

Article

Flame Spray Pyrolysis Engineering of Nanosized Mullite-Bi₂Fe₄O₉ and Perovskite-BiFeO₃ as Highly Efficient Photocatalysts for O₂ Production from H₂O Splitting

Pavlos Psathas ¹, Maria Solakidou ¹ , Asterios Mantzanis ¹  and Yiannis Deligiannakis ^{1,2,*} 

¹ Laboratory of Physical Chemistry of Materials and Environment, Department of Physics, University of Ioannina, GR45110 Ioannina, Greece; p.psathas@uoi.gr (P.P.); maria-sol@windowslive.com (M.S.); asteriosmantzanis@gmail.com (A.M.)

² Institute of Environment & Sustainable Development, University Research Center of Ioannina (URCI), GR45110 Ioannina, Greece

* Correspondence: ideligia@cc.uoi.gr

Abstract: Bi-Fe oxides are stable materials with potential photocatalytic activity under solar light photons. So far, however the photocatalytic potential of pure-phase nanosized mullite-Bi₂Fe₄O₉ has not been studied. Usually, synthesis of pure-phase nanosized mullite-Bi₂Fe₄O₉ is hampered by co-formation with perovskite BiFeO₃. Herein we demonstrate that pure-phase mullite-Bi₂Fe₄O₉ nanoparticles prepared by Flame Spray Pyrolysis (FSP) technology are highly efficient O₂ production photocatalysts, achieving >1500 μmol g⁻¹h⁻¹. This outperforms all -so far reported- O₂ production Bi-Fe-O photocatalysts. We present an FSP-based process for production of a versatile Bi-Fe-O platform, that can be easily optimized to obtain 100% mullite-Bi₂Fe₄O₉ or 100% perovskite-BiFeO₃ or their heterojunctions. The phase-evolution of the Bi-Fe-O materials has been studied by XPS, Raman, and EPR spectroscopies. Short post-FSP annealing process impacts the photoactivity of the BiFeO₃ and Bi₂Fe₄O₉ in distinct ways. Fe²⁺ centers in BiFeO₃ can improve dramatically its O₂ production efficiency, while solid-melt formation in Bi₂Fe₄O₉ is a limiting factor.

Keywords: Flame Spray Pyrolysis; photocatalysis; Bismuth Iron Oxide; mullite; perovskite; oxygen evolution reaction; defects



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1. Introduction

Exploitation of solar photons via photocatalysis is an established green technology approach [1]. Achievement of efficient photocatalytic oxygen evolution reaction (OER) using H₂O as substrate is a challenging task [2,3]. In this context, bismuth-based nano photocatalysts, such as BiVO₄ [4,5] and Bi₂WO₆ [6] have emerged as promising Bi-based materials for OER. Recently, BiFeO₃ has been demonstrated as a potent O₂ evolving photocatalyst [7,8]. More generally, the perovskite-BiFeO₃ phase is renowned for its multiferroic attributes, which possess simultaneously ferroelectric and magnetic order properties [9]. Its small band-gap in the range of 2.1–2.8 eV [10] renders BiFeO₃ visible-light active [7,8]. Interestingly, the mullite-phase Bi₂Fe₄O₉ has also a bandgap in the visible photons range of 2.1–2.3 eV [11]. In general, Bi-Fe oxides are stable materials, as exemplified for BiFeO₃ under photocatalytic conditions [12]. However, the efficiency of mullite-Bi₂Fe₄O₉ for photocatalytic O₂ production from H₂O has not been assessed so far.

On the other hand, both BiFeO₃ and Bi₂Fe₄O₉ materials have been reported to achieve satisfactory photocatalytic degradation of organic pollutants, such as methylene blue (MB), Rhodamine Blue (RhB) [13,14], and Bisphenol-A [15]. Yang et al. [16] have reported [BiFeO₃/Bi₂Fe₄O₉] heterostructures with enhanced RhB photodegradation, which was attributed to the alignment of their conduction and valence bands. Recently, Zhang et al. [17] reported photocatalytic water-splitting by BiFeO₃, while Humayun et al. [18] have reported a porous BiFeO₃/TiO₂ nanohybrid with enhanced H₂ production performance.

Recently, we have developed a Flame Spray Pyrolysis (FSP) process for the synthesis of BiFeO_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanomaterials [19] which could be adjusted to consist of 100% BiFeO_3 nanophase or 100% $\text{Bi}_2\text{Fe}_4\text{O}_9$ as well as the mixed-phase heterojunction BiFeO_3 : $\text{Bi}_2\text{Fe}_4\text{O}_9$.

In the present work, the FSP-made Bismuth Iron Oxide (BFO) nanophases were optimized for enhanced photocatalytic O_2 -evolution from H_2O . Our research revealed that post-FSP annealing has a profound impact on the optimal OER-efficiency of the FSP-made BFO nanophases. To understand the underlying mechanisms we have used a combination of XRD, XPS, Raman, and EPR spectroscopies for a comprehensive study of the OER efficiency vs. the lattice and electronic configuration of BFO materials. Our strategy was based on two steps: first, the use of FSP for controllable synthesis of the pure BFO nanophases i.e., 100% BiFeO_3 or 100% $\text{Bi}_2\text{Fe}_4\text{O}_9$ as reported in our recent work [19]. For completeness, a mixed-phase 50/50 BiFeO_3 / $\text{Bi}_2\text{Fe}_4\text{O}_9$ was also prepared. Second, each BFO nanophase was annealed under O_2 -atmosphere for various short-periods and temperatures. As we show herein, these post-FSP annealing protocols, even for a very short time such as 30-min, impact the photoactivity of the BiFeO_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$ in distinct ways. Fe^{2+} -centers formed in BiFeO_3 can improve dramatically its O_2 production efficiency. On the other hand, $\text{Bi}_2\text{Fe}_4\text{O}_9$ was sensitive to solid-melt formation, which was a limiting factor in its photoactivity. Technology-wise, the present work shows that by diligent control of the FSP parameters combined with short post-FSP annealing, can take advantage of the versatility of FSP for scalable production of nanomaterials with controlled phase/size and defects [20,21] to achieve highly efficient O_2 evolving photocatalyst. Moreover, the present research data reveal -for the first time in literature- that the optimized mullite- $\text{Bi}_2\text{Fe}_4\text{O}_9$ phase is a highly efficient O_2 evolving photocatalyst over performing BiFeO_3 . Together with quantum chemical calculations, we use EPR and XPS data to analyze the underlying mechanism which relates the energy level profile of the BFO phases with the h^+ efficiency in O_2 production from H_2O .

2. Materials and Methods

2.1. Flame Spray Pyrolysis (FSP) Synthesis of Nanocatalysts

The BFO nanomaterials were produced in a single-nozzle FSP reactor [19]. In brief, the stock solutions contained Fe(III) acetylacetonate (97% Aldrich, St. Louis, MO, USA) dissolved in xylene, and Bismuth(III) acetate (99.99% Aldrich) dissolved in 2-Ethylhexanoic acid (EHA). The precursor solution for production of BiFeO_3 phase had a molar ratio of $[\text{Fe}] = 0.1 \text{ M}$, and $[\text{Bi}] = 0.1 \text{ M}$, while for production of $\text{Bi}_2\text{Fe}_4\text{O}_9$ phase we have used $[\text{Fe}] = 0.134 \text{ M}$, $[\text{Bi}] = 0.066 \text{ M}$. In all cases, the total metal concentration was set to $[\text{Fe}] + [\text{Bi}] = 0.2 \text{ M}$ and the solvents [xylene:EHA] volume ratio was (1:1). The parameters of the FSP process consisted of a precursor flow rate of 3 mLmin^{-1} and a dispersion oxygen flow rate of 7 Lmin^{-1} (Linde 99.999%). The flame was enclosed with two metallic tubes of a total 44 cm height. With the assistance of a vacuum pump (Busch, Maulburg, Germany), the produced particles were deposited on a glass microfiber filter with a binder (Albet Labscience, Hahnemuehle, Dasen, Germany, GF 6 257) and collected by scraping the powder from the filter. The produced nano photocatalysts were stored in glass vials under an inert Argon atmosphere, until use.

