

# **Cu-substituted lanthanum ferrite perovskites: preparation, characterization and photocatalytic activity in gas-solid regime under simulated solar light irradiation**

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## **Abstract**

LaFeO<sub>3</sub> perovskites both bare and containing 5 to 40 mol% of Cu(II) substituting Fe(III) have been prepared by the citrate autocombustion synthesis method and used as heterogeneous photocatalysts for the degradation of 2-propanol in gas-solid regime under simulated solar light irradiation. The bare LaFeO<sub>3</sub> resulted inactive, however the Cu(II) containing perovskites oxidized 2-propanol to propanone and eventually to CO<sub>2</sub> and H<sub>2</sub>O. The photocatalytic activity of the Cu containing LaFeO<sub>3</sub> perovskites increased by increasing the Cu amount until a 10% of Fe substitution and hence slightly decreased for higher copper content. The powders were fully characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman and diffuse reflectance (DRS) spectroscopies, X-ray photoelectron spectroscopy (XPS), photocurrent measurements, and the photocatalytic activity was correlated with structural and morphological features.

**Keywords:** photocatalysis, LaFeO<sub>3</sub>, perovskite, Cu(II) substituted LaFeO<sub>3</sub>

## 1. Introduction

The role of perovskite oxides ABO<sub>3</sub>, composed of a rare earth cation in the A-site with radius larger than 1.0 Å and a 3d transition metal cation in the B-site with radius in the order of 0.6 - 0.8 Å is prominent in the modern chemical industry. Perovskite materials present excellent conductivity and thermal and chemical stability. In particular, LaFeO<sub>3</sub> with a typical ABO<sub>3</sub>-type perovskite structure has attracted great attention due to its wide application in catalysis, chemical sensing, magnetic materials and as electrode in fuel cells.

Pure lanthanum ferrite (LaFeO<sub>3</sub>) has the orthorhombic ABO<sub>3</sub> perovskite structure. When Fe(III) is substituted into lanthanum ferrite by Cu(II), a solid solution is formed with Cu<sup>2+</sup> (0.72 Å) in the Fe<sup>3+</sup> (0.64 Å) sites. The difference of valence gives rise to a charge imbalance on the B site. As a result, two possible charge compensating mechanisms may occur: the first consists in formation of one oxygen vacancy for two Cu(II) ions added, the second is the change of the iron valence state from Fe<sup>3+</sup> to Fe<sup>4+</sup>. The thermal history and partial pressure of oxygen during the synthesis of the material are reported as key factors in determining the extent of the above mentioned compensation mechanisms. Previous studies reported the simultaneous existence of both oxygen vacancies and tetravalent iron in Cu-substituted lanthanum ferrite samples treated in air.

A solid solution LaFe<sub>1-x</sub>Cu<sub>x</sub>O<sub>3-δ</sub> (LFC), with x up to 0.2, was proposed as catalyst for NO reduction [1,2], and as thermoelectric and cathodic material [3,4]. LaFe<sub>1-x</sub>Cu<sub>x</sub>O<sub>3-δ</sub> crystallizes in a perovskite-type structure ABO<sub>3</sub> with orthorhombic symmetry, and consists of A-site occupied by La ions in 12-fold coordination and B-site occupied by disordered Fe or Cu ions in octahedral coordination [5]. The good catalytic activity for NO and CO reaction is related to the presence of the oxygen vacancies, which play a crucial role on NO adsorption and dissociation [2]. The parent compound LaFeO<sub>3</sub> shows very promising catalytic properties in gas-solid regime; indeed, detailed studies on the catalytic

oxidation of chlorinated volatile organic compounds [6], hydrocarbons [7], and on the catalytic reduction of NO [8] confirmed the broad range of applications.

The physico-chemical features of  $\text{LaFeO}_3$  satisfy also the requirements for its use as photocatalyst.  $\text{LaFeO}_3$  is a charge-transfer-type semiconductor and exhibits an optical band-gap energy between 2.1 eV (for dense polycrystalline samples) and 2.6 eV (for powdered samples) [9,10].

Under visible light irradiation, this compound shows stable photocurrent [11] and photocatalytic activity, although the activity has been reported only in aqueous solution for oxidative degradation of dyes [12-16] and for water decomposition [17].

