Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Facile Synthesis of Porous La-Ti-O and $LaTiO_2N$ Microspheres

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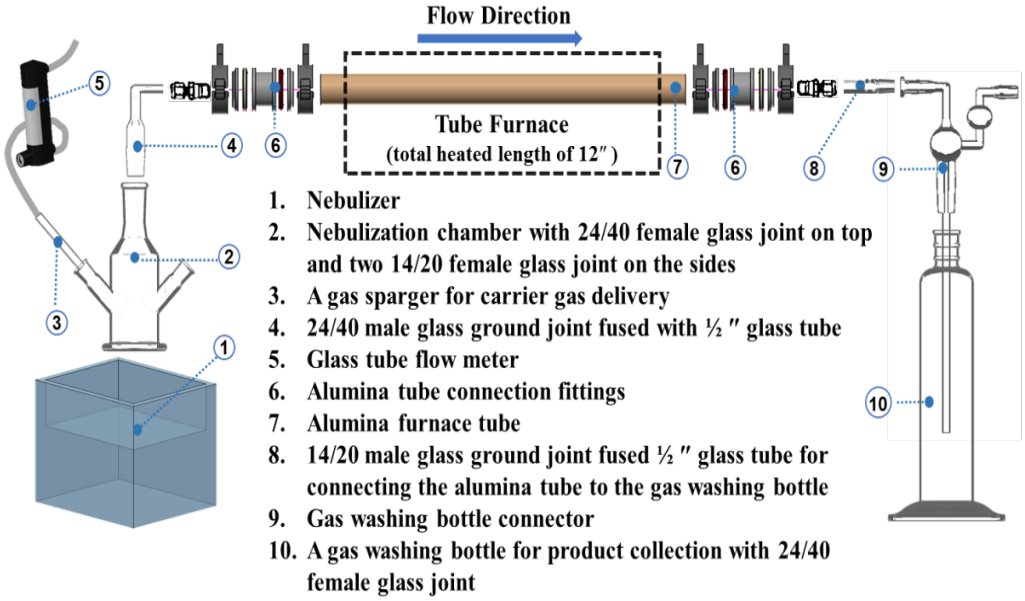

Figure S1: Schematic of the ultrasonic spray synthesis apparatus.

Please see reference 1 for a full description that includes an assembly video.[1] The apparatus consists of a nebulizer, a nebulization chamber, a furnace, a furnace tube and corresponding adapters, and a product collection apparatus. The nebulization source is a Vicks V5100N Ultrasonic Humidifier transducer (1.7 MHz, ~5 W/cm2) and associated electronics fitted in a custom acrylic base filled with water as the coupling media. The nebulization chamber The nebulization chamber consists of a glass 57 mm diameter O-ring groove opening (Chemglass: CG-138-02), two 14/20 ground glass openings to allow for gas inlet and sample refills, and a 24/40 joint to serve as the outlet for the aerosols toward the furnace tube. A Saran wrap membrane is clamped between a Teflon base with an O-ring and the nebulization chamber. The nebulization chamber is then centered above the ultrasonic transducer at a distance of ~2 cm and filled with ~10 mL of precursor solution (room temperature). An alumina tube (1 inch inner diameter, 1.3 inch outer diameter, 21.5 inch length) is used with the single zone furnace (total heating region of ~27.5 cm, 1100 °C maximum). An adapter that utilizes sets of triclamps, fittings, and gaskets is to seal the end of the tube with an airtight Swagelok seal, which connects the tube to the nebulization chamber and collection apparatus through fused silica adapters.

Note: while a Vicks V5100N Ultrasonic Humidifier base was used in the study, the system is adaptable to other household humidifiers and small changes in dimensions without changing the properties of the product.

