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In Tandem Control of La-Doping and CuO-Heterojunction on SrTiO₃ Perovskite by Double-Nozzle Flame Spray Pyrolysis: Selective H₂ vs. CH₄ Photocatalytic Production from H₂O/CH₃OH

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Abstract: ABO₃ perovskites offer versatile photoactive nano-templates that can be optimized towards specific technologies, either by means of doping or via heterojunction engineering. SrTiO₃ is a well-studied perovskite photocatalyst, with a highly reducing conduction-band edge. Herein we present a Double-Nozzle Flame Spray Pyrolysis (DN-FSP) technology for the synthesis of high crystallinity SrTiO₃ nanoparticles with controlled La-doping in tandem with SrTiO₃/CuO-heterojunction formation. So-produced La:SrTiO₃/CuO nanocatalysts were optimized for photocatalysis of H₂O/CH₃OH mixtures by varying the La-doping level in the range from 0.25 to 0.9%. We find that, in absence of CuO, the 0.9La:SrTiO₃ material achieved maximal efficient photocatalytic H₂ production, i.e., 12 mmol g^{−1} h^{−1}. Introduction of CuO on La:SrTiO₃ enhanced selective production of methane CH₄. The optimized 0.25La:SrTiO₃/0.5%CuO catalyst achieved photocatalytic CH₄ production of 1.5 mmol g^{−1} h^{−1}. Based on XRD, XRF, XPS, BET, and UV-Vis/DRS data, we discuss the photophysical basis of these trends and attribute them to the effect of La atoms in the SrTiO₃ lattice regarding the H₂-production, plus the effect of interfacial CuO on the promotion of CH₄ production. Technology-wise this work is among the first to exemplify the potential of DN-FSP for scalable production of complex nanomaterials such as La:SrTiO₃/CuO with a diligent control of doping and heterojunction in a single-step synthesis.

Keywords: strontium titanate; doping; La:SrTiO₃; CuO; heterojunction; FSP; double-nozzle; photocatalysis; hydrogen; CH₄ selectivity



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1. Introduction

Photocatalytic storage of light photons in the form of fuels such as H₂ or CH₄ is globally envisaged as an environmentally benign technology [1,2]. To this front, in the last decades, photocatalytic semiconductors receive great consideration [3].

Strontium Titanate (SrTiO₃) has a classical ABO₃ perovskite structure, with the ideal cubic lattice [4]. SrTiO₃ has received enormous attention as a photocatalyst, oxidative catalyst, or catalyst-support, due to beneficial characteristics such as low price [5], chemical stability, and excellent thermal stability, e.g., melting point as high as 2080 °C, with carbon and sulfur tolerance, adaptability and modifiable oxidative properties [6]. SrTiO₃ has a highly reducing conduction-band-edge energy position (E_{CB}) of −1.2 eV vs. NHE [7,8], which makes it a highly efficient photocatalyst for hydrogen production from H₂O [9]. SrTiO₃ has the disadvantage of a broad 3.2 eV band gap, permitting only the absorption of UV photons, thus to remediate this drawback, a common technique is to apply dopants or heterojunction with other materials [10].

So far, synthesis of nanocrystalline SrTiO_3 has been achieved with various methods, each having distinct advantages/disadvantages [4,11], e.g., solid phase [12] that is a low-cost approach, however, produces rather large particles, sol-gel [11] that gives pure phase small nanoparticles at a higher cost, hydrothermal [5] that produces controllable size but requires long synthesis-times with impurity possibility. Moreover, doping of SrTiO_3 with an appropriate dopant-cation at low concentration, and the formation of heterojunctions between SrTiO_3 and selected co-catalytic particles, pose additional hurdles, complexity, and cost of the synthesis process [13]. In this context, it is of great importance to develop synthesis technologies for high-quality SrTiO_3 in scale-up production, at the same time allowing doping of SrTiO_3 and heterojunction $\text{SrTiO}_3/\text{MO}_x$ formation in one step.

The Flame Spray Pyrolysis (FSP) process is an aerosol combustion technology for nanoparticle synthesis [14–16] that is well-established for industrial-scale production [17,18]. As such, FSP is already used in industry to produce several commonly used metal oxides [19]. FSP utilizes high-temperature combustion, i.e., 1000–2000 K [20], of a precursor containing metal atoms dispersed in an organic solvent, that is sprayed in the form of aerosol droplets. Appropriate selection of precursor mixtures and process parameters allows precise control of the crystal phases [19], devoid of chemical leftovers. So far, FSP has been established for the successful production of a wide range of single-metal oxides [19], however, establishing FSP process parameters for the production of ABO_3 perovskite nanomaterials is typically more challenging, e.g., such as avoiding the formation of the separate oxides AO_n and BO_m . The relative importance of process parameters has been exemplified in our recent works on FSP-engineering of NaTaO_3 [21], $\text{Bi}_2\text{Fe}_4\text{O}_9$ and BiFeO_3 [22,23], W-, Zr-Doped BiVO_4 [24], and by Kudo and Amal for BiVO_4 [25], as well as Abe and Laine for $\text{La}_2\text{Ti}_2\text{O}_7$ [26]. Very recently, the synthesis of SrTiO_3 [27,28] by FSP has been achieved and used for catalytic combustion of CO and CH_4 , however with no reference to photocatalytic evaluation or optimization.

Lanthanum (La) doping of SrTiO_3 has been shown to increase the electrochemical efficiency of the perovskite [29,30], and as co-dopant with other atoms [31,32]. Domen [33,34] and Kudo [35,36] have demonstrated that SrTiO_3 co-doped with La and Rh exhibits high solar-to-hydrogen energy conversion efficiency for water splitting to H_2 . Moreover, selected cations, e.g., La^{3+} , Ce^{3+} , or Nitrogen [8,37] allow control of structural/photo/electronic properties of doped- SrTiO_3 , enhancing the photocatalytic efficiency [38,39]. Thus, SrTiO_3 offers a versatile template, that can be optimized towards specific technologies either via doping or heterojunction engineering.

Surficial heterojunctions of SrTiO_3 with pertinent metal-oxides allow control of the selectivity of surface reactions. More specifically, Cu-atoms and their particles (CuO , Cu_2O , Cu^0) are particularly attractive in photocatalytic processes, since they have been shown to control selectivity towards specific products, i.e., Cu_2O exhibits selectivity towards CH_3OH production and Cu^0 towards hydrocarbons and C_2 products [40,41]. In particular, studies show that CuO clusters on the TiO_2 surface can serve as an efficient co-catalyst to enhance H_2 production [42,43]. Meanwhile, Cu_2O on TiO_2 was also reported to be more suitable for H_2 production, which was attributed to the better energy band alignment between TiO_2 and Cu_2O , which facilitates charge separation [44,45].