The effect of partial substitution of La and/or Fe on the photocatalytic properties of the ferrite has been poorly described in the recent literature. The partial substitution of La with divalent Ca or monovalent Li ions causes an increase of the photocatalytic degradation of methylene blue [18-19]. A similar beneficial effect is obtained by Fe partial substitution with Zn or Mn [20-21]. In these papers it is reported that the cation substitution gives rise to an electronic unbalance compensated by an increment of the oxidation state of a part of Fe(III) to Fe(IV), being oxygen vacancies formed to preserve the electroneutrality. However, in case of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  [11,22] a complex effect on the photoelectrochemical properties has been reported.

To the best of our knowledge, studies on the photoactivity of the solid solution  $\text{LaFe}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  in gas-solid regime are unavailable in the current literature. In this work Cu-substituted  $\text{LaFeO}_3$  perovskites ( $x=0.05, 0.10, 0.20$  and  $0.40$ ) have been prepared by citrate auto-combustion synthesis and their photocatalytic activity was tested by using 2-propanol oxidation in gas-solid regime as a probe reaction, analogously to what reported for other solids [23-25]. Moreover the investigated physico-chemical features have been correlated to the photocatalytic activity.

## 2. Experimental

### 2.1. Perovskites preparation and characterization

Analytical grade  $\text{La}_2\text{O}_3$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ , citric acid, nitric acid and aqueous  $\text{NH}_3$  were used as the starting materials. A specific amount of dried  $\text{La}_2\text{O}_3$  was dissolved in a nitric acid solution to prepare  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . The experimental details have been previously reported [5].  $\text{LaFeO}_3$  (LF),  $\text{LaFe}_{0.95}\text{Cu}_{0.05}\text{O}_{3-\delta}$  (LFC05),  $\text{LaFe}_{0.90}\text{Cu}_{0.10}\text{O}_{3-\delta}$  (LFC10),  $\text{LaFe}_{0.80}\text{Cu}_{0.20}\text{O}_{3-\delta}$  (LFC20) and  $\text{LaFe}_{0.60}\text{Cu}_{0.40}\text{O}_{3-\delta}$  (LFC40) powders were prepared by citrate auto-combustion of the dry gel obtained from a solution of the corresponding nitrates in citric acid solution. The resulting lightweight powders were calcined at  $600^\circ\text{C}$  for 3 h in air. For the sake of comparison a sample (LFC05imp) containing LF and CuO was prepared by the wet impregnation method. In particular 0.025 g  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  were dissolved in water and the solution was poured onto 0.5 g LF sample. After 24 h drying at room temperature, the powder was calcined for 3h at  $400^\circ\text{C}$ , a temperature considerably lower with respect to that reached during the citrate autocombustion method. In this way CuO can be obtained, but solid state interaction and possible diffusion between the two phases are not significant. The phase purity was determined for each composition by powder X-ray diffraction. The patterns were collected at room temperature (Bruker D8 Advance diffractometer) using Cu-K $\alpha$ 1 radiation (40 kV, 40 mA,  $\lambda = 0.15406$  nm); the step scan of  $2\theta$  was  $0.02^\circ$  with a scan rate of  $1.2^\circ \text{ min}^{-1}$ . The crystallite domain size was calculated using the Scherrer equation. The specific surface areas (SSA) of the powders were determined in a Flow Sorb 2300 apparatus (Micromeritics) by using the single point BET method. Scanning electron microscopy (SEM) observations and energy-dispersive X-ray (EDX) analyses were performed on the powdered samples after deposition by sputtering of a thin gold layer, using a FEI Quanta 200 SEM microscope operating in high vacuum at 20 kV. Diffuse reflectance UV-vis spectra were recorded in the range 200-800 nm by using a Shimadzu UV-2401 PC instrument, with  $\text{BaSO}_4$  as the reference sample. Raman spectra were obtained by means of a BWTek-i-Raman Plus System, equipped with a 785 nm diode laser. The measurements were

