

Photocatalytic structures grown on porous and conductive Al_2O_3 –ZnO ceramics prepared with glycerol citrate polyester for solar-driven water splitting

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ABSTRACT

Porous photocatalytic structures hold significant potential for solar-driven water splitting and wastewater treatment. In this work, we present highly conductive and porous Al_2O_3 –ZnO ceramics coated with ZnFe_2O_4 and $\alpha\text{-Fe}_2\text{O}_3$, which were tested for solar-driven water splitting. The photocurrent density of these structures reaches 7.6 mA cm^{-2} at 1.23 V vs. RHE under blue LED illumination (455 nm, 198 mW cm^{-2}) and 0.31 mA cm^{-2} under AM1.5G irradiation. The Al_2O_3 –ZnO ceramics, prepared using glycerol–citrate polyester as both a binder and a foaming agent, exhibit small pores of approximately 100–400 nm and macropores up to several tens of micrometers in diameter. The properties of the resulting photocatalytic structures are discussed based on photoelectrochemical measurements, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy.

1. Introduction

Photocatalytic structures capable of solar-driven water splitting and wastewater treatment are of significant interest, as they enable the simultaneous production of renewable hydrogen fuel and the purification of contaminated water, thereby addressing two of the most urgent global challenges faced by humankind today. A promising strategy for developing such structures is the use of porous and conductive oxide ceramics as free-standing substrates to host photocatalytic coatings [1–5]. The porosity of the ceramics allows the coating to grow not only on the substrate surface but also within its subsurface regions, resulting in a multilayered photoactive structure with an increased reactive area in contact with the aqueous electrolyte. In photoelectrode applications, the conductive and porous ceramic substrate functions both as an efficient electron collector and as a charge-transport pathway to the external circuit [6,7]. Moreover, due to their porosity, these photocatalytic structures can serve as filters for wastewater treatment. Importantly, such filters can be readily regenerated by heat treatment

without compromising their functional properties, thanks to the robustness of ceramics sintered at high temperatures ($>1000^\circ\text{C}$). This resistance of the ceramic substrate to high-temperature treatment distinguishes it favorably from conventional substrates prepared by depositing indium–tin oxide (ITO) or fluorine-doped tin oxide (FTO) onto glass, which begins to deform at temperatures above 600°C . In addition, photocatalytic structures formed on conventional substrates have limited applicability as filters for wastewater treatment, in contrast to those grown on porous ceramic substrates.

The fabrication of photocatalytic structures on ceramic substrates can be achieved using wide-bandgap semiconductors, such as ZnO (3.2 eV), doped with Al to introduce donor states. The prices of ZnO (approximately USD 4.00 per kg) and Al_2O_3 (less than USD 1.00 per kg) are highly attractive compared to that of ITO (at least USD 810 per kg). The high sintering temperature of ZnO-based ceramics ($>1200^\circ\text{C}$ in air) allows these substrates to withstand heat treatments up to 1000°C without undergoing morphological changes. In addition, the transparency of ZnO to solar radiation with wavelengths longer than 388 nm

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allows visible light to penetrate into the subsurface regions of the ceramic substrate, where it can be absorbed by photocatalytic coatings on the grains within the substrate volume. Consequently, these porous photocatalytic structures exhibit an enlarged active surface area. The combination of a multilayered photocatalytic coating with the three-dimensional architecture of the porous ceramic substrate enables efficient light harvesting. Furthermore, the photocatalytic coating on individual ceramic grains can be nanometrically thin, facilitating efficient charge transfer through the photoactive material to the electrolyte with minimal recombination losses (Fig. S1 in the Supplementary Material). As a result, this architecture exhibits enhanced light absorption, reduced recombination of photogenerated charges, and an expanded photoactive surface area.

A variety of techniques and methods have been reported for producing porous ceramic materials. Among these, four widely used approaches are commonly distinguished [8,9]: (i) the use of sacrificial templates as pore-forming agents [10–13]; (ii) replica templating, which enables the formation of ceramic materials with macro- and microstructures that replicate the geometry of the original porous polymer template, decomposing later during high-temperature sintering [14–16]; (iii) partial sintering of ceramics, achieved at lower temperatures or with shorter sintering times than those required for dense material formation [17–19]; and (iv) direct foaming of precursor suspensions, accomplished through mechanical frothing, chemical blowing via gas-releasing reactions, or gas injection [20–22]. Among these approaches, direct foaming is an inexpensive and effective technique with promising potential for the industrial production of porous ceramic materials [8,20–22]. In foaming by chemical blowing, the porosity of the resulting material largely depends on the specific chemical blowing agents used to generate gases within the pre-ceramic precursors.