Herein, we employ a Single-Nozzle FSP (SN-FSP) process for the synthesis of La:SrTiO_3 and a Double-Nozzle FSP (DN-FSP) creating a heterojunction of CuO finely dispersed on La:SrTiO_3 in one-step [46,47], see Figure 1. Recently, our group utilized DN-FSP to produce TiO_2 loaded with noble metal particles (>2 nm), to significantly enhance photocatalytic hydrogen production [48]. In the present work, our hypothesis was that an in tandem La-doping of SrTiO_3 heterojunctions with CuO can allow control of the SrTiO_3 electronic/photocatalytic properties, as well as controlled selectivity in photocatalytic products. In this context, our specific aims were: (i) To develop an FSP protocol for the synthesis of La:SrTiO_3 with controlled La-doping; (ii) To advance the FSP protocol to allow heterojunction of CuO on La:SrTiO_3 ; (iii) To study the H_2 vs. CH_4 photocatalytic process in comparison to CuO . For this reason, we have performed photocatalytic studies in an

H₂O/CH₃OH mixture. CH₃OH is a well-known hole-scavenger [49], however, most publications do not examine the CH₃OH involvement in the reaction path and the final products, e.g., eventually CH₄.

2. Materials and Methods

2.1. Flame Spray Pyrolysis (FSP) Synthesis of SrTiO₃ Nanoparticles

The precursor solution contains Strontium acetate (STREM), Titanium(VI) isopropoxide (97%, Aldrich) for the synthesis of perovskite SrTiO₃. For the deposition of cocatalytic metals, i.e., La atoms, with Lanthanum Acetylacetonate (97%, STREM). The Sr and Ti precursors were dispersed in a mixture of Acetic acid and Xylene (1:1 volume ratio), while for the La precursor a mixture of toluene and 2-EHA (1:1 volume ratio) that consisted of approximately 10% of the total volume of the final precursor solution. We underline that it is the control of FSP parameters that allows Sr- and Ti- to be engaged exclusively in the formation of the SrTiO₃ crystals, while La- is introduced as a lattice-dopant.

Double-Nozzle FSP: In the DN-FSP as shown in Figure 1, two FSP-nozzles operate in tandem that are asymmetrically positioned, so that the system generates two different kinds of nanomaterials by controlling the properties of each nozzle independently, where the left FSP-nozzle contained the Sr/Ti/La precursors, while the right FSP-nozzle contained Cu(NO₃)₂·3H₂O (Supelco) in Acetonitrile:Ethyleglycol (1:1 volume ratio). Screening experiments were conducted to find the preferent geometric parameters: α_1 nozzle angle at 20°, and $\alpha_2 = 20^\circ$. The internozzle distance was placed at $x = 8$ cm and the vertical intersection distance of the two flames, above the nozzle, was $b = 10$, see Figure 1C.

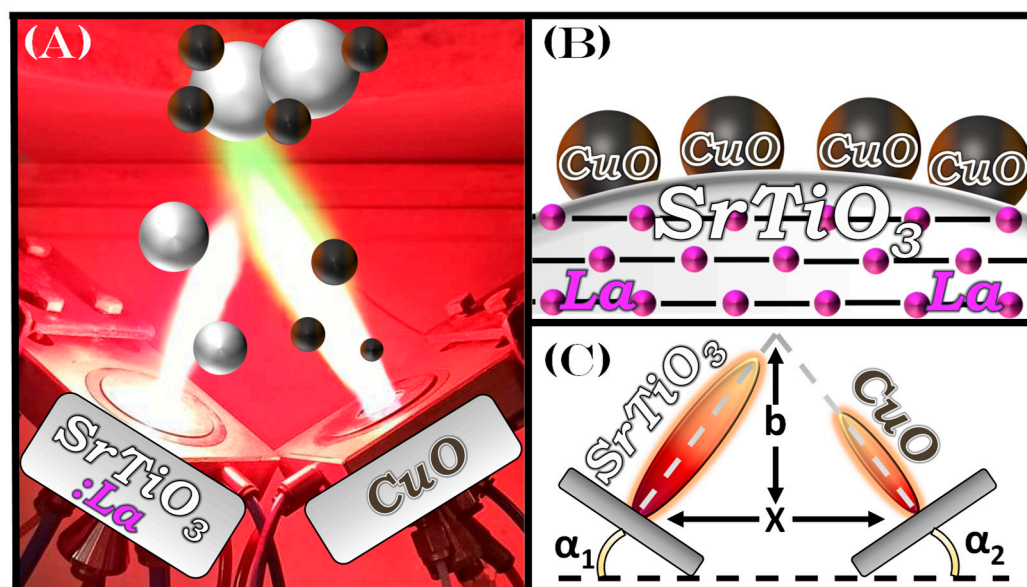


Figure 1. (A) Description of the Double-Nozzle FSP (DN-FSP) set-up, with the SrTiO₃ formation in the left-side nozzle and the CuO formation in the right-side nozzle. (B) Schematic depiction of the structure of the La:SrTiO₃/CuO particle. (C) The geometric parameters for the two nozzles in DN-FSP.

The FSP parameters for the synthesis of the nanoparticles consisted of an oxygen dispersion flow rate of $D = 5 \text{ L min}^{-1}$ (Linde 99.999%) and a precursor flow rate of $P = 5 \text{ mL min}^{-1}$. These D and P rates were also used for both nozzles in the DN-FSP setup. The pilot flame was ignited by premixed O₂ and CH₄ (4 L min^{-1} , 2 L min^{-1}). In the Single-Nozzle as well as in the Double-Nozzle FSP, with the assistance of a vacuum pump (BUSCH), the produced particles were deposited on a glass microfiber filter with a binder (Albet Labscience GF_6_257) and collected by scrubbing the nanoparticles from the filter. The nanomaterials were collected in glass vials under an inert Argon atmosphere, until use.