performed focusing the sample by a 20x magnification lens; spot size was around 50  $\mu\text{m}$ . The accuracy of Raman shift was around 3  $\text{cm}^{-1}$ . The power of the laser used was 10% of the maximum value which is around 300 mW. XPS analysis was performed with a Perkin-Elmer  $\Phi$  5600-ci spectrometer using a non-monochromatized Al/Mg dual anode X-ray source (Al-K $\alpha$  1486.6 eV, Mg-K $\alpha$  1253.6 eV). The samples were analysed as powders mounted on a double-sided adhesive tape. The examined area was 800  $\mu\text{m}$  and the working pressure lower than  $10^{-9}$  mbar. The spectrometer was calibrated by assuming the binding energy (BE) of the Au 4f $_{7/2}$  line at 83.9 eV with respect to the Fermi level. The standard deviation for the BEs values was  $\pm 0.2$  eV. Survey scans were obtained in the 0 – 1200 eV range. Detailed scans were recorded for the La3d, Fe2p, Cu2p, O1s and C1s regions. The BEs shifts due to sample charging were corrected by referencing all the energies to the C1s set at 284.8 eV, arising from the adventitious carbon. The analysis involved Shirley-type background subtraction, non-linear least-squares curve fitting, adopting Gaussian Lorentzian peak shapes and peak area determination by integration. The atomic percentage content was evaluated from peak areas using sensitivity factors supplied by Perkin-Elmer. Compositional data were averaged over three spots on each sample. The experimental uncertainty on the reported atomic composition values does not exceed  $\pm 10\%$ . Photocurrent measurements were performed in a three electrodes electrochemical cell by using a CH Instruments Electrochemical Analyzer. An aqueous Ag/AgCl electrode (AMEL) was used as reference, a platinum foil (surface equal to ca. 0.5  $\text{cm}^2$ ) as the counter electrode and the working electrode consisted of a porous monocrystalline film of the perovskite deposited on a titanium foil. The working electrode was prepared as follows: a titanium foil was first cut into 6.2 x 2.1 cm pieces and then degreased by sonication in acetone, rinsed with demineralized water and blown dry in an air stream. 200 mg of the perovskite powder were suspended in 1 ml of absolute ethanol and sonicated for 20 minutes, hence 200  $\mu\text{L}$  of the suspension was drop-casted onto a fixed area (4.2 x 1.7 cm) of the titanium foil using a scotch tape as frame and spacer. The obtained film was dried at room temperature, covered with a glass plate and pressed for 3 minutes at 200  $\text{kg}/\text{cm}^2$  using an IR pressing tool according to a procedure similar to that described in literature [26].

Such a procedure yields an opaque and slightly translucent perovskite layer having an excellent mechanical stability. The working electrode was then placed in the photoelectrochemical cell so that the film was completely immersed in the 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution used as the electrolyte. The photocurrent was measured at the open circuit potential previously recorded for each working electrode. The electrochemical cell was irradiated from the front-side with a 700 W medium pressure Hg lamp, alternating light and dark phases. All the photoelectrochemical tests were carried out at room temperature and under atmospheric air.

## **2.2. Photoreactivity experiments**

The photoreactivity of the perovskites samples in gas-solid regime was evaluated by using a cylindrical Pyrex batch photoreactor (V = 130 ml, external diameter = 93 mm, external height = 22 mm) provided with a silicon/teflon septum. The powders were irradiated from the top by means of a SOLARBOX apparatus (CO.FO.ME.GRA.) equipped with a 1500 W high pressure Xenon lamp placed at a distance of 165 mm from the upper surface of the reactor. The photocatalyst (0.1 g) was placed on the bottom of the photoreactor and O<sub>2</sub> was fluxed for ca. 0.5 h to ensure oxygen saturation. Subsequently, 10 µl of liquid 2-propanol was injected and vaporized into the reactor (2-propanol nominal initial concentration equal to 1.0·10<sup>-3</sup> M). Irradiation started only when the steady state conditions had been achieved, i.e. after that the system was maintained under dark conditions at room temperature to achieve the adsorption equilibrium of the substrate on the catalyst surface. The irradiance reaching the upper surface of the reactor was measured with a Delta Ohm DO 9721 radiometer equipped with a 315-400 nm and 400-950 nm sensors and resulted equal to 10 and 1000 W/m<sup>2</sup>, respectively, by using the previously mentioned sensors. The set-up of the photocatalytic system is showed elsewhere [27].

The runs lasted ca. 6 h and the reacting fluid was analyzed by withdrawing gas samples from the photoreactor by means of a gas-tight syringe. Substrate and intermediates concentrations were measured by using a GC-17A Shimadzu gas chromatograph equipped with a methyl siloxane (30 m

x 320  $\mu\text{m}$  x 0.25  $\mu\text{m}$ ) HP-1 column kept at 40  $^{\circ}\text{C}$  and a FID.  $\text{CO}_2$  was analysed by a HP 6890 Series GC equipped with a packed column GC 60/80 Carboxen-1000 and a TCD.