In this context, the biodegradable and cost-effective thermoset polymer Glycix, developed by Plantic BV in the Netherlands [23], presents a promising option as both a blowing agent and binder in the preparation of porous oxide ceramics for sensor and electrode applications. This polymer is synthesized by reacting citric acid with glycerol at temperatures between 120 and 160 °C for 40–300 min, producing water as a byproduct. Both precursors are inexpensive and readily available, making this approach favorable for large-scale, low-cost production. When the reaction temperature exceeds 150 °C, citric acid undergoes gradual decarboxylation to form itaconic acid, generating CO₂ gas and water vapor, which act as blowing agents. Further polymerization of glycerol and itaconic acid proceeds without foaming. Additionally, foaming can be suppressed if citric acid and glycerol react at temperatures below 100 °C, resulting in a polymer with closed-cell structures [23]. These findings suggest that the type and size of porosity in the resulting ceramics can be controlled by adjusting the reaction temperature.

In addition, the polymerized glycerol-citric acid resin exhibits excellent adhesive properties due to its abundant –OH and –COOH groups, which readily bind to various materials possessing –OH groups on their surfaces [23]. This binding capability is highly beneficial in the preparation of oxide ceramics, where close contact between precursor particles is essential for effective sintering and dopant diffusion. In traditional ceramic production, tight contacts between particles are typically achieved by pressing the precursors at pressures of 45 MPa or higher [24–26]. In oxide powders incorporated into polymerized glycerol-citric acid, the –OH groups present on the surfaces of precursor particles in ceramic slurries can readily bond with Glycix, effectively binding the precursor particles together without the need for pressing. All these beneficial properties of the polymer Glycix can be exploited to produce porous ceramic substrates—for example, those based on wide-bandgap semiconductors such as ZnO—for the fabrication of photocatalytic ceramic structures with enhanced surface area, which is critical for achieving efficient photocatalytic performance. Moreover, the photocatalytic properties of ZnO-based ceramics can be further

improved by depositing Fe-containing compounds. Iron oxides, zinc oxide, and zinc ferrite (ZnFe₂O₄) are non-toxic materials with promising potential for wastewater treatment due to their antibacterial and antioxidant properties [27,28].

In this work, we present photocatalytic structures for solar-driven water splitting, grown on highly conductive and porous Al₂O₃–ZnO ceramics coated with Fe-containing compounds. To the best of our knowledge, this is the first report of photocatalytic structures formed on porous Al₂O₃–ZnO ceramics used as free-standing substrates, prepared with Glycix serving as both a binder and a foaming agent. The study reports and discusses data from X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, energy-dispersive X-ray spectroscopy, scanning electron microscopy, photoelectrochemical measurements under AM 1.5G irradiation, as well as morphology and electrical conductivity analyses.

2. Material and methods

Porous and conductive Al₂O₃–ZnO ceramics were prepared using Al₂O₃ (2 mol%) and ZnO (98 mol%) precursors purchased from Aldrich, each with a purity of no less than 99.5 %. The oxide powders were mixed in an agate mortar for 45 min with distilled water and then dried at 120 °C for 3 h. Subsequently, the Glycix polymer was added to the dried mixture.

The Glycix polymer was prepared by mixing citric acid and glycerol in a 50:50 M ratio. In some cases, as described below, a corresponding percentage of triethanolamine was used to partially replace glycerol. The oxide powder mixture and Glycix were combined in a 55:45 wt ratio and mixed for 10 min in a silicone bag. The resulting mixture was then pressed into circular discs (9 mm in diameter and approximately 2 mm thick) using a Teflon mold under a pressure of 370 kPa. These pellets were subsequently heat-treated at 170 °C in air for 2 h in a FELISA FE-291D oven to induce polymerization and foaming, as well as to promote binding between the powder particles. In some experiments, polymerization and foaming were instead achieved using an LG MH1449CR microwave operating at 1120 W for 60 s.

The resulting samples were placed in an Al₂O₃ boat inside a tubular furnace (model Barnstead F21135) and heated in air at a rate of 1 °C/min to 550 °C to remove the polymer. After dwelling at 550 °C for 1 h, the furnace was cooled to room temperature at a rate of 10 °C/min. Subsequently, the samples were placed in a tubular furnace (model CTF 17/300) and sintered under vacuum (21 kPa) at 1100 °C for 30 min, with both heating and cooling rates set to 5 °C/min. The vacuum was generated using a PFEIFFER Duo 1.6 forevacuum pump, which operated for 15 min every hour to maintain a vacuum level of 21 kPa.

Sintering under vacuum was employed to induce non-stoichiometry in the ZnO-based ceramics and thereby further increase the conductivity of Al-doped ZnO by generating intrinsic defects such as zinc interstitials, oxygen vacancies, and surface defects. These defects can be ionized at room temperature and act as electron donors [29–31]. In addition, oxygen vacancies can enhance diffusion and mass transport between ceramic grains at high temperatures, promoting effective neck formation and intergranular bonding [32], which can result in highly conductive electrical contacts between the ceramic grains.