For convenience, herein the produced materials, listed in Table 1, are codenamed as follows: X_{La}:STO/Y_{Cu} where STO = SrTiO₃, X the nominal % La-content per weight of SrTiO₃, Y = the nominal % Cu-content per weight of SrTiO₃. In this way, we have prepared 0.9La:STO and 0.35La:STO, respectively, listed in Table 1. For the DN-FSP experiments, we have produced STO/2Cu, STO/1.2Cu, and STO/0.5Cu, respectively. Finally the 0.25La:STO/0.5Cu produced by DN-FSP is codenamed as La:STO/Cu.

2.2. Photocatalytic Evaluation

Photocatalytic experiments were performed in a double-walled photochemical reactor (Toption instrument co. Ltd.) with a total reaction volume of 340 mL, at a temperature of 25 ± 2 °C, controlled by a recirculation chiller cooling system. The UV source was a 250 W Mercury lamp, positioned at the geometrical center of the photoreactor inside the quartz-immersion well. The irradiation power at the experimental mean distance of 3 cm was 0.5 W cm^{-2} as measured with a power meter (Newport model, 1918-C).

A Gas-Chromatography System combined with a Thermal-Conductivity-Detector (TCD-Shimadzu GC-2014, Carboxen 1000 column, Ar carrier gas) was used to identify and quantify the produced H₂ and CH₄ gases. In each experiment, 50 mg of the catalyst was suspended in 200 mL Milli-Q water and 50 mL methanol (20% per volume) as a hole-scavenger. Photo-deposition of Pt-cocatalyst was implemented to increase the photocatalytic production, using hydrogen hexachloroplatinate (IV) hydrate, (H₂PtCl₆·H₂O, 99.9%, Alfa Aesar). The error bars of approximately 8%, for the photocatalytic products H₂ and CH₄, reflect the detection uncertainty and statistical deviation after three catalytic runs.

2.3. Characterization of Materials

XRD measurements were carried out to identify the crystal phase identification and structural properties of the materials, using a Bruker D8-Advance diffractometer with a Cu source ($K\alpha$, $\lambda = 1.5418 \text{ \AA}$), with operation parameters of 40 KV generator voltage and 40 mA current. The particle crystal size (d_{XRD}) as obtained from the XRD data was calculated with the Scherrer Equation (1)

$$d_{\text{XRD}} = \frac{K \lambda}{(\text{FWHM}) \times \cos \theta} \quad (1)$$

where $K = 0.9$, $\lambda = 1.5418 \text{ \AA}$, and FWHM is the full-width at half-maximum of the XRD peaks [50].

Transmission Electron Microscopy analysis was used to map the particle morphology. The amount of La-atoms and Cu-atoms of the nanomaterials was calculated by a home-built Energy-Dispersive X-Ray Fluorescence (EDXRF), and an annular 241 Am radioisotopic source was used for sample excitation. The source is fixed coaxially above a CANBERRA SL80175 Si(Li) detector (5 mm crystal thickness, 80 mm² area), with a 25 µm thick Be window and an energy resolution of 171 eV for the 5.9 keV Mn $K\alpha$ line. Spectral analysis was carried out using the WinQxas software package (International Atomic Energy Agency, 1997–2002). Quantitative analysis was based on in-house standard samples and the construction of calibration curves.

The morphology and phase composition of the La:STO/Cu particle was studied using an FEI Talos F200i field-emission (scanning) transmission electron microscope (Thermo Fisher Scientific Inc., Waltham, MA, USA) operating at 200 kV, equipped with a windowless energy-dispersive spectroscopy microanalyzer (6T/100 Bruker, Hamburg, Germany).

The Specific Surface Area (SSA) and the pore size of the nanomaterials were measured by a Quantachrome NOVAtouch_LX2 to record the N₂ adsorption-desorption isotherms at 77 K. The SSA was calculated using the absorption data points in the range of 0.1–0.3 relative pressure P/P_0 . While the pore radius analysis was obtained by the BJH method [51] in the range of 0.35–0.99 P/P_0 .

Diffuse-Reflectance UV-Vis absorption spectra were recorded with a Perkin Elmer Lambda-35 spectrometer with BaSO₄ powder used as a background standard, operating at

room temperature for the wavelength range of 200–800 nm, while the band gap energy (E_g) was calculated using the Kubelka–Munk method [52].

The oxidation state of the Sr, Ti, O, and Cu atoms was monitored by X-ray photoelectron spectroscopy (XPS), using a SPECS spectrometer equipped with a twin Al-Mg anode X-ray source and a multi-channel hemispherical sector electron analyzer (HSA-Phoibos 100), a monochromatized Mg $K\alpha$ line at 1253.6 eV, analyzer pass-energy at 15 eV, and the base pressure at $2\text{--}5 \times 10^{-9}$ mbar. The binding energies were determined vs. the energy of C1s carbon peak at 284.5 eV. The peak deconvolution was performed employing mixed Gaussian–Lorentzian functions, using WinSpec software, developed at the Laboratoire Interdisciplinaire de Spectroscopie Electronique, University of Namur, Belgium.

3. Results

3.1. SrTiO₃-Based Perovskite Nanoparticle Synthesis by FSP

Highly crystalline SrTiO₃ has been successfully produced by Single-Nozzle FSP, see XRD data in Figure 2A. The distinct peaks 2θ at 22.71, 32.34, 39.91, 46.43, 52.29, 57.74, 67.78, and 77.13 degrees, confirm the formation of pure cubic perovskite SrTiO₃ structure (JCPDS74–1296). All diffraction peaks are assigned to Miller indices of the (100), (110), (111), (200), (210), (211), (220), and (310) planes for the cubic perovskite structure (Pm3m), with no traces of other crystalline byproducts, such as TiO₂ or Sr-oxide.