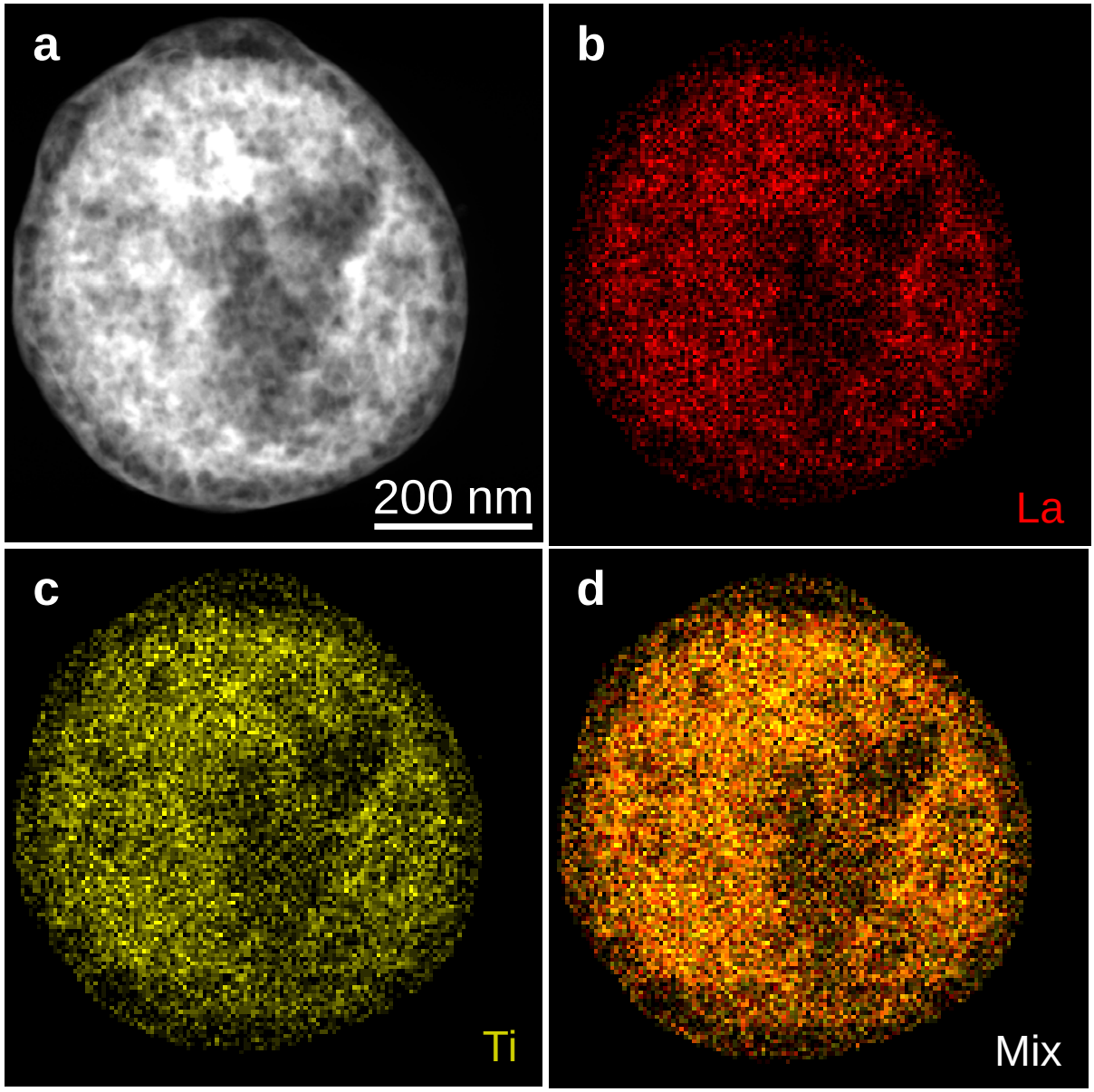

Figure S2. a) Scanning transmission electron microscope image and b-d) EDX elemental maps where red is La and yellow is Ti. An overlay of the La and Ti maps is shown in d.