The iron-compound coating was deposited onto the prepared Al₂O₃–ZnO substrates using metal-organic chemical vapor deposition (MO-CVD) in a horizontal cold-wall chamber. Iron(III) 2,4-pentanedionate (Sigma-Aldrich) was employed as the precursor, while air served as the carrier gas at a flow rate of 1.3 L/min. The chamber pressure was maintained at 2.13 kPa, and the precursor temperature was set to 131 °C. The coatings were grown on ceramic substrates held at a constant temperature of 380 °C for 30 min.

After deposition, the samples were annealed in air using a Thermo-lyne furnace to crystallize the iron-compound coating. Each sample was gradually inserted into a preheated furnace at 800 °C over the course of 1 min, held at that temperature for 30 min, and then gradually removed

over another minute. It was expected that high-temperature annealing at 800 °C would produce a well-crystallized photocatalytic coating of iron compounds on the surface of the Al_2O_3 -ZnO substrate. After cooling to room temperature, a silver electrode for external connection was applied with a quick-drying paste (SPI Supplies, 05002-AB) on the uncoated side of the substrate. After drying the Ag paste at 100 °C for 1 h in air, the samples underwent heat treatment under vacuum (21 kPa) at 425 °C for 1 h. This step was carried out to compensate for the reduction in substrate conductivity caused by oxygen absorption during the prior heat treatment in air at 800 °C for 30 min. Then, the Ag electrode was soldered to an insulated wire, and the contact area was sealed with hot paraffin (Bemis, "M") to complete the fabrication of the photoelectrode.

Electrochemical measurements were performed using an Autolab PGSTAT204 potentiostat in a three-electrode configuration. A platinum wire served as the counter electrode, the hematite-coated ceramic substrate functioned as the working electrode, and an Ag/AgCl (saturated KCl) electrode was used as the reference. A 0.1 M NaOH solution prepared in demineralized water (pH 12.65) served as the electrolyte. Potentials versus the reversible hydrogen electrode (RHE) were calculated using the Nernst equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} + 0.1976 \text{ V}.$$

Photocurrents were recorded under illumination from a solar simulator (PICO G2V, AM1.5G) with a spectral bandwidth of 350–1100 nm and an intensity of 79.1 mW cm^{-2} , as well as from a blue LED source (455 nm, 198 mW cm^{-2} ; Thorlabs M455L2). Cyclic voltammetry measurements were conducted under dark conditions, continuous AM1.5G illumination, and chopped blue LED light at a frequency of 0.03 Hz. The LED driver was controlled using custom MATLAB software. The incident photon-to-current efficiency (IPCE) was evaluated using the following equation [33]:

$$\text{IPCE}(\lambda) = I_{\text{ph}}(\text{mA/cm}^2) \times 1239.8 (\text{V} \times \text{nm}) / [P_{\text{light}}(\text{mW/cm}^2) \times \lambda(\text{nm})]$$

where J_{ph} is the photocurrent density measured under illumination with wavelength λ and light intensity P_{light} . The electrical conductivity of the samples was measured using the van der Pauw method. Measurements of photocurrent density and conductivity were performed on a set of ten samples. The reported values of photocurrent density and conductivity represent the averages, with relative deviations not exceeding 6 % for photocurrent and 4 % for conductivity.

Electrochemical impedance spectroscopy (EIS) was performed using an Autolab unit in the frequency range of 0.01 Hz–1 kHz with an AC signal amplitude of 10 mV at a fixed DC bias of 1.1 V vs. RHE. The photoelectrode was measured first under dark conditions and then under continuous illumination with blue light from a Thorlabs M455L2 LED. The impedance data were analyzed using Nova 2.1.8 software (Metrohm Autolab B.V.) with an equivalent circuit consisting of a Bis-quert #3 transmission-line element connected in series with a resistor.

X-ray diffraction patterns were obtained using a Siemens D5000 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$). The patterns were recorded at a scan rate of $0.02^\circ/\text{s}$ over a 2θ range of 10 – 100° , with an accelerating voltage of 35 kV and a current of 24 mA. Phase identification was carried out using Match! software in conjunction with the Crystallography Open Database (COD). The morphology of the materials was examined using scanning electron microscopy (SEM, TESCAN Vega 3) equipped with a Bruker detector for energy-dispersive X-ray spectroscopy.

X-ray photoelectron spectroscopy was performed using a Thermo Scientific K-Alpha spectrometer equipped with a monochromated Al $\text{K}\alpha$ X-ray source (1486.6 eV), with the instrument calibrated to the C 1s peak at 284.8 eV. Prior to surface analysis, the samples were introduced into the load lock and degassed to pressures approaching 1×10^{-8} Torr for 24 h. Subsequently, the samples were transferred to the analysis chamber, where measurements were carried out at a residual pressure of approximately 1×10^{-9} Torr.