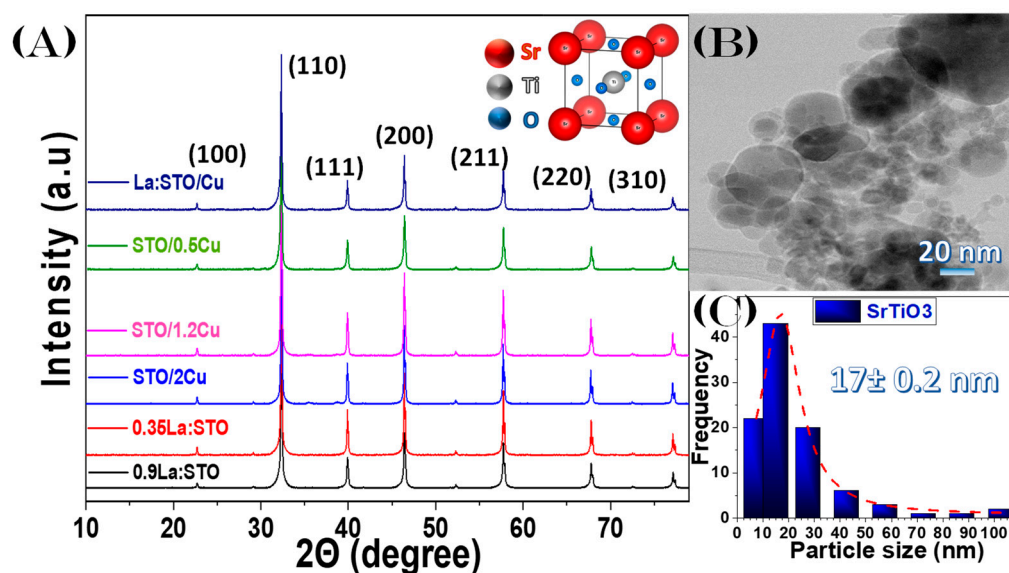


Figure 2. (A) XRD patterns for the SrTiO₃ nanomaterials. *Inset:* The unit-cell structure of the cubic SrTiO₃ structure. (B) TEM image of the pristine SrTiO₃ particle. (C) Size distribution graph obtained from several TEM images.

The d_{XRD} values calculated by the Scherrer method [50], listed in Table 1, indicate d_{XRD} sizes in the range of 45–55 nm. The TEM images of the pristine SrTiO₃, show the formation of quasi-spherical particles with a distribution of particle sizes, see Figure 2B, as commonly observed in FSP-made particles [19]. Specifically, according to TEM, the FSP-made SrTiO₃ includes a few large particles with diameters of 40–50 nm and many smaller particles with diameters below 20 nm. The ensuing particle-size distribution calculated from the TEM images, Figure 2C, shows a mean size of $d_{\text{TEM}} = 17 \pm 0.2$ nm as obtained from a Gaussian fitting. Comparison of d_{XRD} and d_{TEM} exemplifies the well-known effect of large particles to predominate the diffraction peaks in XRD, thus d_{XRD} overestimates the average particle size.

Table 1. Structural Characteristics of La:SrTiO₃, SrTiO₃/CuO, and La:SrTiO₃/CuO nanoparticles.

Nanomaterial ¹	La-, Cu-Content XRF Analysis (%wt)	d_{XRD} (nm) (± 4)	SSA (m ² g ⁻¹) (± 0.5)	Total Pore Volume (cm ³ g ⁻¹) ($\pm 0.02 \times 10^{-2}$)	Band Gap E_g (eV) (± 0.1)
<i>Single-Nozzle FSP</i>					
Pristine SrTiO ₃	La:0 /Cu:0	45	32.3	0.14×10^{-2}	3.2
0.9La:STO	La:0.93 $\pm$ 0.05 /Cu:0	47	53.1	0.39×10^{-2}	3.2
0.35La:STO	La:0.36 $\pm$ 0.05 /Cu:0	55	57.5	0.36×10^{-2}	3.2
<i>Double-Nozzle FSP</i>					
STO/2Cu	La:0.05 $\pm$ 0.05 /Cu:2 $\pm$ 0.1	53	34.9	0.12×10^{-2}	3.2
STO/1.2Cu	La:0/Cu:1.2 $\pm$ 0.1	49	32.1	0.11×10^{-2}	3.2
STO/0.5Cu	La: 0.05 $\pm$ 0.05 /Cu:0.5 $\pm$ 0.1	45	32.0	0.11×10^{-2}	3.2
La:STO/Cu	La: 0.26 $\pm$ 0.05 /Cu:0.5 $\pm$ 0.1	52	37.3	0.16×10^{-2}	3.2

¹ X_{La}:STO/Y_{Cu} where STO = SrTiO₃, X = the nominal % La-content per weight of SrTiO₃, Y = the nominal % Cu-content per weight of SrTiO₃.

In Figure 3A, HRTEM images for La:STO/Cu are shown. Distinct Miller planes of CuO (110) are resolved with $d = 2.75 \text{ \AA}$ [53], showing that CuO particles are deposited on the surface of the SrTiO₃ particle. These CuO particles are small, <2 nm, therefore they are not detected in the XRD. Figure 3C–F present the scanning-TEM images for the Ti, Sr, La, and Cu atoms mapping for material La:STO/Cu. Importantly, Figure 3E demonstrates that the La atoms are evenly dispersed throughout the whole volume of the SrTiO₃ particle. This verifies the atomic distribution of La, i.e., without La-clusters. The STEM for Cu atoms, Figure 3D, verifies the formation of dense/particle structures on SrTiO₃. Caution is drawn to the fact that the faint blue hue in Figure 3D is the enhanced emissions from Cu-grid atoms employed for the TEM measurements that are in proximity to the Sr-atoms. These are secondary Cu-electrons enhanced via Strontium excitations. Thus, in Figure 3F, only the particles inside the white circle are actual CuO particles, showing that CuO particles are found only on the surface of the SrTiO₃.