### 3. Results and Discussion

#### 3.1. Bulk and textural physico-chemical characterization

Figure 1 reports the XRD patterns of the  $\text{LaFe}_{1-x}\text{Cu}_x\text{O}_{3.8}$  perovskite samples. For  $x = 0$  to 0.20 an orthorhombic single phase was found, while for  $x = 0.40$  a mixture of lanthanum ferrite,  $\text{La}_2\text{CuO}_4$  (JCPDS 038-0709) and  $\text{CuO}$  (traces) (JCPDS 048-1548) was observed. Samples of  $\text{LaFe}_{1-x}\text{Cu}_x\text{O}_{3.8}$  have the same basic structure of  $\text{LaFeO}_3$ . The lattice parameters exhibit very small changes with varying  $\text{Cu(II)}$  content, in agreement with ref. [5].

FIGURE 1

Table 1 reports the crystalline phases present in the samples together with the size of the crystallites (ranging between 17 and 43 nm), calculated by using the Scherrer formula. The specific surface areas (SSA) of the samples, included in Table 1, are quite low and similar for each sample due to the high temperature reached during the preparation.

TABLE 1

SEM images, shown in Figure 2, evidence that all the prepared samples consist of almost spherical agglomerates of particles whose shapes are similar. The size of the agglomerates ranges between 40 and 70 nm. However, some differences can be evidenced between the LF, LFC05, LFC10 and LFC20, LFC40 samples (the last one is not shown being morphologically similar to LFC20). Indeed, only in

the last two samples several or almost all of the particles appear merged, indicating that a sintering effect occurred in the presence of higher amounts of Cu(II).

EDX atomic percentage values are listed in Table 2, where the atomic percentages reported are the average of at least ten values recorded on different agglomerates. The LF and LFC05 samples are very homogeneous; in fact, very low oscillations of the atomic percentage were observed by analyzing different areas of their surface. Conversely, for LFC10, LFC20 and LFC40 slightly higher oscillations in the metals content and in the dimension of the agglomerates were observed. Notwithstanding the average percentages of La, Fe and Cu measured by EDX resulted close to their nominal compositions when considering a very large number of agglomerates. Notably the figures for Cu and La were always higher or lower, respectively, than the nominal values. These findings can be explained by considering a partial superficial Cu segregation.

#### FIGURE 2 and TABLE 2

Further information on the structure of the samples are given by Raman spectroscopy. Figure 3 shows the spectra of LF and LFC samples. The Raman spectrum of LF sample shows the presence of bands at ca. 73, 100, 150, 176, a doublet at 262 and 287, 430 with a shoulder at 409, 625 and 1335  $\text{cm}^{-1}$ . LF presents the orthorhombic symmetry and crystallized with the distorted orthorhombic perovskite structure in agreement with results previously reported for powders prepared at 600°C [5]. Popa et al. observed a spectrum very similar to that reported in Figure 3 (a) for a distorted orthorhombic perovskite structure  $\text{LaFeO}_{3+\delta}$  [28].

#### FIGURE 3

The Raman bands of the Cu doped perovskites are less intense and with higher luminescence increasing the Cu amount. Raman spectroscopy is a very sensitive technique to structure distortion



and oxygen vacancies. For LFC05 and LFC10 the recorded Raman bands are essentially those assigned to the bare  $\text{LaFeO}_3$  and consequently we can assume a certain additional distortion of the perovskite crystalline with respect to the parent LF cell. Remarkably, the band recorded at ca.  $625 \text{ cm}^{-1}$  for LF sample is clearly shifted in the LFC05 and LFC10 samples where it appears at ca.  $555 \text{ cm}^{-1}$ . This shift can be ascribed to the oxygen vacancies in the perovskite deriving from a strong distortion of the anionic lattice, as suggested by Lee et al. [29]. Also modification in the crystallites size giving rise to crystal imperfections may be responsible for the lower intensity of the Raman modes. LFC20 and particularly LFC40 (not shown) samples presented strong problems of luminescence hampering their Raman study.

The Kubelka-Munk transformation of the diffuse reflectance spectra of the samples,  $F(R_\infty)$ , shown in Figure 4 A, evidences a strong absorption in the visible region. The observed behaviour can be assigned to the band-gap energy due to the electronic transitions from the valence band (mainly constituted of strongly mixed  $e_g$  states of Fe  $3d$  and O  $2p$  states) to the conduction band ( $t_{2g}$  states of Fe  $3d$ ) [30]. The optical band gap energies of the perovskites were estimated, assuming a direct allowed transition, by extrapolating a linear fitting in the Tauc plot [31], i.e.  $(F(R_\infty) \cdot E)^2$  vs the incident light as shown in Figure 4B. Two slightly different energy values can be obtained from this method and this finding can be explained by considering that the presence of oxygen vacancies can create intermediate energy levels. Moreover the different size of the crystallites could be also invoked. Although, according to the previous characterization results, LF, LFC05, LFC10 and LFC20 samples consist of a single crystallographic phase, the presence of two different structures, corresponding to the distorted perovskite lattice by virtue of the oxygen defects, cannot be excluded. Interestingly, LFC40 Tauc plot shows only one electronic transition, indicating that the perovskite structure in this case is less distorted than for the samples with lower amount of Cu.