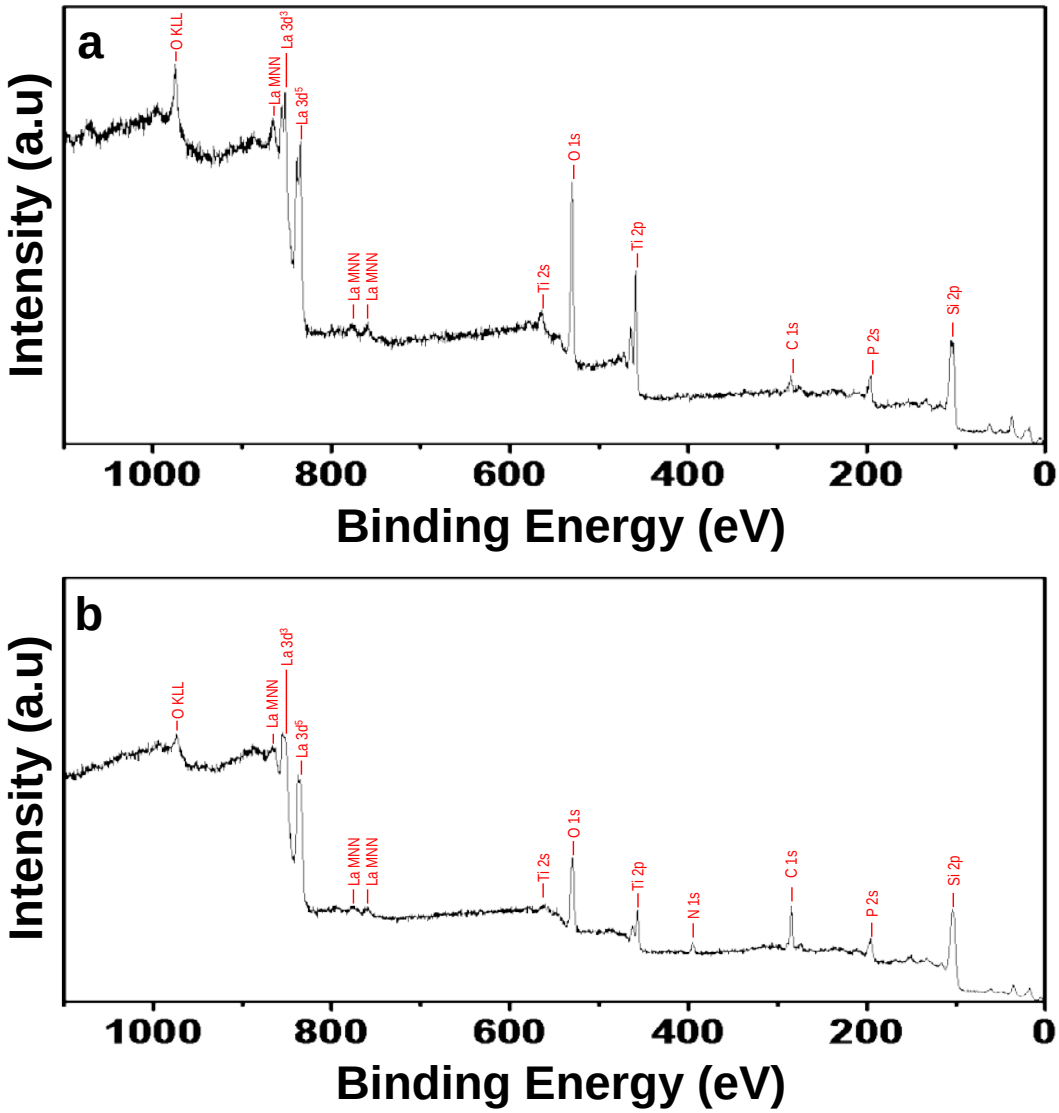

Figure S3. XPS survey scans of a) LTO-USS and b) LTON-USS.