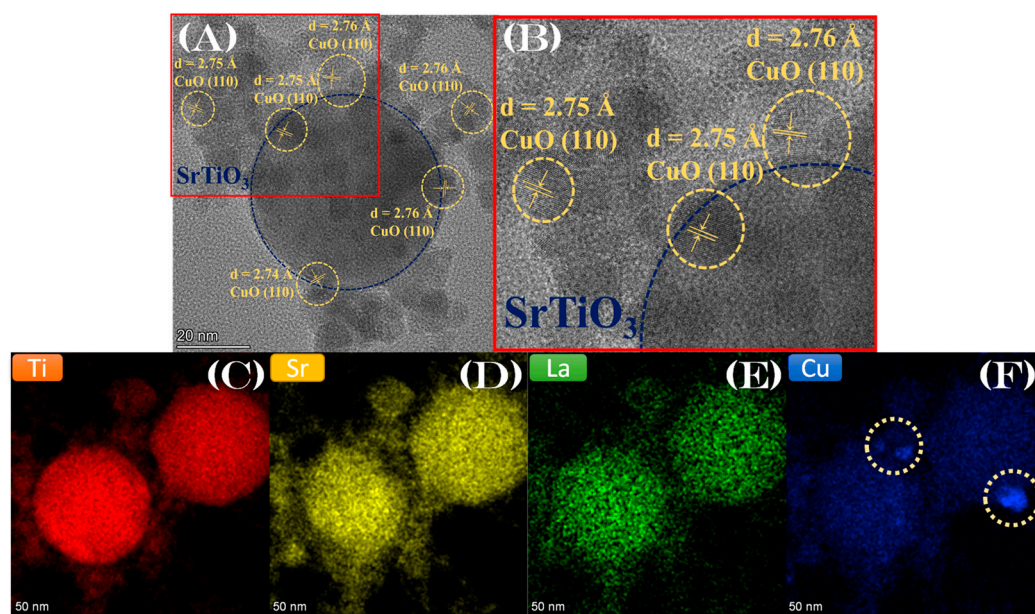


Figure 3. (A,B) HRTEM images for the particle La:STO/Cu, with the distinct miller planes of CuO (110) deposited on the SrTiO₃ surface. (C–F) Scanning-TEM images with Ti, Sr, La, and Cu atom mapping for material La:STO/Cu.

La-doped SrTiO₃ produced by Single-Nozzle FSP retain their high crystallinity and purity, i.e., no secondary phases are formed, such as La₂O₃. La-doping is evidenced by a pink-hue color developed in La:SrTiO₃ vs. the white SrTiO₃. Upon increasing La-doping, the SrTiO₃-particle size tends to increase, i.e., from 45 nm d_{XRD} to 55 nm d_{XRD} . Strikingly, the Specific Surface Area increases also, see Table 1. This counterintuitive observation is further analyzed in the BET-data analysis hereafter.

Double-Nozzle FSP used to form the SrTiO₃/CuO heterojunctions, retains the high crystallinity of SrTiO₃, see XRD data in Figure 2A, with a tendency towards larger particle sizes at increased Cu-content. In agreement with previous reports [28], this can be attributed to the increased contribution to the increased enthalpy that is added due to the second flame, thus increasing the overall synthesis temperature, and extending the temperature at the stage of agglomeration.

The N₂-adsorption isotherms for selected nanomaterials are presented in Figure 3A, while the data for nanomaterials with different CuO percentages are shown in Figure S1 in the Supporting Information. All nanomaterials have the characteristic of a type-IV isotherm. The SSA values and pore-volume analysis, see Figure 4B, reveal some interesting trends: in the Single-Nozzle FSP, the La-doped particles show an increase in their SSA values, see Table 1. However, taking into account the XRD data, this increased SSA is not concurring with the particle size. More insightful information is obtained by examining the pore size and pore volume trends, see Figure 4B, which reveals an increase in pore volume upon La-doping. Typically, in literature, SrTiO₃ particles are reported to possess a total pore volume in the range of 15 cm³ g^{−1} [18,54], which is in the same range observed for our pristine SrTiO₃ nanomaterial, Figure S2 in the Supporting Information. Upon La-doping, a sharp increase is observed for the SSA, but more importantly a 3-fold increase in the pore volume to 39 cm³ g^{−1}. This trend can be attributed to a geometrical effect as depicted in the scheme in Figure 4. This is a result of the FSP process, where the La-doping decreases the packing/aggregation of the SrTiO₃, even though some SrTiO₃ might grow bigger. It is worth mentioning the relatively high surface area and pore volume in our nanomaterials, i.e., compared vs. previous synthesis methods for SrTiO₃ that possessed low SSA, i.e., due to the application of high calcination temperatures [5,55].

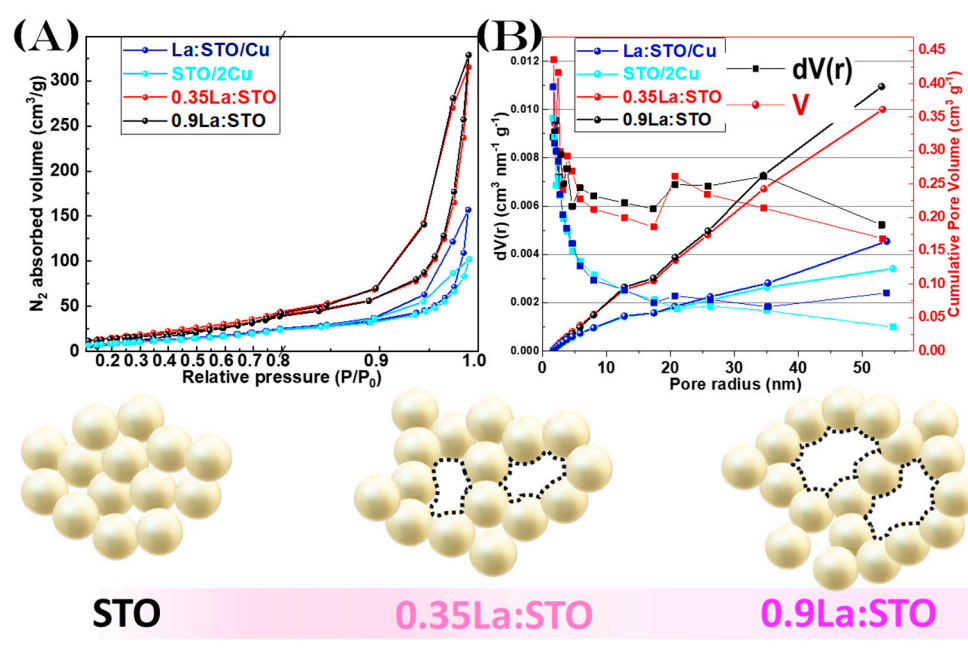


Figure 4. (A) Nitrogen adsorption isotherms for the SrTiO₃-based nanoparticles. (B) The corresponding pore-size distribution plot using the BJH method and the Cumulative Pore Volume. *Bottom:* Schematic visualization of the La-doping effect on the nanomaterial aggregation.

3.2. Spectroscopic Characterization

3.2.1. Diffuse Reflectance UV-Vis Spectroscopy

SrTiO₃, as a semiconductor, has been shown to possess an indirect bandgap of 3.25 eV and a direct bandgap of 3.75 eV [56]. It has been shown that La or Nb-dopings, or oxygen vacancies can produce an *n*-type alteration in the Density of States (DOS) [56], i.e., extra DOS are formed within the band gap right below the Conduction Band bottom. In our data in Figure 5B, the indirect band gap has been calculated using the Kubelka–Munk method [52]. Notice that its absorption starts at 390 nm [57], resulting in all the nanomaterials having *E_g* values close to 3.2 eV, listed in Table 1. Lanthanum/Copper incorporation in the SrTiO₃ materials fundamentally changed the color of the nanoparticles, with a purple hue observed after the lanthanum doping, while a drastic brown tint was observed for the 2% CuO heterostructure [28], which is clearly visible from extra absorption in the 400–580 nm range, Figure 5A.

