## Supplementary Information for

## "Surfactant-free Synthesis of Three-dimensional Perovskite Titania-based Micron-scale

## Motifs Used as Catalytic Supports for the Methanol Oxidation Reaction"

Nathaniel Hurley,<sup>1</sup> Luyao Li,<sup>1</sup> Christopher Koenigsmann,<sup>2</sup> and Stanislaus S. Wong<sup>1,\*</sup>

Email: stanislaus.wong@stonybrook.edu; sswong@bnl.gov

<sup>1</sup>Department of Chemistry, State University of New York at Stony Brook,

Stony Brook, NY 11794-3400

<sup>2</sup>Department of Chemistry, Fordham University,

Bronx, NY 10458

\*To whom correspondence should be addressed.



Figure S1. SEM images of CTO, annealed at various temperatures, including (A) 600°C, (B)

700°C, (C) 800°C, (D) 900°C, (E) 1000°C, and (F) 1100°C, respectively.



**Figure S2.** XRD patterns of a CTO powder sample calcined at (A) 1100°C; (B) 1000°C; (C) 800°C; and (D) 600°C, respectively, as well as of the (E) CTO intermediate. The data on all samples were acquired without an acid wash.



**Figure S3.** SEM images of TiO<sub>2</sub> rod-like impurities and "sea urchin" motifs within isolated (A) CTO and (B) STO samples, respectively, prior to the 'nitric acid' wash.



**Figure S4.** XRD patterns of a BTO powder sample, calcined at (A) 1100°C, (B) 1000°C, (C) 900°C, and (D) 800°C, respectively, as well as of the (E) BTO intermediate. The data on all samples were obtained without an acid wash. Triangles indicate the presence of BaTi<sub>5</sub>O<sub>11</sub> peaks.



**Figure S5.** SEM images of BTO, annealed at various temperatures, including (A) 600°C, (B) 700°C, (C) 800°C, (D) 900°C, (E) 1000°C, and (F) 1100°C, respectively.



**Figure S6.** SEM images of STO annealed at various temperatures, including (A) 600°C, (B) 700°C, (C) 800°C, (D) 900°C, (E) 1000°C, and (F) 1100°C, respectively.



**Figure S7.** XRD patterns of annealed, hydrothermal-derived, and ultra-small STO samples as compared with the standard STO reference pattern.



**Figure S8.** XRD patterns of the TiO<sub>2</sub> 3D precursor templates along with the commercial TiO<sub>2</sub> nanoparticles, with both samples compared with respect to the anatase TiO<sub>2</sub> database standard.



**Figure S9.** TEM images of Pt particles deposited onto the various different perovskite and standard samples that were analyzed. These systems include (A) Pt/CTO, (B) Pt/STO, (C) Pt/BTO, (D) Pt/STO hydrothermal, (E) Pt/STO ultra-small, (F) Pt/TiO<sub>2</sub> commercial, and (G) Pt/TiO<sub>2</sub> precursor templates, respectively.



**Figure S10.** CV curves for reference standards of (A) Pt/STO hydrothermal, (B) Pt/STO ultrasmall, (C) Pt/TiO<sub>2</sub> commercial, and (D) Pt/TiO<sub>2</sub> template systems, respectively

Material System	Specific activity (mA / cm <sup>2</sup> )		Mass Activity (mA / mg)		Specific Surface Area
	0.7 V	0.8 V	0.7 V	0.8 V	(m <sup>2</sup> /g)
Pt / CTO -	0.033	0.151	1.920	8.780	5.80
annealed					
Pt / STO -	0.030	0.138	1.150	5.300	3.85
annealed					
Pt / STO -	0.016	0.030	0.103	0.198	0.65
hydrothermal					
Pt / STO	0.018	0.032	0.056	0.099	0.31
(ultra-small)					
Pt / BTO -	0.021	0.114	1.200	6.420	5.70
annealed					
Pt / TiO <sub>2</sub> templates	0.008	0.012	0.024	0.035	0.28
Pt / TiO <sub>2</sub>	0.033	0.104	0.197	0.624	0.60
(commercial)					

**Table S1.** MOR data obtained for all samples, including specific and mass activity readings, in

 addition to specific surface area values.



**Figure S11.** Chronoamperometry measurements collected at 0.8 V of reference standard systems associated with Pt/STO hydrothermal (orange), Pt/STO ultra-small (teal), Pt/TiO<sub>2</sub> commercial (black), and Pt/TiO<sub>2</sub> templates (purple), respectively, obtained within an Arsaturated 0.1 M perchloric acid solution + 0.5 M MeOH medium for 3600 sec.