Post-FSP annealing: Post-FSP annealing was performed in a Thermawatt furnace, (Thermawatt, Athens, Greece) where a standard mass of 100 mg of nanomaterial was inserted in the tubular compartment under atmospheric O_2 . We found that nano-BFO [19] phase-transitions occur at temperatures $\sim 130^\circ\text{C}$ lower than in bulk BFO [22]. Herein after several screening experiments, we have found that post-FSP periods of $t_{\text{anneal}} = 5$ to 120 min and $T_{\text{anneal}} = 550\text{--}700^\circ\text{C}$ values allowed us to span the appropriate phase-transitions in conjunction with the photocatalytic performance. Based on this, we discuss in detail $t_{\text{anneal}} = 5, 30, 60, 120 \text{ min}$ since these provide the full O_2 performance variation, i.e., $t_{\text{anneal}} = 5 \text{ min}$ was best for photocatalytic performance of BiFeO_3 while $t_{\text{anneal}} = 60 \text{ min}$ was best for photocatalytic performance of $\text{Bi}_2\text{Fe}_4\text{O}_9$.

2.2. Characterization of the Nanomaterials

2.2.1. Material Morphology

Powder X-ray Diffraction (pXRD) was carried out on a D8 Advance Bruker diffractometer with a Cu source ($K\alpha$, $\lambda = 1.5418 \text{ \AA}$), with operation parameters to be 40 mA current and 40 KV generator voltage. All structural parameters obtained from the pXRD data were calculated via Rietveld analysis using the Profex software, to determine the percentage of the $\text{BiFeO}_3/\text{Bi}_2\text{Fe}_4\text{O}_9$ crystal-phases for each BFO material.

Transmission Electron Microscopy (TEM) images were taken with a JEOL JEM-2100 electron microscope equipped with a LaB_6 filament, operating at 200 kV accelerating voltage.

N_2 -Adsorption-desorption Brunauer–Emmett–Teller (BET) adsorption-desorption isotherms were recorded at 77 K using a Quantachrome NOVA touch LX². Outgassing was performed at 150 °C for 16 h under vacuum. The absorption points in the relative pressure P/P_0 range of 0.1–0.3 were used to calculate the specific surface area (SSA). The absorption data points in the P/P_0 range = 0.35–0.99 were used for the pore radius analysis by the BJH method, while the total pore volume was obtained at the $P/P_0 = 0.99$ data point. The complete adsorption-desorption isotherm data are in Figure S1.

2.2.2. Optical Spectroscopy

Diffuse-Reflectance UV-Vis spectra (DRS-UV/Vis) were recorded with a Perkin Elmer Lambda-35 spectrometer, operating at room temperature, using BaSO_4 powder as a background standard.

Fourier Transformed Infrared (FTIR) spectra were collected using an-IR Nicolet IS5 system equipped with the OMNIC software package, in the wavenumber range 400–4000 cm^{-1} , for materials dispersed in KBr pellets.

Raman HORIBA-Xplora Plus spectrometer, equipped with an Olympus BX41 microscope was used to record Raman spectra. A 785 nm diode laser was used as an excitation source, and the laser beam was focused on the sample with the microscope. Before measurement, each powder material was softly pressed between two glass plates to form a pellet. A laser intensity of 15 mW was used, we found after trial-and-error that at this low-intensity, the crystal phase remained unchanged. Typically, good signal-to-noise Raman spectra were recorded for 15 accumulations at 30 s.

X-ray photoelectron spectroscopy (XPS) spectra were collected 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). The base-pressure at the measurement was $2\text{--}5 \times 10^{-9}$ mbar. In all experiments, the monochromatized Mg $K\alpha$ line was set at 1253.6 eV, and the analyzer pass-energy at 20 eV. The binding energies were calculated vs. the energy of C_{1s} carbon peak at 284.5 eV. The peak deconvolution for the Shirley background and peak deconvolution was performed employing mixed Gaussian–Lorentzian functions in the least-squares curve-fitting, using WinSpec software, developed at the Laboratoire Interdisciplinaire de Spectroscopie Electronique, University of Namur, Belgium.

2.2.3. Theoretical Modeling (DFT) Calculations

Theoretical calculations were conducted for the $\text{BiFeO}_3\text{-R3C}$ [23] and $\text{Bi}_2\text{Fe}_4\text{O}_9\text{-Pbam}$ structures [24], using DFT as implemented in the Quantum Espresso software [25]. The projector augmented-wave (PAW) method was used to describe the core pseudopotential and the generalized gradient approximation (GGA) as simplified by Perdew, Burke, and Ernzerhof (PBE) and it was used for exchange-correlation effects. Pseudopotentials containing 15 valence electrons were used for Bi ($5d^{10}, 6s^2, 6p^3$), 16 valence electrons for Fe ($3s^2, 3p^6, 3d^6, 4s^2$) and 6 valence electrons for O ($2s^2, 2p^4$). A plane-wave energy cutoff of 70.8 Ry was used for the $\text{BiFeO}_3\text{-R3C}$ structure and the $\text{Bi}_2\text{Fe}_4\text{O}_9\text{-Pbam}$ structure. Both structures were relaxed until the forces acting on each atom were $<10^{-3} \text{ eV/\AA}$. For geometry optimization and electronic structure calculations, $(3 \times 3 \times 3)$ and $(9 \times 9 \times 9)$ Monkhorst-Pack k-point grids were used respectively. Considering the strong correlations in transition

metal oxides, we used the DFT+U approximation in the approach of Cococcioni and de Gironcoli [26] with a U-value of 4 eV applied on both structures.

2.3. Photocatalytic O₂ and •OH Generation

2.3.1. Electron Paramagnetic Resonance (EPR) Spectroscopy (•OH Generation)

A Bruker ER200D spectrometer equipped with an Agilent 5310A frequency counter was used, operating at X-band (9.61 GHz). The spectrometer was running under homemade software based on LabView. In situ illumination of the samples inside the EPR cavity was performed using a 450 W Xe light lamp (Oriel model 66929), equipped with a 400 nm cut-off filter. For determination of •OH, the reaction mixture was prepared using 1 mL of ultrapure Milli-Q water (Millipore, Burlington, MA, USA) contained 0.4 mg of each BFO material and 0.12 mg of H₂AuCl₄•3H₂O, or 0.14 mg of H₂Pt₄Cl₆•H₂O, which mixed with 2 mM of spin trap DMPO (5,5-dimethylpyrroline-(2)-oxyl, Aldrich). From this stock suspension, 20 µL were inserted into glass capillaries. To avoid the interference of sulfate-hydroxyl radicals, we have recorded EPR spectra without the presence of Na₂S₂O₈. Irradiation was carried out in-situ at the EPR cavity, for periods from 30 s up to 5 min. Quantitative analysis of the •OH was done using DPPH (1,1-Diphenyl-2-Picrylhydrazyl, Alfa Aesar, Haverhill, MA, USA) as a spin standard [27], and the double integral of the EPR signals.