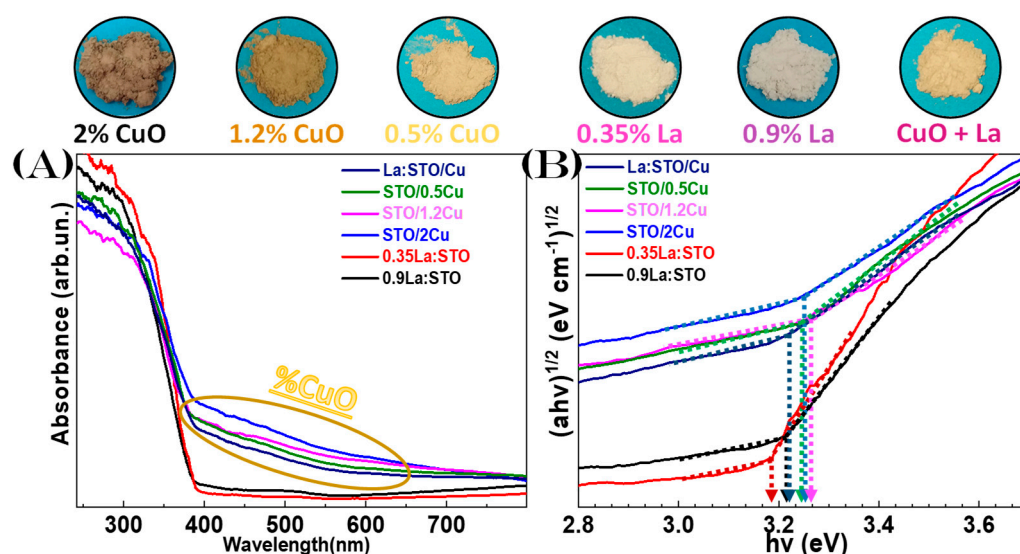


Figure 5. (A) DRS-UV-Vis data for the SrTiO₃ particles. (B) Tauc-Plots with the dotted arrows show the calculated bandgap. *Side-photos:* The powder nanoparticles showcase the color shift.

Overall, the present DRS-UV-Vis analysis verifies that the electronic structure of the SrTiO₃ semiconductors produced by SN-FSP and DN-FSP, as well as their trends upon La-doping and Cu-heterojunction, are in accordance with literature data.

3.2.2. X-ray Photoelectron Spectroscopy

XPS data for Sr- or O-atoms are presented in Figure 6A,C, respectively. Figure 6B presents Cu-XPS data, there is an emphasis on copper in order to confirm the oxidation state of the Cu-NPs. The material STO/2Cu, i.e., with the higher Cu-loading is exemplified, since it possessed strong Cu-XPS signals, to ascertain the Cu-oxidation state with precision. La-could not be detected by XPS in any of our materials.

In Figure 6B, the binding energies located broadly at 932.8 eV and 952.7 eV correspond to the Cu 2p_{3/2} and Cu 2p_{1/2}, respectively [58,59], while the presence of a strong satellite signal at 941 eV and the broader peaks of Cu 2p_{3/2} and Cu 2p_{1/2} indicate that the Cu atoms are in the Cu(II) oxidation state [58,59]. Thus, XPS results confirm that the heterostructure is indeed SrTiO₃/CuO. This is in agreement with the FSP settings, i.e., the P/D = 5/5 produces a typical oxidizing environment [19] that in our Cu-precursor promotes the formation of CuO. The binding energies at 132.2 eV and 134 eV were identified as the Sr 3d_{5/2} and Sr 3d_{3/2}, corresponding to the Sr²⁺ state of the SrTiO₃ [60,61], Figure 6A. For the oxygen species, Figure 6C, three peaks were observed, with the binding energies at 528.9 eV that can be attributed to lattice oxygen species of the SrTiO₃ crystal structure [61,62]. The 531.1 eV is attributed to chemisorbed oxygen, and lastly, the peak at 532.4 eV is attributed

to adsorbed oxygen on the particle surface or hydroxyl groups [61,62]. The oxygen species from the partially substituted materials, i.e., 0.25%La/0.5%CuO have distinctly different intensity ratios of the (lattice) vs. (chemisorbed) oxygen species. This can be possibly attributed to oxygen vacancies that are created from the bending of the lattice, impacting the adsorption and efficiency of the oxygen species at the catalyst surface [61,62]. For the Ti 2p, all materials have peaks located at 457.7 eV and 463.4 eV, which are the binding states of Ti 2p_{3/2} and Ti 2p_{1/2}, respectively, that correspond to typical Ti⁴⁺ states, Figure S3 in the Supporting Information.