The density (D) of Al_2O_3 -ZnO ceramics was estimated using Archimedes' principle according to the equation: $D = D_0 m_1/(m_1 - m_2)$, where D_0 is the density of water (0.9971 g cm^{-3} at 25 °C), and m_1 and m_2 are the mass of sample measured in air and in water, respectively. The textural properties of the materials were determined by nitrogen adsorption at -196°C using a 3Flex Micromeritics sorptiometer. Prior to analysis, the samples were degassed under a nitrogen atmosphere at 90 °C for 1 h and at 350 °C for 4 h. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method, based on sorption data in the relative pressure range of 0.05–0.3. The average pore size was determined using the Barrett–Joyner–Halenda (BJH) method [34]. Raman spectra were acquired using a NT-MDT NTEGRA Spectra instrument, with excitation provided by a 532 nm laser at a power of 2 mW.

3. Results and discussion

The obtained structures were characterized by XRD, XPS, Raman spectroscopy, EIS, SEM, and EDS, and were evaluated as photoelectrodes for solar-driven water splitting.

Fig. 1 shows the XRD pattern of Al_2O_3 -ZnO ceramics prepared from precursor mixtures pressed at 150 MPa without polymer additives and coated with a layer of Fe compounds. The XRD data reveal the presence of three phases: ZnO (zincite), ZnFe_2O_4 (franklinite), and ZnAl_2O_4 (gahnite), with contents of 93.6 %, 4.8 %, and 1.6 %, respectively. ZnFe_2O_4 formation is likely induced by the high annealing temperature (800 °C for 30 min in air) required to crystallize the Fe-compound coating deposited by MO-CVD, while ZnAl_2O_4 forms during the sintering of Al_2O_3 -ZnO ceramics at 1100 °C for 30 min. Raman spectroscopy was employed to confirm the presence of the ZnAl_2O_4 phase.

Fig. 2 shows the Raman spectra recorded on the surface of a bare Al_2O_3 -ZnO substrate (curve 1) and on the substrate coated with an Fe-containing compound at two different locations (curves 2 and 3). The spectrum of the bare substrate exhibits an intense peak at approximately 443 cm^{-1} and a broad band near 1150 cm^{-1} , both attributable to ZnO [32,35,36]. In turn, the spectrum recorded at the first point on the Al_2O_3 -ZnO substrate with the coating (Fig. 2, curve 2) exhibits peaks at 356 and 651 cm^{-1} , along with a broad band near 500 cm^{-1} , indicative of ZnFe_2O_4 [37,38]. No evidence of iron oxides—such as hematite

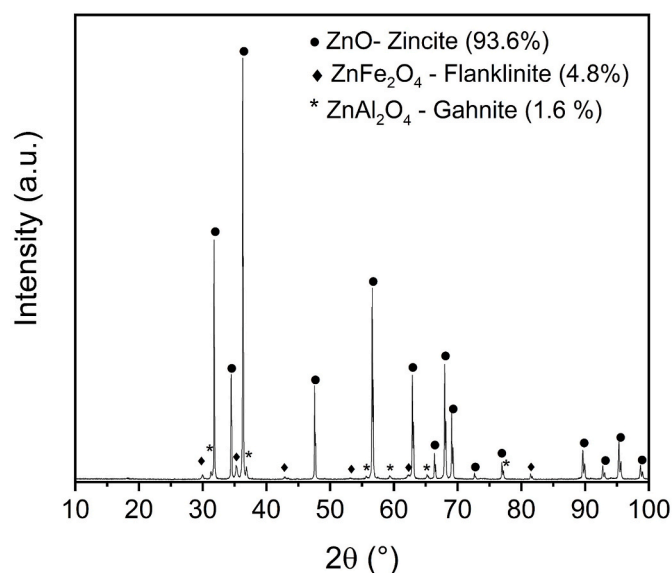


Fig. 1. XRD patterns of Al_2O_3 -ZnO ceramics with a Fe-containing coating, annealed in air at 800 °C for 30 min, and subsequently heat-treated under vacuum (21 kPa) at 425 °C for 1 h. The ceramics were prepared from Al_2O_3 and ZnO precursors compressed at 150 MPa without polymer additives.