2.3.2. Photocatalytic O₂ Evolution Measurements

Experiments were performed into an immersion-well reactor (Photochemical Reactors Ltd., Reading, UK, Model 3210), a total reaction volume of 300 mL, at temperature 25 ± 3 °C being controlled by tap-water cooling. The light source was a medium-pressure mercury lamp (Model Oriel 3010, 125 W, total light flux 7 × 10¹⁸ photons/s), inserted into the glass-reactor. This irradiation set-up allowed only radiation with λ > 380 nm photons to excite the photocatalysts. In each experiment, 50 mg of the catalyst was suspended into 150 mL Milli-Q water which contained 0.1M NaOH (pH~12.8) and 0.02 M Na₂S₂O₈ as an electron acceptor (final concentration of catalyst 0.33 g/L). Experiments with Pt⁰, Au⁰, or Ag⁰ were realized using hydrogen hexachloroplatinate (IV) hydrate, (H₂Pt₄Cl₆•H₂O, 99.9 %, Alfa Aesar), hydrogen tetrachloroaurate (III) trihydrate (HAuCl₄•3H₂O, 99.9 %, Alfa Aesar), and Silver nitrate (I) (AgNO₃, 99.9 %, Sigma Aldrich). In all experiments, the cocatalytic noble-metal particles were photo deposited in-situ: after the addition of all compounds in the reactor, an irradiation period of 15 min was necessary to achieve the in-situ reduction of the Pt, Au, or Ag cations [28].

Before each catalytic run, the suspension was purged with Ar gas (99.9997%) for at least 1 h so as to remove atmospheric gases. Quantitative monitoring of produced O₂ was done via a continuous on-line Gas Chromatography System combined with a Thermo-conductive Detector (TCD- Shimadzu GC-2014, Carboxen 1000 column, Ar carrier gas).

3. Results

3.1. Structure and Morphology

3.1.1. XRD and TEM Structures

According to XRD, Figure 1A, the material BFO1(5) obtained for T_{anneal} = 550 °C/t_{anneal} = 5 min material possesses the characteristic XRD peaks of the perovskite structure of the BiFeO₃ with an R3c space group [29], and the most distinct Miller planes {012}, {104}, {110}, discerned at the XRD figure. Longer t_{anneal} resulted in sharper XRD diffraction peaks, indicating improved crystallinity of the BiFeO₃ phase [30]. The as-prepared BFO material, i.e., not-annealed, showed poor crystallinity (Figure S2). The short residence time of the particles in our FSP reactor i.e., milliseconds [20,21], does not allow full-growth of the BFO crystal structure. Thus, for the Bi-based materials, a post-FSP annealing step is necessary to obtain the fully crystalline particles [19]. The BFO3(60) material obtained at T_{anneal} = 700 °C/t_{anneal} = 60 min exhibits high-quality diffraction peaks of the orthorhombic-Bi₂Fe₄O₉ Pbam structure [31] with prominent peaks from the crystal planes {001}, {121}, {211}, {130}. The annealing period of 60 min was the minimal required to

achieve 100% pure $\text{Bi}_2\text{Fe}_4\text{O}_9$ phase i.e., shorter annealing times at $T_{\text{anneal}} = 700^\circ\text{C}$, resulted in mixed-phase $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{BiFeO}_3$ with increasing BiFeO_3 at shorter t_{anneal} . At prolonged $t_{\text{anneal}} = 120$ min, a rapid decline of crystal quality was observed due to the formation of solid melts [19]. Exemplifying this case, BFO3(120) has less sharp XRD peaks (Figure S3).

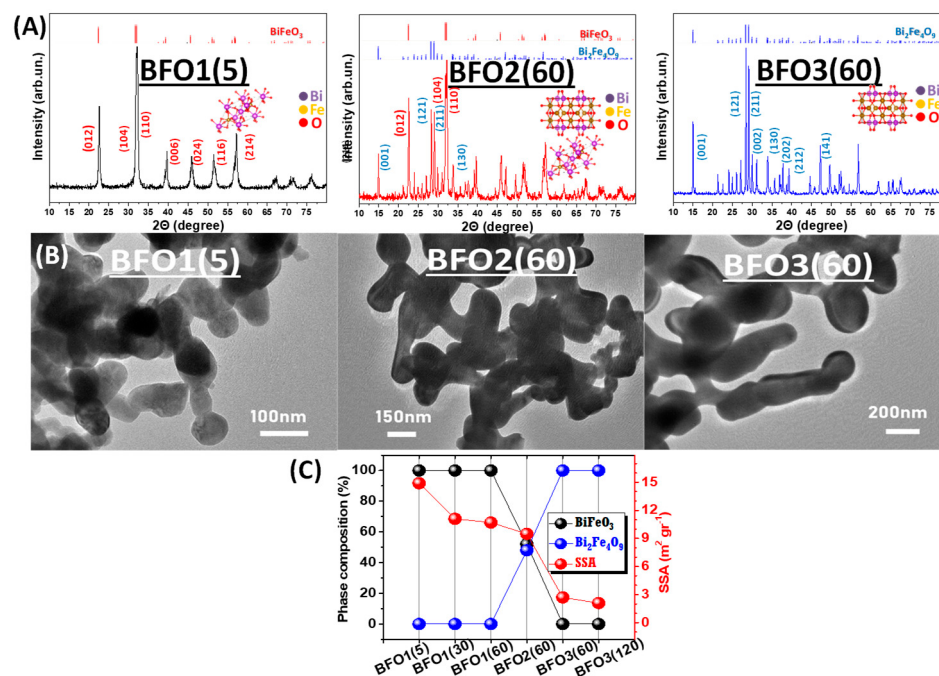


Figure 1. (A) XRD patterns for the BFO1(5), BFO2(60), BFO3(60) materials. The reference Miller-planes' reflections for BiFeO_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$ phases are shown in the graph's top. (B) TEM images, (C) Percentage of crystalline phases, and SSA for the various annealing protocols (see details in Table 1).

Table 1. Structural Characteristics of the present FSP-made BFO materials.

Photocatalyst	Annealing T/Time (°C)/(Min)	%Crystalline Phase Fraction		Crystallite Size (nm)		SSA ($\text{m}^2 \text{g}^{-1}$)	Total Pore Volume ($\text{cm}^3 \text{g}^{-1}$)	Band Gap E_g (eV)
		BiFeO_3	$\text{Bi}_2\text{Fe}_4\text{O}_9$	d_{BET}	d_{TEM}			
BFO1(5)	550/5	100	0	48	55	14.1	4.01×10^{-2}	2.1
BFO1(30)	550/30	100	0	64	-	12.1	2.83×10^{-2}	2.1
BFO1(60)	550/60	100	0	67	-	10.7	2.81×10^{-2}	2.1
BFO2(60)	625/60	52	48	75	130	9.5	2.11×10^{-2}	2.08
BFO3(60)	700/60	0	100	268	240	2.7	0.56×10^{-2}	2.05/1.55
BFO3(120)	700/120	0	100	336	-	2.1	0.46×10^{-2}	2.05/1.55