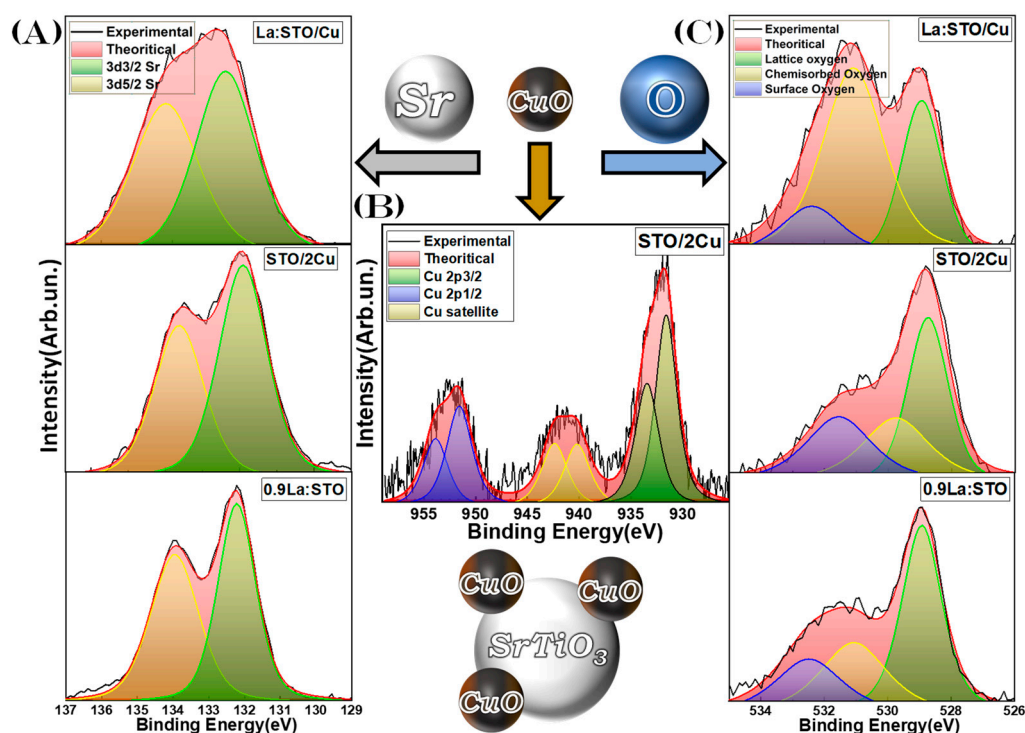


Figure 6. (A) Sr 3d_{5/2} and Sr 3d_{3/2} XPS spectra for 0.9La:STO, STO/2Cu, and La:STO/Cu materials. (B) Cu 2p_{3/2} and Cu 2p_{1/2} XPS spectra of STO/2Cu for the binding energies. (C) Oxygen XPS spectra of 0.9La:STO, STO/2Cu, and La:STO/Cu.

Overall, the present XPS data show that the FSP-made nano SrTiO₃ consists of typical Ti⁴⁺ states with some O vacancies in all materials. In STO/Cu, the CuO particle was confirmed by XPS in accordance with the oxidizing FSP process used herein.

3.3. Photocatalytic Evaluation

Photocatalytic results for photocatalytic hydrogen production of the materials were evaluated using a mixture of H₂O/CH₃OH as a catalytic substrate. The only products were H₂ or CH₄, in all cases. The gas-production data are shown in Figure 7A,B for H₂ or CH₄, respectively. The corresponding rates are presented in Figure 7C,D, respectively. The highest H₂-yield was 11980 μmol g^{−1} h^{−1}, achieved by the 0.9%La:SrTiO₃, which is ~500% higher than for pristine SrTiO₃ with H₂-yield 2760 μmol g^{−1} h^{−1}. A clear beneficial trend is observed, i.e., higher La-doping promotes H₂ production. This trend is in agreement with the literature [31,32]. Herein, however, we focus attention on the relative rates for CH₄ also.

From Figure 7 we observe that in the absence of CuO, the production of CH₄ from the photoreduction of methanol was minimal. The SrTiO₃/CuO heterostructure portrays very different results, with the 2%CuO having almost the same H₂ production as the pristine SrTiO₃, however, there is a sharp increase in the CH₄ (76 to 136 μmol g^{−1} h^{−1}). This selectivity towards CH₄ is apparent for all CuO heterojunctions. Decreasing CuO content resulted in higher H₂ and CH₄ production, 2%CuO increasing the production to 704 μmol g^{−1} h^{−1} CH₄. Notice that with increasing Cu-loading the SrTiO₃ particle surface

is fully covered with CuO, which in turn might act as an inhibitor of light-absorbance by the SrTiO₃. This ‘darkening’ effect plays a key role in diminishing the photocatalytic activity, i.e., both H₂ and CH₄. Most interestingly, the material 0.25%La/0.5%Cu showed an enhanced H₂/CH₄ selectivity, with the CH₄ reaching 1469 $\mu\text{mol g}^{-1} \text{h}^{-1}$ and H₂ to 5907 $\mu\text{mol g}^{-1} \text{h}^{-1}$.

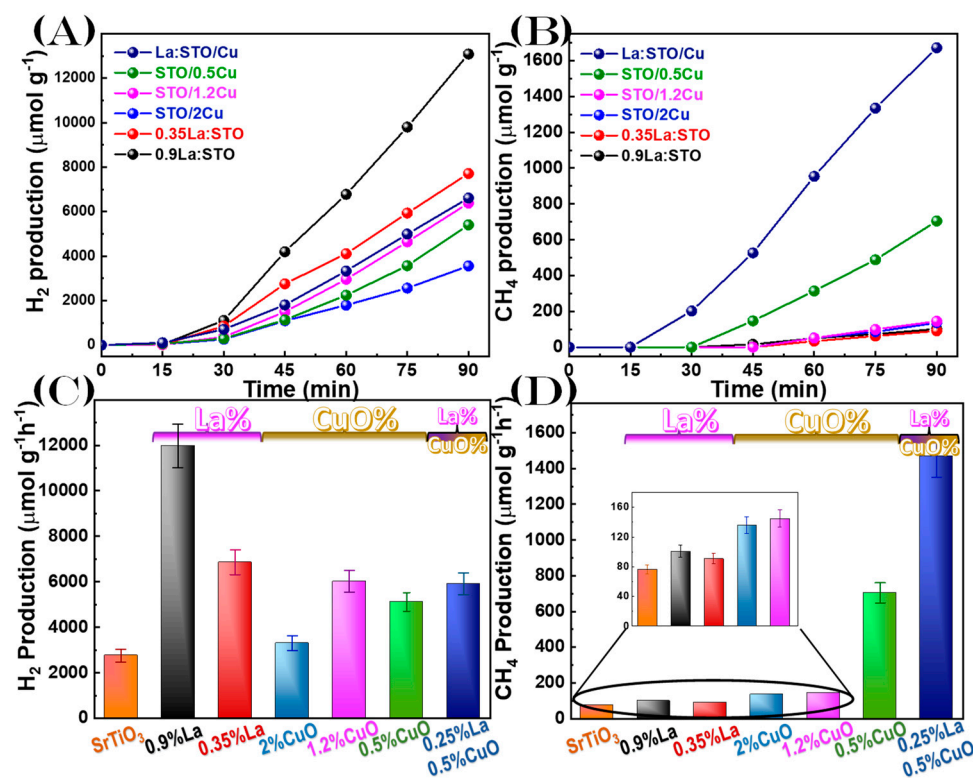


Figure 7. Photocatalytic production by the nanomaterials from an H₂O/CH₃OH mixture. (A) H₂-gas vs. time. (B) CH₄-gas vs. time. (C, D) the corresponding gas production rates (μmol per gr catalyst per hour).