Table 1 reports the estimated band gap values of the samples. LF sample shows two band gap energies of 2.56 and 2.64 eV. The onset of the linear increase in diffuse reflectance spectrum has been taken often as the band gap energy. However this kind of approach does not lead to an accurate estimation,

in fact the reported optical band gap for  $\text{LaFeO}_3$  varies from 2.1 to 3.85 eV [32]. These discrepancies may result from different particle sizes and synthesis routes, but they also depend on the graphical determination technique applied. In order to correctly determine the optical band gap it is necessary to consider the type of transition that occurs [33]. The theoretical value has been estimated as 2.6 eV [9,10,29], in good agreement with the obtained values. Notably, when Cu(II) partially substitutes Fe(III), no significant changes in the band gap is observed indicating that the presence of  $\text{Cu}^{2+}$  does not significantly modify the UV absorption properties of the LF perovskite.

#### FIGURE 4 A and B

XPS analysis was adopted to evaluate the surface composition of the samples in order to shine some light on the above reported photoactivity trends. For the whole set of specimen signals from lanthanum, iron, oxygen, and carbon were obtained. Copper was always detected with the exception of the LF sample. In all perovskite powders, the binding energy pertaining to the O1s lines agrees well with oxygen in the perovskite lattice, which is peaked at 529.2 eV [34]. A second component on the higher energy side is clearly observed at *ca.* 531 eV and may be likely assigned to a partial hydroxylation and/or carbonatation at the perovskitic surface (see Figure 5A). This hypothesis is supported by considering the C1s line profile shown in Figure 5B. Along with the component of adventitious carbon (284.8 eV), a high energy contribution at 289.4 eV is present in all samples and can be associated with the formation of surface carbonates [34]. It is worth highlighting that the relative intensity of the two components for both O1s and C1s regions is significantly dependent on samples composition. In particular, it is evident an increase in the O1s and C1s high energy components associated with surface carbonates as a function of the dopant amount. The trend is shown in Figure 5 at increasing copper doping levels. The formation of carbonates, as a consequence of the interaction with  $\text{CO}_2$ , can be attributed mostly to the structural properties of the copper lanthanum ferrites. The ideal perovskite structure ( $\text{ABO}_3$ ) is cubic with the larger A site cations located at the corners of the cube, the B-site ions at the body centre, and the oxygen ions at the centres of the faces. The oxide anion is coordinated by two relatively small and rather polarizing Fe/Cu

cations, while it is only weakly polarized by the larger La cations. The surface oxide ions present an average coordination lowered to one, and as a consequence they show strong nucleophilicity, responsible for the attack of CO<sub>2</sub> to the cation atom giving rise to stable surface carbonates [35].

Notably, enhancing the intensity of the X-ray source (by using Al instead of Mg as the anode) results in a lower intensity of the high energy O1s and C1s peaks thus confirming that the species responsible for these signals are segregated on the surface of the samples.

The only exception is represented by the impregnated sample whose O1s and C1s high energy components present the lowest intensity compared to the whole set of samples. Indeed, solid state reactions can be neglected due to the mild thermal treatment to which this sample was subjected. We also observe that in the O1s spectrum of the 20% Cu-doped perovskitic powder the carbonate component is dominant thus suggesting the prevalence of this phase on the sample surface.