Overall, the XRD data for BFO reveal that the FSP-made BFO undergoes phase-evolutions from amorphous to BiFeO_3 , then to $\text{Bi}_2\text{Fe}_4\text{O}_9$, and finally to solid-melt, increasing $T_{\text{anneal}} = 550 \rightarrow 700^\circ\text{C}$ and t_{anneal} . These trends can be better visualized in Figure 1C. In order to gain insight into the relation of the BFO structures vs. the photocatalytic performance, we focus on pure phase BiFeO_3 & $\text{Bi}_2\text{Fe}_4\text{O}_9$ with varying degrees of crystallinity, quality, and defects. In this context, a ~1:1 mixed-phase material BFO2(60) that is $\text{BiFeO}_3/\text{Bi}_2\text{Fe}_4\text{O}_9$ heterostructure, has been obtained by $T_{\text{anneal}} = 625^\circ\text{C}/t_{\text{anneal}} = 60$ min post-FSP annealing. Table 1 and Figure S3, provide the full set of all pertinent structures produced by the controlled [$T_{\text{anneal}}, t_{\text{anneal}}$] protocols. In BFO1 or BFO2, at a given T_{anneal} , upon prolonged t_{anneal} , the particle crystallinity was increased. In contrast, the pure- $\text{Bi}_2\text{Fe}_4\text{O}_9$ nanophases, showed a striking degradation in crystallinity at prolonged $t_{\text{anneal}} = 120$ min, due to solid-melt formation. It is underlined that, based on the Rietveld analysis of the XRD data, the particles were found to have only the pure phases, i.e., without characteristic peaks from impurities or secondary phases, such as Bismuth-oxides and the more troubling

$\text{Bi}_{25}\text{FeO}_{40}$ or Fe_2O_3 that are usually difficult to eliminate in solid-state or wet synthesis methods [32]. The Rietveld-XRD analysis of mixed-phase BFO2(60) (Figure S4), shows that it consists of 52% BiFeO_3 /48% $\text{Bi}_2\text{Fe}_4\text{O}_9$ phases. Thus, BFO2(60) represents a ~1:1 heterojunction BiFeO_3 : $\text{Bi}_2\text{Fe}_4\text{O}_9$.

The TEM images of the catalysts, (Figure 1B), confirm the increase in particle size, upon increase of T_{anneal} and t_{anneal} . The annealed materials appear to retain rod-like morphology with neck-sintering between neighboring particles, as observed originally for the FSP-BFO particles [19]. FSP-made Bi-based perovskites such as BiVO_4 nanoparticles [33] present the same elongated morphology. The TEM size distribution, (Figure S5), reveals that all materials had a size distribution with a 30% span of the mean d_{TEM} value. The SSA analysis and total pore volume (Figure S1), allow the d_{BET} size calculation using the empirical Equation (1):

$$d_{\text{BET}} = 6000/\text{SSA} \times \text{density} \quad (1)$$

All materials had relatively low SSA $\sim 14.1 \text{ m}^2 \text{ g}^{-1}$ for BFO1(5), which dropped under longer annealing time at $10.7 \text{ m}^2 \text{ g}^{-1}$ for BFO1(60), and more severely at higher T_{anneal} i.e., $2.7 \text{ m}^2 \text{ g}^{-1}$ for BFO3(60).

3.1.2. Diffuse Reflectance Uv-Vis Spectroscopy: Band-Gap Estimates

All our BFO materials showed characteristic broad absorption from 200 nm to 600 nm, with a maximum in visible wavelengths 400–480 nm, corresponding to their dark-brown colors (inset photo in Figure 2A). The bandgap energy E_g calculated from the Tauc plot [34], was derived using the Kubelka-Munk transformation (2):

$$\alpha h\nu = K(h\nu - E_g)^p \quad (2)$$

The value of the p -index signifies the direct or indirect band transitions in a semiconductor [35]. i.e., $p = 1/2$ for a direct-band transition, $p = 2$ for indirect-band transition. So far, there is not a clear agreement in the literature whether the optical transitions in BiFeO_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$ phases are direct or indirect [10].

Thus, herein the direct transitions are assumed ($p = 1/2$) for the main DRS-UV/Vis absorbance peaks of BiFeO_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$ phases. In addition, a secondary transition was consistently observed for $\text{Bi}_2\text{Fe}_4\text{O}_9$, which is usually identified as an indirect transition, marked by the dashed arrow in Figure 2A. The direct bandgap of the perovskite phase BiFeO_3 has been reported to be in the range of 2.1–2.8 eV [10]. For the mullite-type $\text{Bi}_2\text{Fe}_4\text{O}_9$, E_g is expected in the range of 2.1 to 2.3 eV [11]. Also, for the $\text{Bi}_2\text{Fe}_4\text{O}_9$, a secondary smaller bandgap 1.6 eV [36] is usually evident by the absorbance peak at $\sim 700 \text{ nm}$, suggested to originate from the $d-d$ transition of Fe atoms [37]. Our data agree with the literature, with $E_g = 2.1 \text{ eV}$ for BFO1(5), $E_g = 2.08 \text{ eV}$ for BFO2(60), while the BFO3(60) has $E_g = 2.05 \text{ eV}$. All other FSP-made catalysts prepared for various t_{anneal} have E_g in the range 2.0–2.1 eV, (Figure S6). The secondary bandgap of 1.6 eV is evidenced in the spectrum of BFO3(60) with 100% $\text{Bi}_2\text{Fe}_4\text{O}_9$. In the BFO2(60) this absorbance-hump at 700 nm, is lower in accordance with the lower 48% content in $\text{Bi}_2\text{Fe}_4\text{O}_9$. The indirect-transitions have typically lower absorbance cross-sections [2,35] since they require a transition of the photoactivated electron between energy states with different lattice-vector k [35] between different Brillouin zones. In the context of photocatalysis, an indirect transition can inhibit the recombination of the photoexcited e^-/h^+ pairs [2,35], improving photocatalytic performance.

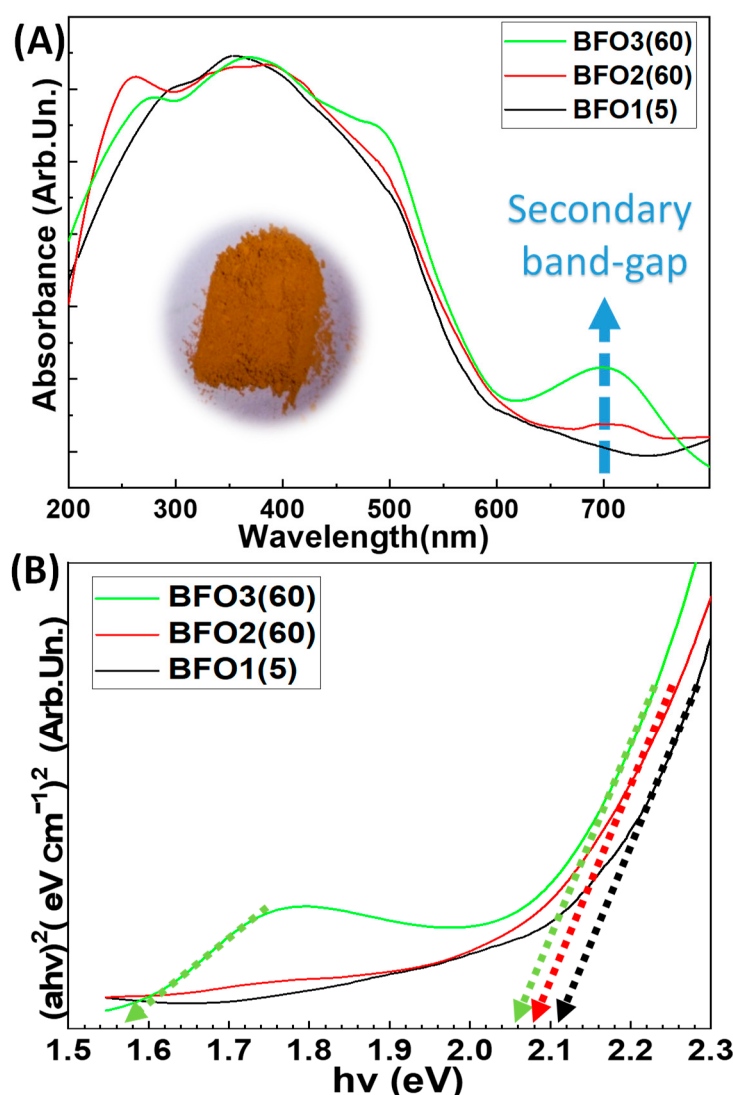


Figure 2. (A) DRS-UV/Vis spectra of the BFO materials. *Inset:* the BFO3(60) powder color. (B) The Tauc plot for each material, with the tangential dashed lines marking the estimated band-gap.