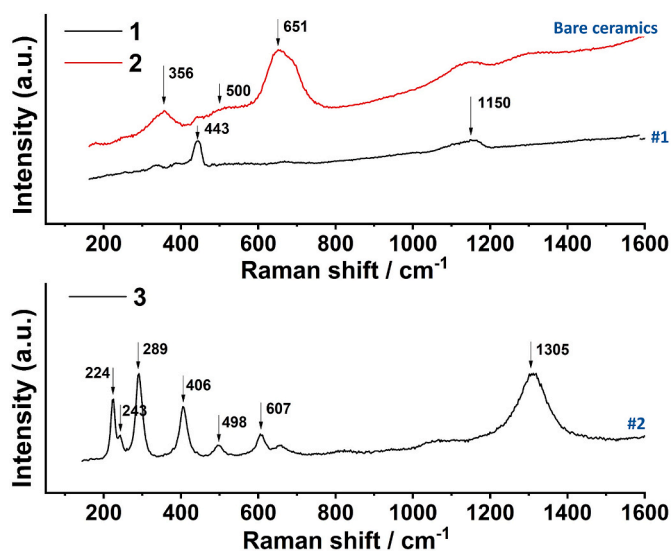


Fig. 2. Raman spectra of bare $\text{Al}_2\text{O}_3\text{-ZnO}$ ceramics (curve 1) and of ceramics coated with an Fe-containing compound (curves 2 and 3). Curves 2 and 3 were recorded at two different points (#1 and #2) on the same sample.

($\alpha\text{-Fe}_2\text{O}_3$) or maghemite ($\gamma\text{-Fe}_2\text{O}_3$), which exhibit peaks below 300 cm^{-1} and around 1300 cm^{-1} [38,39] —was observed in these data. However, the spectrum recorded at the second point on the Fe-coated surface (Fig. 2, curve 3) clearly shows the presence of hematite, with peaks at 224, 243, 289, 406, 498, 607, and 1305 cm^{-1} , consistent with literature data [39]. Additional measurements at different points on the coating also confirmed the presence of hematite and zinc ferrite.

The XRD pattern (Fig. 1) did not reveal the presence of the $\alpha\text{-Fe}_2\text{O}_3$ phase, most likely because its concentration was below the detection limit of the diffractometer. To further detect the hematite phase, a sample with an Fe coating grown for a longer time (50 min) to form a thicker layer was prepared and analyzed in grazing-incidence mode. However, the resulting XRD pattern also showed no evidence of hematite (Fig. S2). These results suggest that the photocatalytic layer on the $\text{Al}_2\text{O}_3\text{-ZnO}$ ceramics consists primarily of ZnFe_2O_4 , formed during annealing at 800 °C for 30 min, while the $\alpha\text{-Fe}_2\text{O}_3$ detected by Raman spectroscopy is present only in low concentrations, likely as a thin film with a thickness comparable to the XPS probing depth (less than 10 nm) and only in localized regions on the sample surface.

Fig. 3 shows the high-resolution XPS spectra of the Fe 2p, O 1s, and Zn 2p signals recorded on the surface of $\text{Al}_2\text{O}_3\text{-ZnO}$ ceramics coated with Fe compounds. The corresponding survey spectrum is presented in Fig. S3 (Supplementary Materials), where signals from oxygen, zinc, iron, and carbon are observed. The high-resolution Fe 2p spectrum exhibits two photoelectron peaks, Fe 2p_{3/2} and Fe 2p_{1/2}, at binding energies of 711.1 eV and 725.1 eV, respectively (Fig. 3a, curve 1). The Fe 2p_{3/2} peak is accompanied by a satellite at 719.6 eV, shifted 8.5 eV to higher binding energy relative to the main peak. These features are characteristic of Fe^{3+} species in $\alpha\text{-Fe}_2\text{O}_3$ and ZnFe_2O_4 [40–42].

For $\text{Al}_2\text{O}_3\text{-ZnO}$ ceramics coated with Fe compounds, the O 1s signal appears as a peak centered at a binding energy of 529.9 eV, which can be deconvoluted into two components at 529.81 eV and 531.11 eV (Fig. 3b, curve 1). The peak at 531.11 eV is associated with chemisorbed oxygen species and hydroxyl groups, whereas the peak at 529.81 eV is attributed to lattice oxygen bonded to metal cations in ZnFe_2O_4 [43]. For bare $\text{Al}_2\text{O}_3\text{-ZnO}$ ceramics, the O 1s peak appears at a slightly higher binding energy than in ceramics coated with ZnFe_2O_4 and $\alpha\text{-Fe}_2\text{O}_3$, specifically 530.3 eV and 529.9 eV, respectively (Fig. 3b, curve 2). This shift is attributed to differences in the oxygen environments within the crystal lattices of these materials.