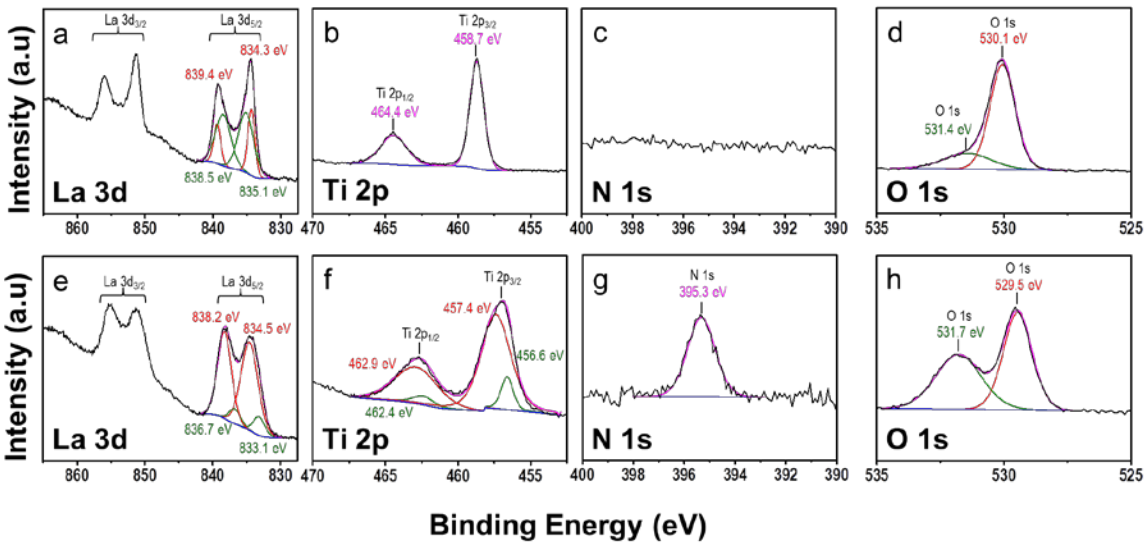

Figure S4. High resolution XPS spectra for the La 3d, Ti 2p, N 1s, and O 1s regions of LTO-USS (a-d) and LTON-USS (e-h). Black traces represent experimental data, red and green traces show individual peak deconvolutions, blue represents the calculated background, and magenta traces show the overall calculated peak envelope.