3.1.3. FT-IR, Raman Spectroscopy

In all cases, the BiFeO₃ phase can be discerned from two characteristic peaks at 445 cm⁻¹ and 557 cm⁻¹, due to the Fe-O bond stretching and bending vibrations from octahedral FeO₆ groups of BiFeO₃ [38,39]. The Bi₂Fe₄O₉ phase has a more complex structure and it contains both octahedral FeO₆ and tetrahedral FeO₄ units [40], thus its FT-IR spectrum is characterized by several bands of lower intensity than BiFeO₃ [41]. We can identify the Bi₂Fe₄O₉ phase by focusing on the bands at 441 cm⁻¹, 609 cm⁻¹, and the more prevalent 814 cm⁻¹. Noticeably, the FTIR spectrum for BFO1(5) shows weak peaks around 1250–1500 cm⁻¹, (inset zoom of Figure 3A), which are indicative of traces of hydrocarbons in BFO1(5). These peaks were also observed in the as-prepared materials (not shown). These traces are eliminated upon longer t_{anneal} and higher T_{anneal} (Figure S7). Such traces of hydrocarbons are known to be potential leftovers from the FSP combustion process [42]. The short t_{anneal} of 5 min in BFO1(5) is not enough to fully combust them. As we show hereafter, these hydrocarbon traces cause reduction of some Fe-centers forming Fe²⁺ in BFO1(5). The mixed-phase material BFO2(60) contains the characteristic peaks of both BiFeO₃ and Bi₂Fe₄O₉ phases, in accordance with XRD results. The characteristic Raman peaks are marked with the corresponding dotted lines. The BFO1(5) i.e., 100% BiFeO₃ has two characteristic Raman peaks at 136 cm⁻¹ and 170 cm⁻¹, accompanied by seven weaker

peaks in the range of 260 cm^{-1} to 520 cm^{-1} [43,44], while the BFO3(60) i.e., $\text{Bi}_2\text{Fe}_4\text{O}_9$, exhibits multiple bands at 87, 207, 283, 331, 365, 430, and 552 cm^{-1} [45] (Figure S8).

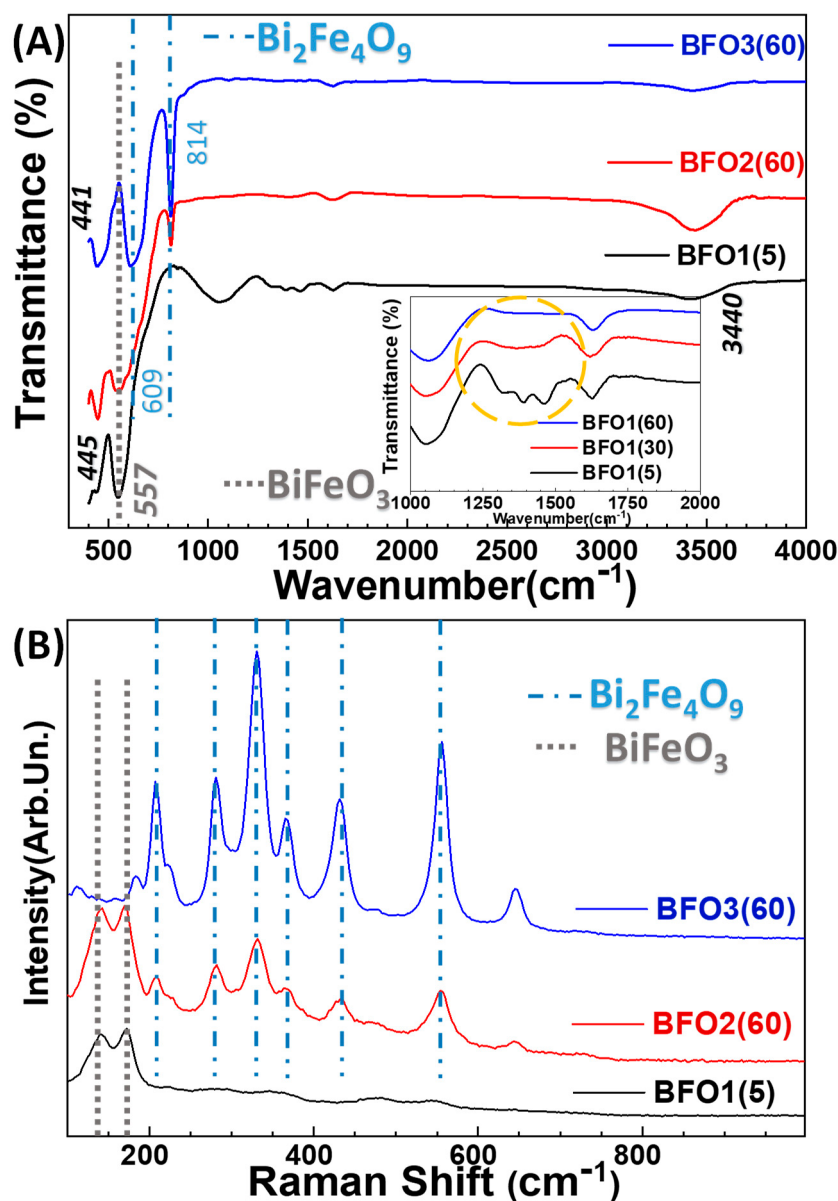


Figure 3. (A) FT-IR spectra for BFO materials in the range 400 to 4000 cm^{-1} . *Inset:* zoom into the hydrocarbon's region. (B) Raman spectra for BFO materials. In both graphs, characteristic peaks that differentiate the two phases BiFeO_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$ are marked with dashed lines.

Thus, from the present FT-IR and Raman data, it is confirmed that BFO1(5) is a 100% BiFeO_3 , BFO3(60) is a 100% $\text{Bi}_2\text{Fe}_4\text{O}_9$, while the BFO2(60) is a mixed phase. Our XRD, FTIR, Raman data provide clear evidence that the BFO materials are devoid of any secondary phase.

3.1.4. X-ray Photoelectron Spectroscopy

The XPS spectra for the Fe2p energy range, Figure 4, present two sets of doublets corresponding to Fe^{3+} : the doublet at 710 and 712 eV is assigned to $\text{Fe}^{3+}2p_{3/2}$, while the 723.5 and 725.5 eV are assigned to $\text{Fe}^{3+}2p_{1/2}$ [46]. The characteristic $\Delta E = 13.5\text{ eV}$ splitting is typical for the spin-orbit coupling of the $\text{Fe}^{3+}2p$ [47]. The weak-peak at $\sim 718\text{ eV}$ is the satellite of the $\text{Fe}^{3+}2p_{3/2}$ at approximately 6 to 8 eV from the binding energies of the

$\text{Fe}^{3+}2p_{1/2}$ [46]. In addition, the Fe-XPS spectrum of BFO1(5), Figure 4A, contains peaks at 706.2 eV that correspond to the $\text{Fe}^{2+}2p_{3/2}$ and the 719.7 eV at $\text{Fe}^{2+}2p_{1/2}$ [48], confirming that BFO1(5) contains Fe^{2+} atoms (approximately 10–15%). This can be attributed to the reduction of Fe^{3+} centers, by traces of small hydrocarbons, leftover during the FSP process [42] i.e., as evidenced by the FT-IR data (Figure 3A). Noticeably, Fe^{2+} atoms were not detected in the XPS spectra in the as-prepared BFO material, [19], nor in the other BFO materials prepared at longer t_{anneal} or higher T_{anneal} . The population of the Fe^{2+} centers was maximum in the shortly-annealed BFO1(5) and declined rapidly upon longer $t_{\text{anneal}} = 30$ or 60 min (Figure S9). Thus, the XPS data together with the FT-IR data, show that 5 min at 550 °C allowed the optimal formation of Fe^{2+} centers in BFO1(5) as a consequence of the interaction with the hydrocarbon's traces. Theoretical DFT calculations, discussed hereafter, reveal that these Fe^{2+} atoms have a significant impact on the energy level positioning of the CB and VB edge of BiFeO_3 , and this has a beneficial effect on photocatalytic O_2 production.

