyzed via this method.

Nitrogen physisorption was measured with an ASAP 2010 adsorption analyser (Micrometrics) at 77 K. Prior to the measurements, the samples were degassed at 120 °C for 12 h. The Brunauer-Emmett-Teller (BET) surface area was determined from the relative pressure range between 0.06 and 0.2. X-ray diffraction (XRD) patterns were collected at room temperature on a Stoe STADI P transmission diffractometer using Cu K $\alpha_1$  radiation. For the supporting information, XRD patterns were measured on a Stoe theta/theta diffractometer in Bragg-Brentano geometry (reflection) using CuK $\alpha_{1,2}$ . The measured patterns were evaluated qualitatively by comparison with entries from the ICDD-PDF-2 powder pattern database.

Mott-Schottky measurements were conducted on electrodes made by coating a slurry of the asprepared KLTO sample onto a fluorine doped tin oxide (FTO) substrate. The slurry was prepared by mixing 100 mg of the KLTO sample powder, 300  $\mu$ L de-ionized (DI) water, 10  $\mu$ L acetylacetone (Sigma-Aldrich) and 5  $\mu$ L Triton X-100 (Sigma-Aldrich). The mixture was stirred for 2 h and then coated as a thin film onto the conducting side of the substrate using an automatic laboratory drawdown machine (Auto-Draw III) with a #4 rod. After that, the coated substrate was heated at 200 °C for 2 h to dry the film. The Mott-Schottky measurements were performed at 10 Hz and 100 Hz in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution (pH = 8.2) with a Biologic VMP3 potentiostat. The reference electrode used was a saturated calomel electrode (SCE) and the counter electrode was a Pt wire.

#### References

S1. Yang, T.; Gordon, Z.D.; Chan, C.K. Synthesis of hyperbranched perovskite nanostructures. *Crystal Growth and Design*, 13, 3901- 3907 (2013).

**Supporting Figures** 



**Figure S1.** XRD pattern of KLTO synthesized in 100 mL hydrothermal reactor with P25 as precursor and KLTO peaks compared to the reference pattern for  $K_{0.469}La_{0.531}TiO_3$  (PDF 89-4930).



**Figure S2.** TEM images of KLTO synthesized in 100 mL hydrothermal reactor with P25 as precursor showing (a) the overall morphology at low magnification, and (b) the KLTO nanowires along with the P25 nanoparticles at higher magnification.



**Figure S3**. XRD pattern of KLTO synthesized with  $Ti(OEt)_4$  precursor after long HCl etching time (KLTO-L). The new reflection indicated by the arrow may be from  $H_2La_2Ti_3O_{10}$ . The XRD pattern was collected in a Bragg-Brentano geometry using CuK $\alpha_{1,2}$  radiation.



**Figure S4.** KLTO nanoparticles (a) TEM images, (b) XRD pattern, (c) Photocatalytic  $H_2$  generation in 10 vol% methanol compared to hyperbranched KLTO – S.



**Figure S5.** TEM image of KLTO after Pt deposition by impregnation and heating at 300 °C (thermal decomposition). (a) Low magnification image showing the hyperbranched morphology. (b) High magnification image reveals that no Pt particles are visible.



**Figure S6.** TEM image of KLTO with Pt decoration by impregnation after the photocatalytic test, with many Pt nanoparticles observed across the sample.



**Figure S7.** TEM image of KLTO with Pt decorated by photodeposition after the photocatalytic test, with few Pt particles scattered across the sample.