The Zn 2p spectrum of ceramics coated with Fe compounds exhibits

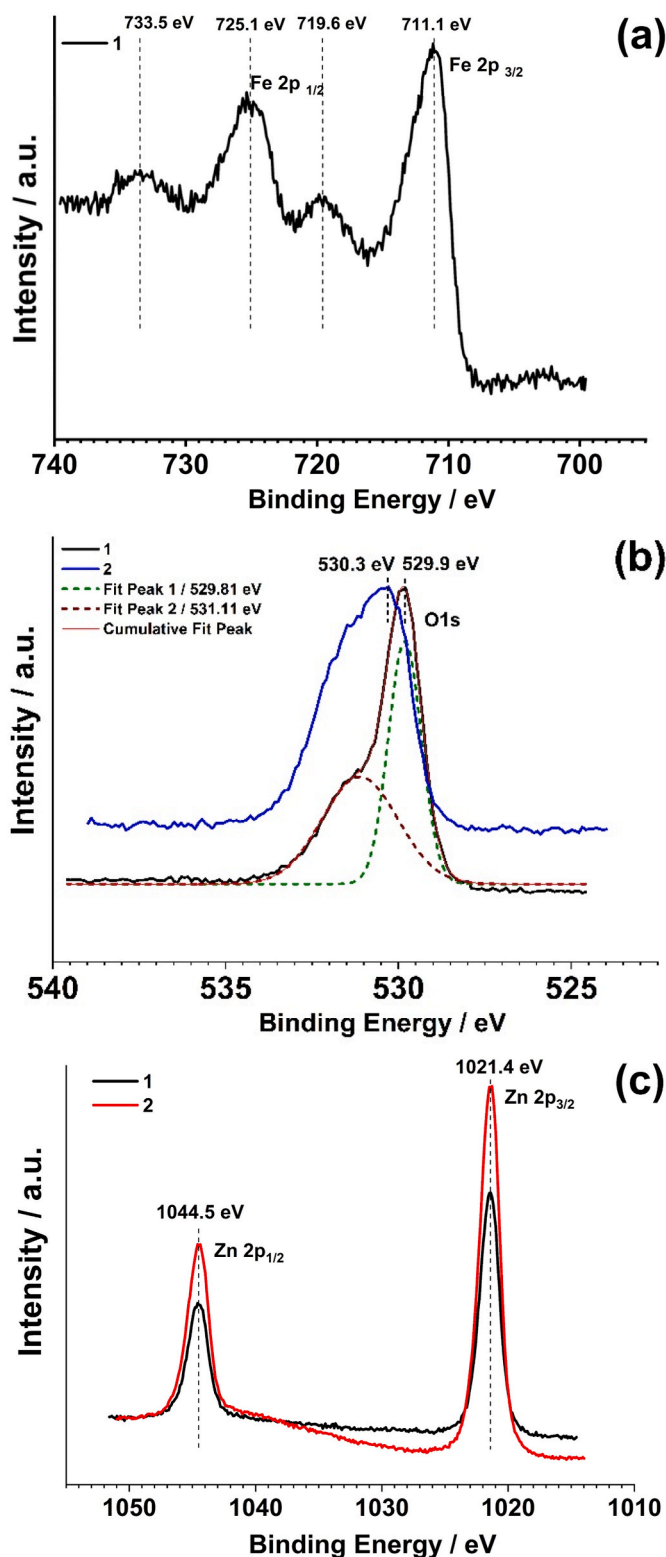


Fig. 3. XPS spectra of (a) Fe 2p, (b) O 1s, and (c) Zn 2p recorded on the surface of $\text{Al}_2\text{O}_3\text{-ZnO}$ ceramics with (curve 1) and without (curve 2) a coating.

two well-resolved peaks, Zn 2p_{3/2} and Zn 2p_{1/2}, centered at binding energies of 1021.4 eV and 1044.5 eV, respectively (Fig. 3c, curve 1). The same peak positions are also observed in the spectrum of bare $\text{Al}_2\text{O}_3\text{-ZnO}$ ceramics (Fig. 3c, curve 2). These results indicate the presence of Zn^{2+} species in tetrahedral O^{2-} coordination on the examined surfaces of both structures and are consistent with literature values for

ZnO and ZnFe₂O₄ [41,44,45].

Fig. 4 presents SEM micrographs of bare Al₂O₃-ZnO ceramics sintered under vacuum, with and without the addition of the polymers Glycix and triethanolamine. The ceramics prepared without polymers exhibit distinct morphologies in the bulk (Fig. 4a) and at the surface (Fig. 4e). The cross-sectional micrograph of a fractured sample (Fig. 4a) reveals a well-sintered material containing closed pores ranging from 100 to 500 nm. In contrast, the surface region of the same sample (Fig. 4e) consists of small, interconnected grains sized between 100 and 400 nm, forming an open-porosity network. This morphology extends to a depth of up to 10 µm from the sample surface and may result from the extensive loss of fine surface particles that were removed along with the air during vacuum pumping.

In the samples with polymer additives (Fig. 4f–h), the grain size also falls within the range of 100–400 nm; however, the grains in these ceramics appear more rounded than those in ceramics sintered without polymers. These morphological differences are attributed to the binding effect of Glycix, which promotes the agglomeration of small precursor particles during mixing and ensures their subsequent retention at the surface during vacuum pumping. Unlike the ceramics synthesized without polymer additives, those prepared with Glycix exhibit similar morphologies at both the surface and in the bulk.