## FIGURE 5

Regarding La3d and Fe2d peaks, their band-shape and energy position are typical for lanthanum iron oxides. The La 3d<sub>5/2</sub> peak centered at *ca.* 834.2 eV shows the typical complex structure of core-level photoemission spectra of the light rare earth compounds; i.e., in addition to the well-known spin-orbit multiplet splitting, a characteristic satellite structure is present, which has been mainly attributed to final-state effects or to charge-transfer coexcitations. The observed intensity ratio between the satellites and the main peaks is the same for all samples indicating that doping with copper in different amounts does not influence the chemical state of lanthanum [36]. For the Fe 2p<sub>3/2</sub> peak the binding energy value is centered at 710.5 eV and the profile is typical of Fe(III) ions in oxidic environment [37]. All samples show a depletion of Fe on the surface as already observed in similar systems [38]. For all samples, lanthanum is clearly overabundant when compared to the nominal amount. This behaviour was already observed in similar compounds and can be attributed to the “basic” properties of La and its tendency to segregate in surface and react with atmospheric CO<sub>2</sub>. Regarding the Cu2p

peak, the measured BE ( $j = 3/2$  at *ca.* 934 eV) value is characteristic for Cu(II) ions in oxide environment.

Table 3 summarizes the nominal and measured Fe/Cu and La/(Fe+Cu) molar ratios.

TABLE 3

For all of the samples the measured Fe/Cu ratio values are lower than the nominal ones. In the case of the impregnated sample this result can be explained by taking into account the above mentioned negligible defectivity of this sample so that copper is probably present in the form of CuO islands on the surface of LF.

For samples prepared by citrate autocombustion method, instead, the lower measured ratios which decrease by increasing the copper content, can be attributed to iron depletion on the surface. This indicates that the surfaces of the powders are richer in copper the higher its nominal content is. The comparison of the measured La/(Fe+Cu) ratios with the theoretical ones reveals that the  $\text{Cu}^{2+}$  substitute  $\text{Fe}^{3+}$  ions giving rise to surface defectivity. In fact, the measured values are very close to 1.0 for LFC05, LFC10 and LFC20 samples as the molar amount of La is similar to that of (Fe+Cu). On the contrary, the measured value is lower than the nominal one for the impregnated sample because Fe/La and Cu are present probably as separated phases and the molar amount of (Fe+Cu) results higher than that of La.

### **3.2. Photocatalytic activity in gas-solid regime**

Blank reactivity experiments were performed under the same experimental conditions used for the photo-reactivity runs but in the absence of catalyst, oxygen or light. No reactivity was observed in all these cases so that it was concluded that the contemporary presence of  $\text{O}_2$ , catalyst and irradiation is necessary for the occurrence of 2-propanol degradation. For some selected experiments the photocatalyst was recovered and reused twice more and its photoactivity was virtually unchanged,

although a slight decrease was observed after each run. It is worth mentioning that the system placed in the SOLARBOX apparatus was cooled by means of forced air recirculation, however the temperature inside the reactor reached a constant value of 120 °C. Blank tests were carried out to ascertain that the influence of the temperature on the photoactivity was negligible. The initial concentration of 2-propanol measured in the reacting system after ca. 30 minutes of its injection was ca. one half that expected, indicating that all of the perovskites showed strong 2-propanol adsorption under dark conditions.

Figure 6 reports the values of 2-propanol concentration vs. irradiation time for runs carried out in the presence of the perovskites. 2-Propanol concentration continuously decreased whilst propanone concentration firstly increased, reached a maximum value and then slowly decreased. Propanone was the main intermediate product. As evident by a perusal of Figure 6, CO<sub>2</sub> was detected as a reaction product only by using the copper containing perovskites and its concentration was ca. one order of magnitude lower than the stoichiometric one. The carbon atom mass balance considered as the sum of the concentrations of substrate and products was never achieved. The propanone amount, measured in vapor phase, never reached the stoichiometric value that should be obtained from 2-propanol degradation, probably because also propanone and/or CO<sub>2</sub> were adsorbed on the catalyst surface.

#### FIGURE 6 (A)-(E)

From the observation of the data reported in Figure 6 it can be concluded that the Cu(II) content in the perovskite influenced the photocatalytic activity of the solids. The LF perovskite showed an initial increase of 2-propanol concentration attributed to the photo/thermal desorption of the substrate from the solid surface, however the evolution of the 2-propanol substrate during the run evidenced that this material showed a negligible photocatalytic activity. Increasing the amount of Cu(II) substituting Fe(III) sites in the perovskites, gave rise to higher photocatalytic activity. The LFC05 material also presented a certain photo-thermal desorption during the first 90 minutes of reaction and hence a

decrease of 2-propanol concentration. During the first 90 minutes an increase in the propanone concentration was also observed. Afterwards the propanone amount in the gas phase remained constant. LFC10, LFC20 and LFC40 showed an analogous qualitative photocatalytic behaviour with a decrease of the 2-propanol substrate and a contemporary increment of the propanone and CO<sub>2</sub> concentrations up to a plateau, although the photocatalytic activity of the LFC10 sample appeared to be the highest in terms of consumed 2-propanol and produced CO<sub>2</sub>. For all of the three perovskite samples, the plateau of the propanone concentration corresponded to ca. 10<sup>-4</sup> M after ca. 60 minutes of irradiation, whereas the CO<sub>2</sub> plateau concentrations were ca. 2.5·10<sup>-5</sup>, 5·10<sup>-5</sup>, 4.5·10<sup>-5</sup> and 3.0·10<sup>-5</sup> M for LF05, LFC10, LFC20 and LFC40, respectively and they were reached after ca. 120-150 minutes of irradiation, depending on the sample.