Overall, the present data in Figure 7 show that: (i) in all instances, La-doping greatly increases the photocatalytic activity, (ii) CuO on SrTiO₃ drives the products toward the reduction of CH₃OH to CH₄. Importantly, after the photocatalytic application, the particles fully retained their structure as evidenced by XRD data, see Figure S4 in the Supporting Information.

4. Discussion

The present data show that FSP offers a versatile technology for the production of nano SrTiO₃, La:SrTiO₃, SrTiO₃/CuO, and La:SrTiO₃/CuO. These materials show significant photocatalytic activity that can be tailored towards either pure H₂ production or CH₄/H₂ production from an H₂O/CH₃OH mixture. Table 2 allows a comparison of H₂ photogeneration by the present FSP particles vs. literature, SrTiO₃-based nanocatalysts. From Table 2, and the literature generally, the use of methanol or ethanol as a sacrificial agent to enhance CH₄ production has not been reported so far. Most research publications utilize Xenon radiation, with the highest yields shown in Table 2, although there are several with UV irradiation.

In the case of SrTiO₃, full exploitation of its band gap > 3.2 eV dictates the use of UV light, in order to maximize the H₂ yield [63–67], in comparison with visible-light H₂ production [68,69]. In this context, Table 2, shows that the FSP-made 0.9%La:SrTiO₃ nanocatalyst has the highest yield vs. literature data on pertinent La:SrTiO₃ materials, although the irradiation method that was used herein (UV-Lamp) definitely boosts the photocatalytic efficiency. So far, stabilizing CuO or Cu₂O NPs on metal oxides with lower conduction-band positions is a common strategy to enhance photocatalytic H₂ production

compared with pristine CuO and Cu₂O [70,71]. In this context, it was reported that coupling Cu₂O with TiO₂ or ZnO leads to higher H₂ photoproduction [70,72]. Although there are no previous data on CH₄ production promotion by SrTiO₃/CuO or La:SrTiO₃/CuO heterojunctions, some insights can be gathered from other systems. For example, Xiong et al. demonstrated that on a TiO₂-Pt-Cu₂O nanohybrid, Cu₂O promotes the CH₄ production and at the same time suppresses the H₂ evolution, whereas Pt favors H₂O activation [73]. Moreover, Chen et al. had shown that the co-existence of Cu¹⁺/Cu⁰ species on TiO₂ enhances the photocatalytic efficiency, by increasing the lifetime of electrons leading to an enhancement of CO₂ hydrogenation. In the same study, the reduction of CuO to Cu⁰ was found to be more efficient for the photocatalytic production of CH₄. A Cu-Cu₂O/TiO₂ hybrid has shown an excellent selectivity for CH₄ which is attributed to the suppression of CO formation from Cu⁰ species while Cu¹⁺ species act as the active sites for CH₄ production [74]. All these data pose the possibility that the promotion of CH₄ production by SrTiO₃/CuO or La:SrTiO₃/CuO heterojunctions might involve the formation of Cu¹⁺ or Cu⁰ species at the SrTiO₃/CuO interface.

Table 2. Hydrogen production rates and conditions reported for similar particles/methods.

Photo Catalyst	Synthesis Method	Cocatalyst (wt%)	Light Source	Reaction Solution	H ₂ Yield (umol g ⁻¹ h ⁻¹)	Ref.
0.9%La: SrTiO ₃	FSP	1% Pt	Hg (250 W)	H ₂ O + 20% CH ₃ OH	11,978	This work
0.25%La:SrTiO ₃ /0.5% CuO	FSP	1% Pt	Hg (250 W)	H ₂ O + 20% CH ₃ OH	5907	This work
Ag-STO	Microwave-assisted hydrothermal	2% Ag	UV-low pressure Hg	50% H ₂ O + 50% ethanol	463	[63]
Pt- SrTiO ₃	Polymerized-Complex	0.32% Pt	Hg (500 W)	Pure water + 40% methanol	3200	[64]
Nanofibers SrTiO ₃	Electrospinning method	-	Hg (450 W)	Pure water + 40% methanol	160	[65]
La: CoO/SrTiO ₃	Solid statereaction	-	Hg (400 W)	Pure water + Na ₂ CO ₃	2800	[66]
Na:SrTiO ₃	polymerizable complex emulsion	0.3% Rh	Hg (450 W)	Pure Water	1600	[67]
Macroporous SrTiO ₃	polymerization method	0.7% Pt	Xe (300 W)	Pure water + 25% methanol	3599	[68]
g-C ₃ N ₄ /Rh-SrTiO ₃ /RGO	Multiple methods	0.58% Rh	Xe (260 W)	Pure water + 10% TEOA	3467	[69]

5. Conclusions

In the present work, we introduce Double-Nozzle Flame Spray Pyrolysis technology as a synthesis method for production of nano SrTiO₃ perovskites, with in tandem control of La-Doping of SrTiO₃ crystal plus a CuO/SrTiO₃-heterojunction. The proposed FSP technology allows controlled production of La:SrTiO₃, SrTiO₃/CuO, or La:SrTiO₃/CuO with fundamental advantages of the one-step production, and the potential for scalable production of complex nanomaterials.

The resulting nanomaterials showed distinct structural-electronic properties, with the La-doping inducing a characteristic increase in SSA via the formation of larger pore voids. Diligent control of the La-doping and SrTiO₃/CuO heterostructure allowed a selective control of photocatalytic production of H₂ or CH₄ from an H₂O/CH₃OH mixture. La-doping in all cases increased the photocatalytic activity of SrTiO₃ nanocatalysts, with the 0.9La:STO showing a benchmark H₂-production rate of 12 mmol g⁻¹ h⁻¹. The incorporation of CuO drastically shifted the selectivity from H₂ toward CH₄. The highest production was achieved with in tandem incorporation of La and CuO, i.e., La:SrTiO₃/CuO catalyst, with a CH₄ production rate of 1.5 mmol g⁻¹ h⁻¹.

Thus, the present work exemplifies FSP as a potent technology for the production of complex nanocatalysts, at the same time bringing new insights into photocatalysis for H₂/CH₄ production.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano13030482/s1>, Figure S1: Pore distribution and N₂ adsorption-desorption isotherms of SrTiO₃ with 2%, 1.2%, and 0.5% CuO materials; Figure S2: XRD and N₂ adsorption-desorption isotherm of the pristine SrTiO₃; Figure S3: XPS data for the nanomaterials for the Ti binding energies; Figure S4: XRD data for the before and after photocatalysis.

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