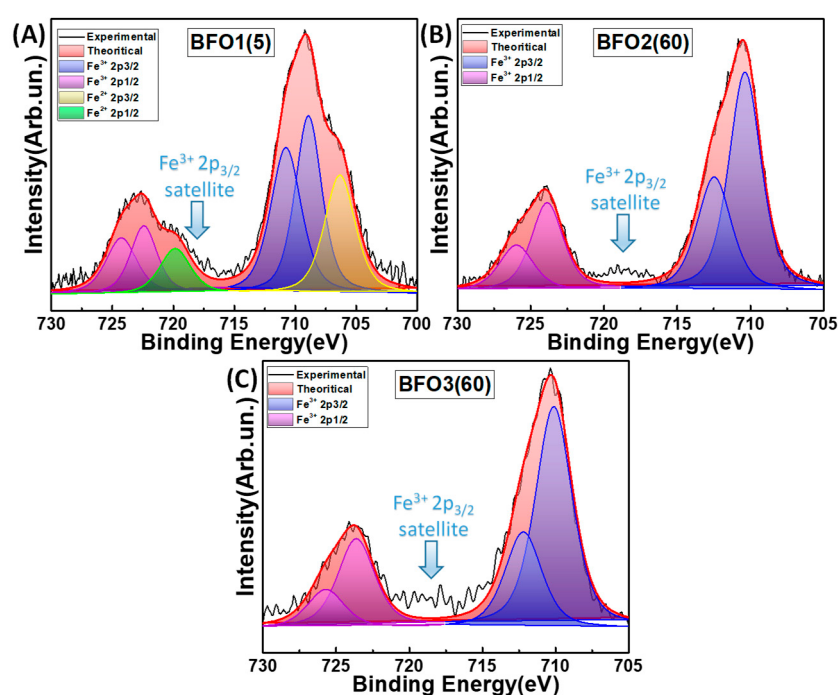


Figure 4. Fe-XPS spectra of (A) the BFO1(5), (B) BFO2(60), and (C) BFO3(60) materials, with the corresponding fitted $\text{Fe}^{3+}2p_{3/2}$, $\text{Fe}^{3+}2p_{1/2}$, and the $\text{Fe}^{2+}2p_{3/2}$, $\text{Fe}^{2+}2p_{1/2}$ peaks.

A complete set XPS data for all BFO materials Fe (Figure S9), Bi (Figure S10) and O (Figure S11) show the characteristic peaks at 164.4 eV and 159 eV, with a spin-orbit splitting value ~ 5.4 eV of the two states $\text{Bi } 4f_{5/2}$ and $\text{Bi } 4f_{7/2}$ in accordance with the literature [49]. The O-XPS spectra exhibit the characteristic peak at 532 eV due to oxygen adsorbed on the surface of and hydroxyl groups, while the peak at 530.1 eV is due to O-Fe units of the crystals structure [50,51].

3.2. Photocatalysis

3.2.1. Photocatalytic O_2 Production from H_2O

The Conduction Band (CB) energy position of BiFeO_3 was found to be at +0.34 eV vs. NHE, and the Valence Band (VB) position at 2.44 eV. Similarly, $\text{Bi}_2\text{Fe}_4\text{O}_9$ has a CB-edge at +0.36 eV and VB-edge at 2.41 eV (Table S1). These are in agreement with literature values of CB-edge +0.51 eV for BiFeO_3 and CB-edge +0.5 eV for $\text{Bi}_2\text{Fe}_4\text{O}_9$ [52,53]. As the energy level of $\text{O}_2/\text{H}_2\text{O}$ is at +1.23 eV vs. NHE, both materials are suitable for oxidation of water. Using

$\text{Na}_2\text{S}_2\text{O}_8$ as electron scavenger [7], the overall photocatalytic reaction proceeds according to the reactions scheme Figure 5C, and reaction (3):

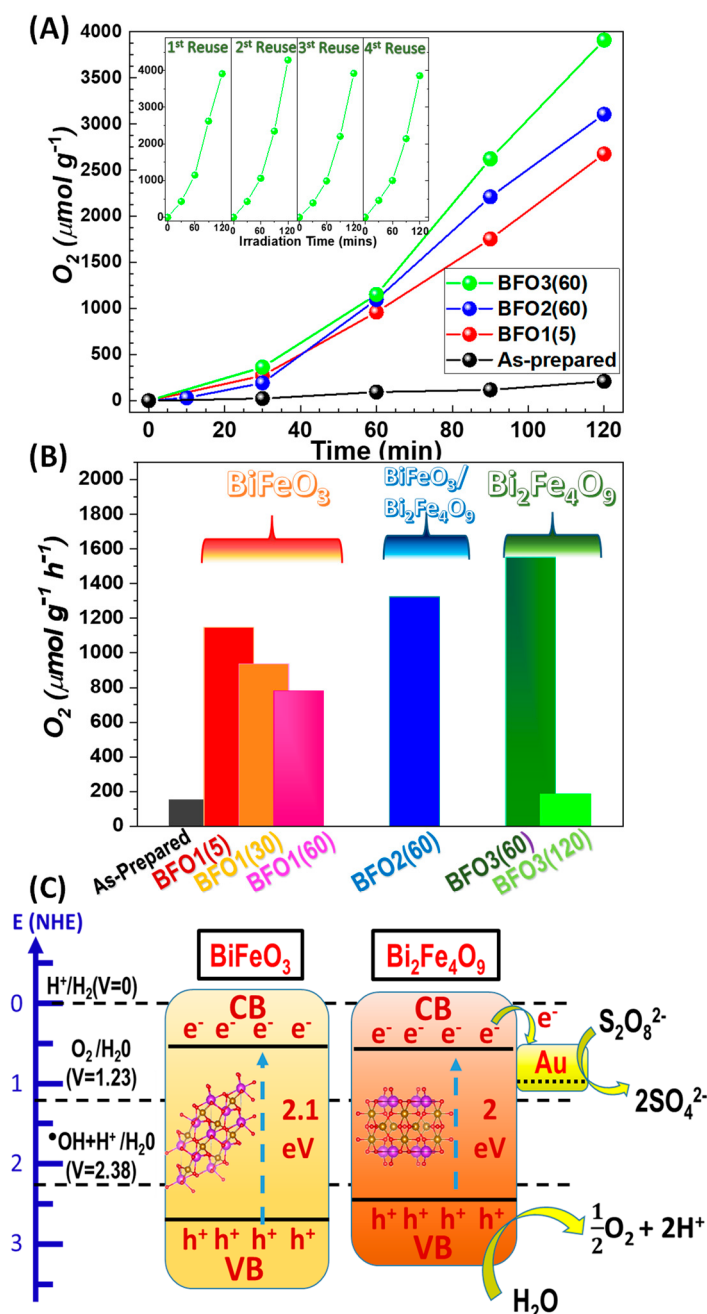


Figure 5. (A) Kinetics of photocatalytic O_2 production by the BFO photocatalysts. Inset, Reuse study of the BFO3(60) photocatalyst. (B) The photocatalytic O_2 -production per h, for all the studied BFO. (C) a reaction scheme of the photocatalytic reaction process.