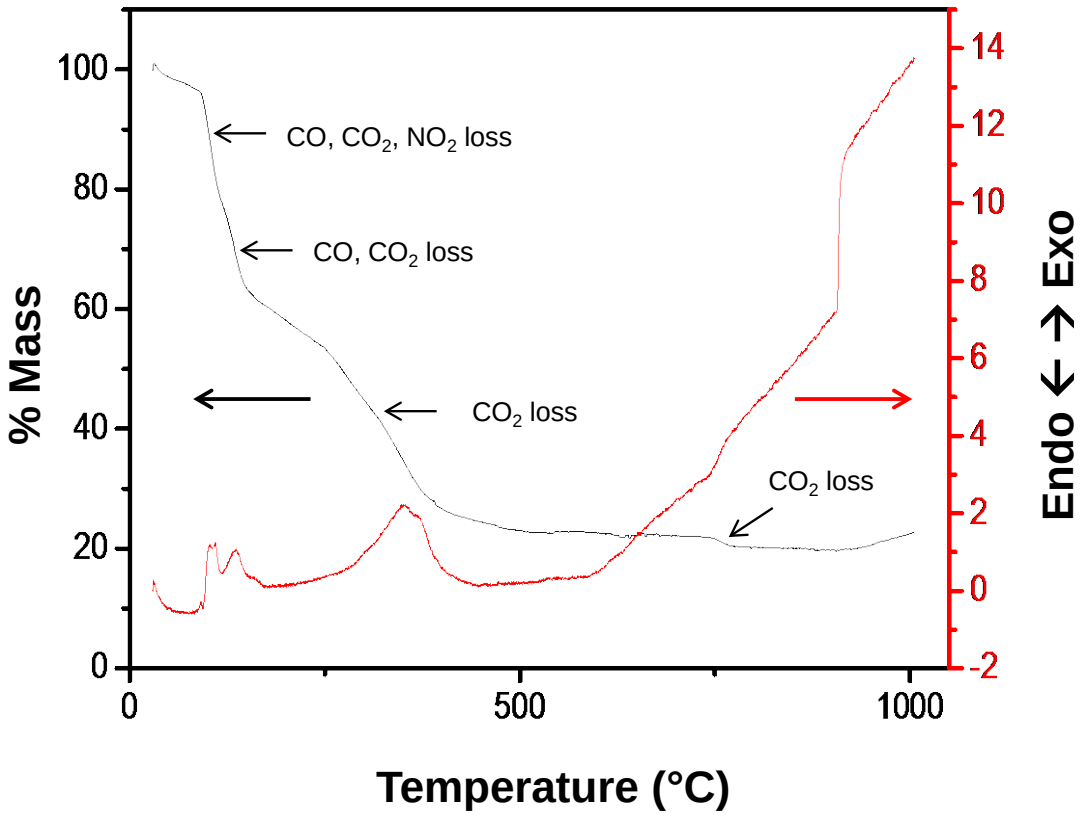

Figure S5. TGA/DSC/EGA of the dried LTO-USS precursor solution. Mass loss events are labeled, with the primary gaseous species detected by mass spectrometry indicated.

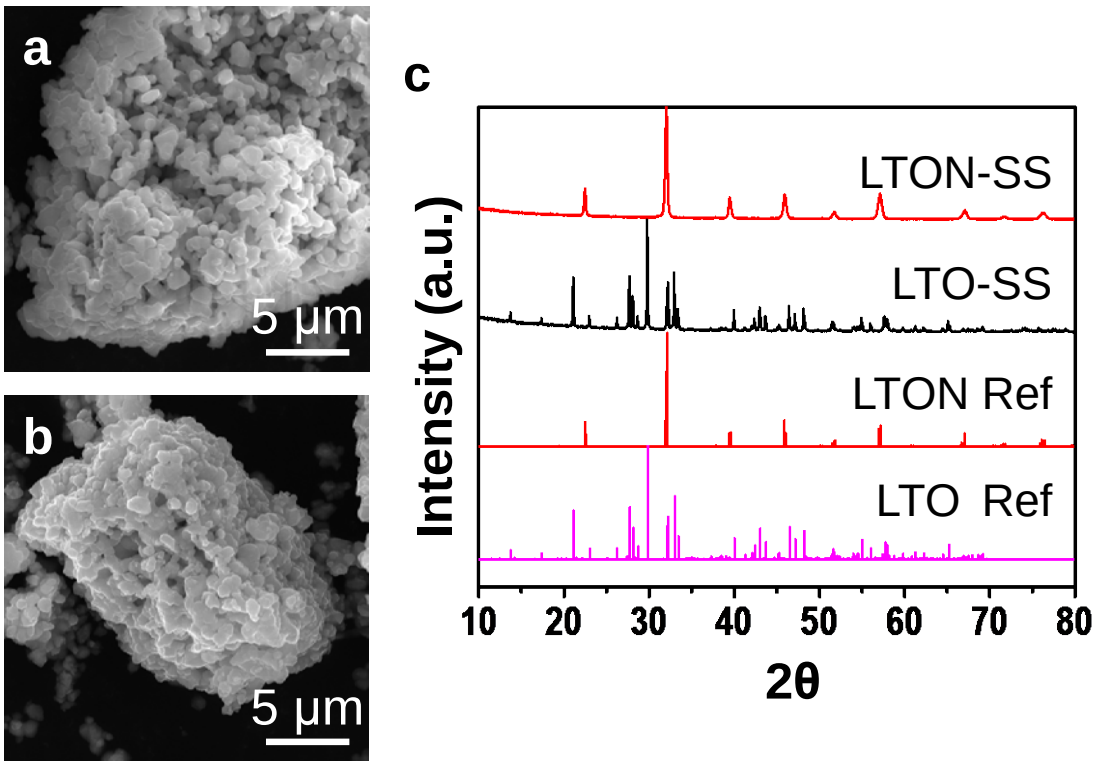

Figure S6. SEM images of a) LTO-SS, b) LTON-SS and c) their corresponding XRD patterns. LTO Ref and LTON References correspond with monoclinic $La_2Ti_2O_7$ (ICDD PDF 01-070-0903) and orthorhombic $LaTiO_2N$ (ICDD PDF 01-079-6426), respectively.