Notably the lower the copper content, the more intense the photo/thermal desorption processes of 2-propanol were. In fact, once the lamp was switched on, 2-propanol desorbed from the catalyst surface in higher extent for the sample without copper (LF) with respect to the Cu containing perovskites. It should be considered that the disappearance of 2-propanol masked the photodesorption process when the photo-activity of the samples was higher.

The photocatalytic tests reported in Figure 6 were carried out by using the same amount of photocatalyst and under the same experimental conditions, therefore, they are quantitatively comparable because the powders presented similar specific surface areas.

By taking into account the XPS results it is possible to explain the better oxidation ability of the powders containing Cu(II). It has been reported that the oxygen defects could increase the capacity to adsorb molecular oxygen on the perovskite surface [39,40]. In such a way the improvement of the photocatalytic activity can be explained by taking into account the formation of higher amounts of OH radicals formed through interaction of oxygen vacancies generated by substitution of trivalent iron by divalent copper, with water molecules adsorbed on the surface. Moreover, both Cu(II) and oxygen vacancies may act as electron traps decreasing the electron-hole recombination thus enhancing the photocatalytic activity. The higher hydroxylation degree of copper containing samples

is confirmed by the above reported intensities of the O1s signal at 531.3 eV (Figure 5A). The higher surface hydroxylation degree and the presence of stable surface carbonates present opposite influence on the photocatalytic activity. The higher surface hydroxylation increases the number of active sites affording higher photocatalytic activity. On the other hand, the stable surface carbonates may block the active sites depressing the activity. As a consequence the photocatalytic activity of the Cu containing LaFeO<sub>3</sub> perovskites increased by increasing the Cu amount until a 10% of Fe substitution and hence slightly decreased for higher copper content. These results allow to explain also the reason why the carbon balance during the photocatalytic degradation of isopropanol was always not respected. In fact, the CO<sub>2</sub> produced through photo-oxidation of the organic substrate easily could adsorb onto the surface so that only a very low amount could be detected in the reaction atmosphere. It is worth to mention that LFC05imp presents photocatalytic activity (not shown) comparable to LFC20 one. However in this case the observed activity is likely due to the presence of heterojunctions between CuO and LaFeO<sub>3</sub> particles. Indeed, the valence and conduction band edges of CuO (VB: +2.66V; CB: +0.96V) and LaFeO<sub>3</sub> (VB: +2.27V; CB: -0.27 V) at pH = 1, [11,41] may afford an efficient spatial charge separation giving rise to lower electron-hole recombination and higher photocatalytic activity. The photo-activity of impregnated samples is under ongoing investigation, however it remains out of the aims of this work, being their morphology very different from that of the samples prepared by the autocombustion method.

In order to study the electronic properties of the LF samples and in particular the possible modification of electron-hole recombination due to the presence of Cu(II) and oxygen defects, the transient photocurrent response of all the materials was recorded for several on-off cycles of UV irradiation. Results are showed in Figure 7.

FIGURE 7

The photocurrent response of the LF sample was very low. Increasing photocurrent responses corresponding to ca.  $2 \cdot 10^{-6}$ ,  $4 \cdot 10^{-6}$  and  $8 \cdot 10^{-6}$  A were observed for LF, LFC05 and LFC10 samples, respectively. For all of the three samples the photocurrent drastically increased in the presence of irradiation (light on), and the photocurrent came back to the original baseline value as soon as the illumination of the photoanode stopped (light off). Moreover, the photocurrent was almost stable during the irradiation time, showing a good mobility of the charge carriers. The above analysis revealed that the Cu presence, at least until 10% of Fe substitution, could effectively reduce the recombination of photo-generated electrons and holes, and produce longer living photo-generated carriers. Accordingly, the photocatalytic activity of LF, LFC05 and LFC10 followed the same trend, being the LFC10 the most active powder. For higher Cu(II) contents, the photoelectrochemical response decreased and accordingly LFC20 and LFC40 samples (which produced a photocurrent response of ca.  $6 \cdot 10^{-6}$  and  $4 \cdot 10^{-6}$  A, respectively) showed lower photocatalytic activity.