Another difference between Al₂O₃-ZnO ceramics sintered with and without polymer additives lies in the type of porosity (Fig. 4). Materials sintered without polymer additives exhibit small pores approximately 100–500 nm in size (Fig. 4a and e). In contrast, ceramics prepared with polymer additives not only retain these small pores but also develop a secondary population of larger, dome-shaped macropores, reaching several tens of micrometers in size (Fig. 4b–d). The number of these macropores increases with the proportion of triethanolamine in the polymer mixture (Fig. 4c and d), indicating the possibility of further engineering the ceramics using other polymer additives in combination with Glycix. These dome-shaped macropores likely form through a blowing effect induced by the release of CO₂ and water vapor during the

polymerization and decarboxylation of Glycix and triethanolamine. In contrast, the smaller pores (~100 nm) are most likely attributable to the irregular shapes of the grains. Thus, the binding effect of the polymers promotes close contact between precursor particles and facilitates grain sintering, whereas the blowing effect gives rise to the large macropores.

The density of the obtained materials decreases from 4.98 g cm⁻³ for ceramics sintered without polymers (sample S1, Table 1) to 1.85 g cm⁻³ for those prepared with Glycix and 20 % triethanolamine (sample S4), whereas the corresponding BET surface area increases from 1.05 to 1.39 m² g⁻¹. These results correlate with the observed changes in porosity, which increases upon polymer addition (Fig. 4b–d). Ceramics prepared with Glycix mixed with triethanolamine exhibit even higher porosity than those obtained with Glycix alone (Fig. 4b–d). Nevertheless, all ceramics show high electrical conductivity, ranging from 1.08 to 1.91 S cm⁻¹ (Table 1). For comparison, Al₂O₃-ZnO ceramics sintered from the

Table 1

Parameters of bare Al₂O₃-ZnO ceramic substrates estimated using the BET, BJH, Archimedes, and Van der Pauw methods.

Sample	Material Preparation (pressure/additive)	Density (g cm ⁻³)	Electrical conductivity (S cm ⁻¹)	Average size of pores (nm)	BET surface area (m ² g ⁻¹)
S1	150 MPa/without polymer	4.98	1.45	below the instrument sensitivity.	1.0485
S2	370 kPa/with Glycix	3.24	1.91	14.158	1.2429
S3	370 kPa/with Glycix and 10 % triethanolamine	2.96	1.47	11.718	1.3871
S4	370 kPa/with Glycix and 20 % triethanolamine	1.85	1.18	11.681	