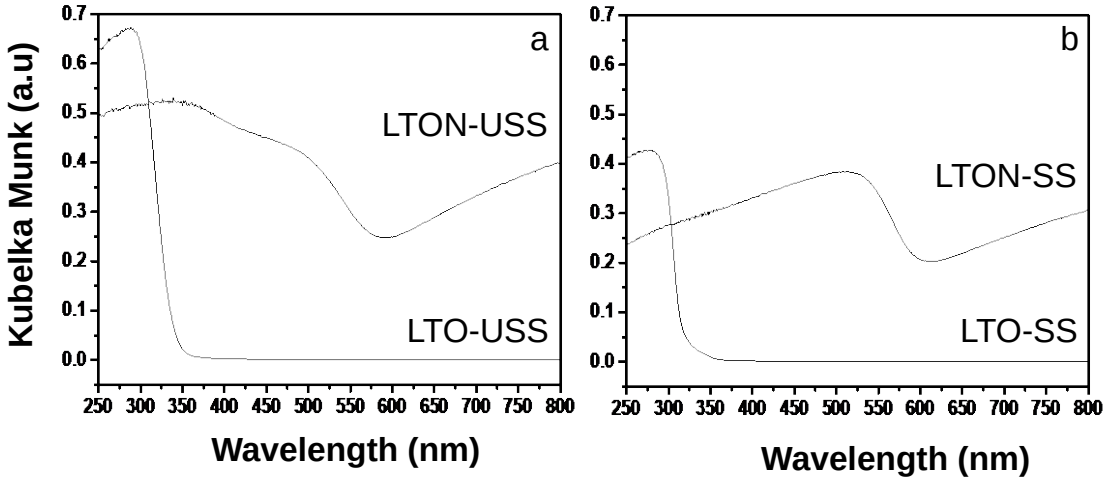

Figure S7. Diffuse reflectance UV-Vis spectra of a) the USS products and b) the SS products.

Rate of incident photon determination.

The rate of incident photons was obtained using the ferrioxalate actinometer procedure detailed in reference 2.[2] A solution of 0.012 M potassium oxalate in 0.5 M sulfuric acid was prepared as described and 10 mL was placed in the photocatalytic reactor. This solution was exposed to light for 15 seconds before being immediately shielded from light. A 1.5 mL aliquot of this solution was mixed with 0.25 mL buffered phenanthroline, followed by a 10x dilution. The absorbance of this dilution at 510 nm was recorded. The same was procedure was performed for a sample that had not been exposed to light. The difference in absorbance between these two species was then used to calculate the concentration of ferrous ions in solution using the equation:

$$moles\ Fe^{2+} = 10 * \left(\frac{V_1 * V_3 * \Delta A}{10^3 * V_2 * l * \varepsilon}\right)$$

where V_1 is the irradiated volume, V_2 is the aliquot of the irradiated solution taken for the determination of the ferrous ion concentration, V_3 is the final volume after complexation with phenanthroline (all volumes in mL), l is the cell path length, ΔA is the difference between the absorbance of the dark and irradiated samples, and ε is the molar absorptivity of the complex ($11100\,\frac{\mathrm{L}}{\mathrm{mol*cm}}$). The moles of photons absorbed by the irradiated solution per hour was then able to be calculated using the equation:

$$\frac{moles\ of\ photons}{hour} = \frac{moles\ of\ Fe^{2+}}{\phi_\lambda * t * F}$$

where ϕ_λ was the quantum yield of ferrous ions (0.94), t was the time in hours, and F was the mean fraction of light absorbed by the solution (assumed to be 1).

References

1 J. Fu, N. N. Daanen, E. E. Rugen, D. P. Chen and S. E. Skrabalak, *Chem. Mater.*, 2017, **29**, 62–68.

2 M. Montalti, A. Credi, L. Prodi and M. Teresa Gandolfi, *Handbook of Photochemistry, Third Edition*, CRC Press, 2006.