The photocatalytic O_2 production data (Figure 5) show that the as-prepared BFO material achieved very low O_2 evolution i.e., $<151 \mu\text{mol g}^{-1} \text{h}^{-1}$. Annealing at short-time $T_{\text{anneal}} = 550^\circ\text{C}$, $t_{\text{anneal}} = 5$ min, had a dramatic effect on the O_2 generation efficiency i.e., $1150 \mu\text{mol g}^{-1} \text{h}^{-1}$ for BFO1(5). Prolongation of t_{anneal} causes a drop in O_2 -production rates i.e., to $900 \mu\text{mol g}^{-1} \text{h}^{-1}$ for $t_{\text{anneal}} = 30$ min, and $780 \mu\text{mol g}^{-1} \text{h}^{-1}$ for $t_{\text{anneal}} = 60$ min.

The trend in BiFeO₃ shown in Figure 5B, implies a key-optimization step occurring at short $t_{\text{anneal}} = 5$ min.

We have performed a screening of the optimal noble metal loading for the O₂ evolution of the BFO materials. By testing loadings of 0.1, 0.5, 1.0, 2.0, 5.0 % *w/w* (data not shown), we concluded the 1.0% to be the best ratio. Lower noble metal loadings were not adequate, while higher loadings (2% *w/w* or 5% *w/w*) inhibited the O₂ production due to coverage of the BFO surface. For example, the 2% *w/w* Au⁰ or 5% *w/w* Au⁰ produced by 30% and 60% less O₂ as it is compared with the 1% Au⁰.

The mixed-phase BFO2(60), ~1:1 BiFeO₃:Bi₂Fe₄O₉, shows an improved O₂ evolution rate 1300 $\mu\text{mol g}^{-1} \text{h}^{-1}$. This is higher than the performance of the best BiFeO₃. Remarkably, the pure Bi₂Fe₄O₉ phase, achieved a significant O₂ evolution rate of 1550 $\mu\text{mol g}^{-1} \text{h}^{-1}$, which is 35% higher than BiFeO₃. In addition, the Bi₂Fe₄O₉ catalyst is stable for 4 catalytic cycles with a minor loss of 5% of its efficiency (inset of Figure 5A), while for all the materials the XRD, Tauc plot and XPS after the photocatalysis are present in (Figure S12).

Overall, we can conclude that:

1. Photocatalytic O₂-evolution is improved significantly on going from BiFeO₃ towards Bi₂Fe₄O₉
2. For materials of the same phase, the annealing protocol parameters, T_{anneal} , t_{anneal} , allow modulation of the O₂ evolution trend. In all cases, longer t_{anneal} is detrimental
3. Bi₂Fe₄O₉ is sensitive to prolonged t_{anneal} , i.e., severe crystal quality deterioration occurs in BFO3(120) and this causes severe deterioration of its photocatalytic activity. In contrast, BiFeO₃ shows less-pronounced effects upon prolonged annealing.
4. The XPS data reveal a correlation trend between the Fe²⁺ centers in BiFeO₃ and O₂ production.

A comparison with literature data for photocatalytic OER vs. pertinent Fe, Bi catalysts, is presented in Table S2 [7,8,54–56]. Our FSP-made BiFeO₃ i.e., BFO1(5), supersedes the performance of Papadas et al. [7] which is comparable to our BFO1(60) catalyst. Among all BFO photocatalysts in Table S2, the FSP made Bi₂Fe₄O₉ (BFO3(60)) is a superior photocatalyst for O₂ production from H₂O, over performing all so far known BFO materials.

3.2.2. Photogenerated Holes of the Photocatalytic Mechanism

In O₂ evolution photocatalysis, oxidation of H₂O by the photogenerated holes is a key-step [2] via the formation of •OH. Herein we have used EPR spectroscopy to monitor in-situ the photogeneration of •OH by the best performing BFO (BFO1(5), BFO2(60), BFO3(60)).

The EPR data show that all the studied BFO catalysts are very efficient in the photogeneration of •OH (Figure 6A). Interestingly, the EPR spectral patterns, have a characteristic 7 line pattern with intensity ratio [1:2:1:2:1:2:1] which is the fingerprint of two •OH trapped/per/DMPO [57]. The so formed structure is known as DMPOX [58]. The reaction path is shown on top of Figure 6. The formation of DMPOX reveals that a high local concentration of •OH occurs [57] during the photoexcitation of the BFO particles. Indeed, quantification of the •OH proves that the BFO creates very high concentrations of •OH up to ~850 $\mu\text{mol/g}$ for BFO3(60). For comparison, a reference P25-TiO₂ irradiated under the same conditions generated 300 $\mu\text{mol/g}$. Comparison between Figures 5B and 6B show a clear trend BFO3(60) > BFO2(60) > BFO1(5), in both •OH generation as well as in O₂ photogeneration efficiency. Accordingly, we conclude that the superior photocatalytic efficiency of BFO3(60) and pure Bi₂Fe₄O₉, originates from the highly efficient photogeneration of the holes in the valence band. To further peer into the band-positioning of our BFO3(60) we have compared the effect of Au⁰, Pt⁰, Ag⁰ as electron acceptors on the O₂ generating efficiency. Interestingly, BFO3(60)/Au⁰ and BFO3(60)/Pt⁰ have almost the same performance, while BFO3(60)/Ag⁰ shows a lower by 25% of the original efficiency (Figure S13). According to the energy-level scheme in Figure 5C, the photocatalytic efficiency can be correlated with the favorable positioning of the conduction-band edge of Bi₂Fe₄O₉ +5 eV vs. vacuum (+0.5 eV vs. NHE) [53] vs. the work function of Pt⁰ ($\phi = 5.6$ eV) and the work function of Au⁰ ($\phi = 5.1$ eV vs. vacuum) [59]. Ag⁰ has a less favorable

positioning work function ($\varphi = 4.2$ eV) [60] vs. the CB of $\text{Bi}_2\text{Fe}_4\text{O}_9$ and this results in lower O_2 photogeneration.

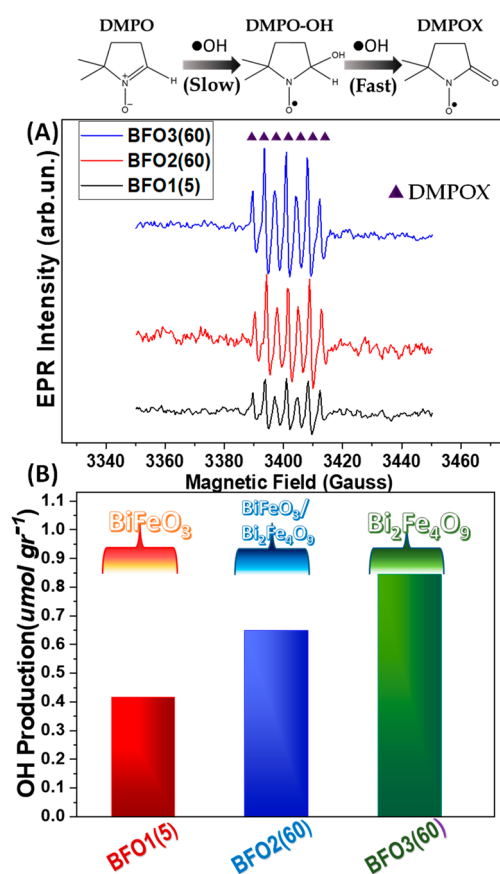


Figure 6. (A) EPR spectra of photogenerated OH-radicals for the three best-performing BFO materials. The detected EPR signals correspond to DMPOX states which is a result of two $\bullet\text{OH}$ trapped per DMPO molecule. (B) Quantitative $\bullet\text{OH}$ -production per gram of photocatalyst.