## **Conclusions**

Cu-substituted lanthanum ferrites with Cu(II) content ranging between 5 and 40% have been obtained by citrate auto-combustion synthesis procedure. These materials have been used for the 2-propanol photocatalytic oxidation in gas-solid regime by using solar simulating light. The substrate was oxidised in the presence of the Cu-substituted lanthanum ferrite giving rise to propanone as the major intermediate product and CO<sub>2</sub> as the final product. All of the perovskites showed a strong adsorption ability for 2-propanol but only those containing Cu(II) exhibit photocatalytic activity. The higher activity of the Cu containing powders was related with the presence of oxygen vacancies and with the reduced electron-hole recombination as also proved through XPS analysis and photocurrent measurements.

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**Table 1.** Physico-chemical characterization of the perovskites used as photocatalysts: morphological and surface features.

Sample	Phase composition	XRD Crystallite size of the perovskite phase (nm)	B.E.T. SSA [m <sup>2</sup> ·g <sup>-1</sup> ]	Band gap [eV]
LF	Perovskite*	43	16	2.56 and 2.64
LFC05	Perovskite*	41	10	2.54 and 2.57
LFC10	Perovskite*	35	13	2.51 and 2.58
LFC20	Perovskite*	21	14	2.46 and 2.51
LFC40	Perovskite*, La <sub>2</sub> CuO <sub>4</sub> , CuO (traces)	17	16	2.47

\*Based on orthorhombic LaFeO<sub>3</sub>.

**Table 2.** Nominal and EDX average (with the maximum oscillation) atomic percentages of La, Fe and Cu, in the perovskite photocatalysts.

Sample	La [%]		Fe [%]		Cu [%]	
	nominal	EDX	nominal	EDX	nominal	EDX
LF	50.0	50±0.5	50.0	50±0.5	0.0	0
LFC05	50.0	49±1	47.5	47±1	2.5	4±1
LFC10	50.0	47±2	45.0	45±1	5.0	7±2
LFC20	50.0	49±2	40.0	39±1	10.0	12±2
LFC40	50.0	48±2	30.0	30±1	20.0	22±2

**Table 3.** Nominal and measured Fe/Cu and La/(Fe+Cu) molar ratios in the perovskite photocatalysts.

	<b>Fe/Cu nominal</b>	<b>Fe/Cu measured</b>	<b>La/(Fe+Cu) nominal</b>	<b>La/(Fe+Cu) measured</b>
LF	-	-	1.00	1.10
LFC05	19.0	5.80	1.00	0.93
LFC10	9.00	5.00	1.00	1.08
LFC20	4.00	2.87	1.00	1.04
LFC05imp	19.00	4.72	0.95	0.70

## CAPTIONS FOR FIGURES

**Figure 1.** XRD patterns as a function of Cu-substitution for the  $\text{LaFe}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  solid solution. Impurity phases are marked with a square ( $\text{La}_2\text{CuO}_4$ ) and a star ( $\text{CuO}$ ).

**Figure 2.** SEM micrographs of (a) LF, (b) LFC05, (c) LFC10 and (d) LFC20 samples.

**Figure 3.** Raman spectra of: (a) LF; (b) LFC05; (c) LFC10; (d) LFC20 samples.

**Figure 4A.** Diffuse reflectance spectra of (a) LF, (b) LFC05, (c) LFC10, (d) LFC20 and (e) LFC40 samples.

**Figure 4B.** Tauc plot of (a) LF, (b) LFC05, (c) LFC10, (d) LFC20 and (e) LFC40 samples.

**Figure 5.** XPS spectra of LF05-IMP, LF, LFC05, LFC10, LFC20 samples: (A) O1s region and (B) C1s region.

**Figure 6.** 2-propanol ( $\blacklozenge$ ), propanone ( $\bullet$ ) and  $\text{CO}_2$  ( $\blacktriangle$ ) concentrations vs. irradiation time for reaction in the gas-solid system in the presence of (a) LF, (b) LFC05, (c) LFC10, (d) LFC20 and (e) LFC40 samples.

**Figure 7.** Transient photocurrent responses for (a) LF, (b) LFC05, (c) LFC10, (d) LFC20 and (e) LFC40 samples.