3.2.3. Insight into the Role of Fe^{2+} Centers in BiFeO_3

The photocatalytic and XPS data indicate that the presence of Fe^{2+} atoms in BiFeO_3 , i.e., BFO1(5) plays a key role in the photocatalytic activity. Intriguingly, no difference was observed in the UV-Vis absorbance profile neither in the E_g value for the Fe^{2+} containing BFO1(5) vs. Fe^{2+} -free BFO(30, 60) materials. To better understand this phenomenon, we have analyzed the energy levels of BiFeO_3 including Fe^{2+} atoms.

For Fe^{2+} free BiFeO_3 the calculated bandgap values are 2.0 eV (indirect, $\text{F}/\Gamma \rightarrow \text{F}$) and 2.1 eV (indirect, $\text{F}/\Gamma \rightarrow \text{Z}$, and $\text{F}/\Gamma \rightarrow \text{L}$). In accordance with previous reports regarding BiFeO_3 [61], the spin-up and spin-down populations are symmetric, due to the antiferromagnetic arrangement of Fe^{3+} magnetic moments. As shown in the DOS plot in Figure 7A, the maximum energy of the Valence-band VB_{max} of BiFeO_3 is dominated by O-2p states, while the CB_{min} by Fe-3d states. The VB_{max} of BiFeO_3 is located between the $\text{F}(0.5,0.5,0)$ and $\Gamma(0,0,0)$ points, and the CB_{min} at the $\text{F}(0.5,0.5,0)$ point, in agreement with the previous reports [62]. In Figure 7B one atom of Fe^{2+} has been introduced per unit cell i.e., for the sake of the discussion we codename it $\{\text{Fe}^{2+}\}\text{BiFeO}_3$, comparing with the DOS for BiFeO_3 (red vs. black lines) reveals that the introduction of Fe^{2+} atoms into the BiFeO_3 lattice causes a downshift of both CB and VB by 0.9 eV, without a change in the band-gap value.

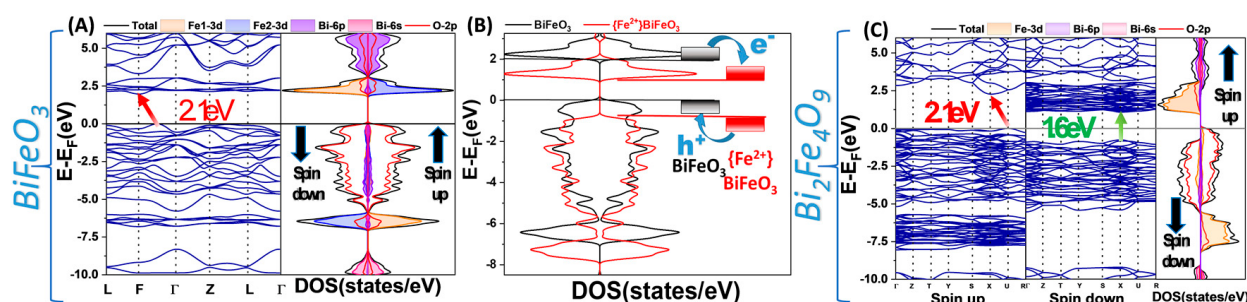


Figure 7. (A) Theoretical energy band-structure and DOS of BiFeO₃. (B) DOS for {Fe²⁺}BiFeO₃ (red lines) vs. BiFeO₃ (black lines). (C) Theoretical energy band-structure and DOS of ferromagnetic Bi₂Fe₄O₉.

The theoretical result is in accordance with the experimental data, EPR, and photocatalysis, which show that {Fe²⁺}BiFeO₃ and BiFeO₃ i.e., materials BFO1(5) and BFO1(30, 60), have similar E_g values. [ii] the downshift of CB by +0.9 eV, towards more positive potentials, enhances the oxidative capacity of the holes in {Fe²⁺}BiFeO₃ vs. BiFeO₃, which shows the BFO1(5) being more photoactive than BFO1(30, 60). Thus, the present theoretical analysis indicates the superior photocatalytic efficiency of BFO1(5) can be attributed to the more positive potential of the CB induced by the presence of Fe²⁺ atoms in the BiFeO₃ lattice.

For completeness, we present the energy-bands and DOS for Bi₂Fe₄O₉ (Figure 7C). In Bi₂Fe₄O₉ the CB_{min} is mainly populated by Fe-3d states and the VB_{max} by O-2p states, as is the case for BiFeO₃. However, in Bi₂Fe₄O₉ the DOS profile is fundamentally more complex than BiFeO₃ i.e., due to the ferromagnetic character Bi₂Fe₄O₉ [45]. More specifically, various transitions are allowed for combination of spin-up/spin-down configurations: a transition with energy 2.1 eV (indirect, U^{up} → X^{up}), one with 1.1 eV (indirect, U^{up} → X^{down}) and 1.6 eV (direct, X^{down} → X^{down}). These are in agreement with the DRS-UV/Vis data where the bands at $E_g \sim 2.1$ eV and ~ 1.6 eV are evidenced in the experimental spectra.

4. Conclusions

The present study shows that FSP-made BFO nanocatalysts can be optimized dramatically for highly efficient photocatalytic O₂ evolution from H₂O, by easy-to-apply short-time post-FSP annealing protocols. In this way, mullite-Bi₂Fe₄O₉ is exemplified, for the first time, to be a highly promising O₂-evolving photocatalyst, outperforming all so far reported BFO nanocatalysts. Spectroscopic and theoretical data show that the post-FSP annealing allows detailed control of the structural and electronic features of Bismuth-Iron-Oxide nanomaterials, however in a distinct manner for BiFeO₃ vs. Bi₂Fe₄O₉. The introduction of Fe²⁺ centers in BiFeO₃ can enhance dramatically the O₂ production efficiency via a downshift of the CB and VB edges. For Bi₂Fe₄O₉, short annealing improves O₂ evolution, while prolonged annealing is detrimental, via deterioration of its crystallinity.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/en14175235/s1>, Figure S1: N₂ adsorption-desorption isotherms for the materials BFO1(5)-BFO3(120). Figure S2: XRD, Tauc plot, and XPS spectra of the As-Prepared BFO material. Figure S3: Powder XRD patterns for the annealing effect on BFO1 and BFO3 materials. Figure S4: Rietveld analysis of the BFO2 material. Figure S5: TEM size distribution of the materials. Figure S6: Tauc plot for the annealing effect on BFO1 and BFO3 materials. Figure S7: FT-IR for the annealing effect on BFO1 and BFO3 materials. Figure S8: Raman for the annealing effect on BFO1 and BFO3 materials. Figure S9: Fe XPS plots for all the materials. Figure S10: Bi XPS plots for all the materials. Figure S11: O XPS plots for all the materials. Figure S12: XRD and Raman for the photocatalytically reused BFO3(60). Figure S13: O₂-photoproduction for Au⁰, Pt⁰, Ag⁰ as electron acceptors for the BFO3(60). Table S1 electronegativity of the materials. Table S2 Literature comparison for the photocatalytic abilities of the materials.

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