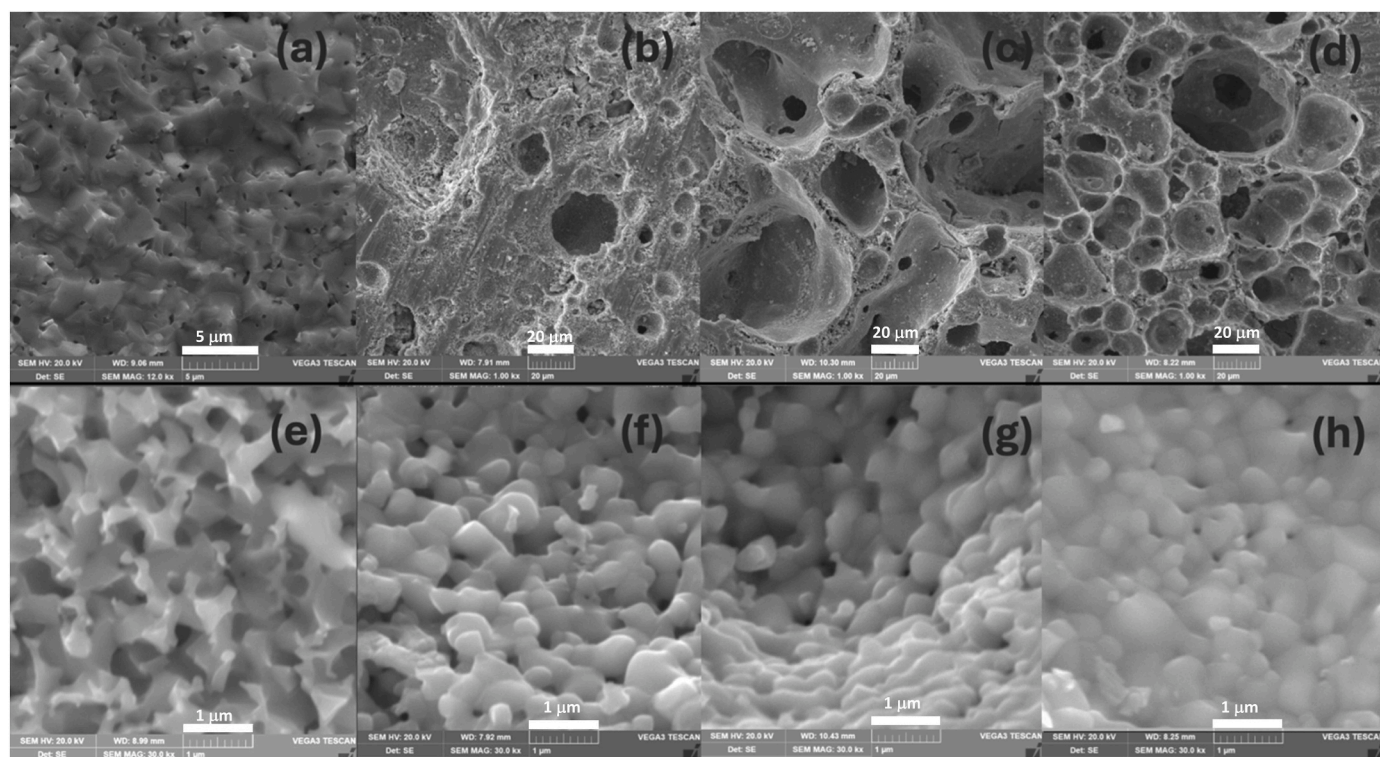


Fig. 4. SEM micrographs of bare Al₂O₃-ZnO ceramics prepared from: (a, e) precursors compressed at 150 MPa without the Glycix polymer, and precursors compressed at 370 kPa with the following additives: (b, f) Glycix; (c, g) Glycix with 10 % triethanolamine; and (d, h) Glycix with 20 % triethanolamine. Micrographs show a cross-section (a) and surface views (b–h) of the corresponding samples.

same precursors in air at 1350 °C for 1 h exhibit a conductivity of approximately 0.044 S cm^{-1} , whereas pure ZnO ceramics display a significantly lower conductivity of $1.08 \times 10^{-6} \text{ S cm}^{-1}$. This indicates that Al atoms act as donor impurities in ZnO, increasing the conductivity by more than three orders of magnitude. In addition, the higher conductivity of the $\text{Al}_2\text{O}_3\text{-ZnO}$ ceramics sintered in vacuum (1.91 S cm^{-1}) compared with those sintered in air (0.044 S cm^{-1}) suggests that the non-stoichiometry developed in the ZnO-based ceramics during vacuum heat treatment promotes the formation of intrinsic defects—such as zinc interstitials, oxygen vacancies, and surface defects—which can be ionized at room temperature and act as electron donors.

Fig. 5 presents micrographs and the elemental map of Fe distribution on the surface of $\text{Al}_2\text{O}_3\text{-ZnO}$ ceramics obtained with and without Glycix. The EDS data show that Fe distribution is not uniform on the surfaces of either ceramic, particularly within the dome-shaped macropores on the sample surface (Fig. 5b). Non-uniform Fe distribution is also evident on the surfaces of individual grains (Fig. 5c), suggesting that the coating thickness varies at different locations on the surface of the same sample, likely due to its 3D surface morphology, which results in a non-uniform distribution of the precursor flux during MO-CVD.

The EDS data recorded in the photoelectrode cross-section (Fig. 5d and e) reveal a high Fe concentration on the surface and in the subsurface region, indicating a photoactive layer with a variable thickness of 5–10 μm . This layer consists of grains coated with $\alpha\text{-Fe}_2\text{O}_3$ and ZnFe_2O_4 ,

which can function as a photocatalytic structure for solar-driven water splitting and wastewater treatment. To evaluate the photocatalytic performance of the synthesized structures and the potential of $\text{Al}_2\text{O}_3\text{-ZnO}$ ceramics as free-standing substrates for hosting the photocatalytic coating, the materials were tested as photoelectrodes in a photoelectrochemical cell.

Fig. 6 shows the EIS data presented as Bode plots for the photoelectrodes prepared from bare ceramics and ceramics coated with the Fe compound (Fig. 6a), along with their corresponding fitting results (Fig. 6b and c). Measurements were performed under dark conditions and under blue LED illumination. The experimental data (Fig. 6a) were modeled using a transmission line model incorporating the Bisquert #3 element [51] in series with a resistor R2, which represents the electrolyte resistance. The transmission line (Fig. 6b) consists of a set of R1 elements reflecting the resistivity of the ceramic substrate, a set of R3 elements associated with the interfacial electron-transfer resistance, and a set of capacitors describing the total interfacial capacitance, which was lumped into a single parameter, C_{total} . The values obtained from fitting are presented in Table 2.

The porous nature of the ceramics results in a relatively high capacitance. The parameters R2 and C_{total} determine the characteristic time constant for interface charging, which for the bare ceramics under dark conditions is 0.31 s ($\tau = R2 \times C_{\text{total}} = 0.31 \text{ s}$). Consequently, high-frequency features cannot be resolved in the obtained EIS data; however,

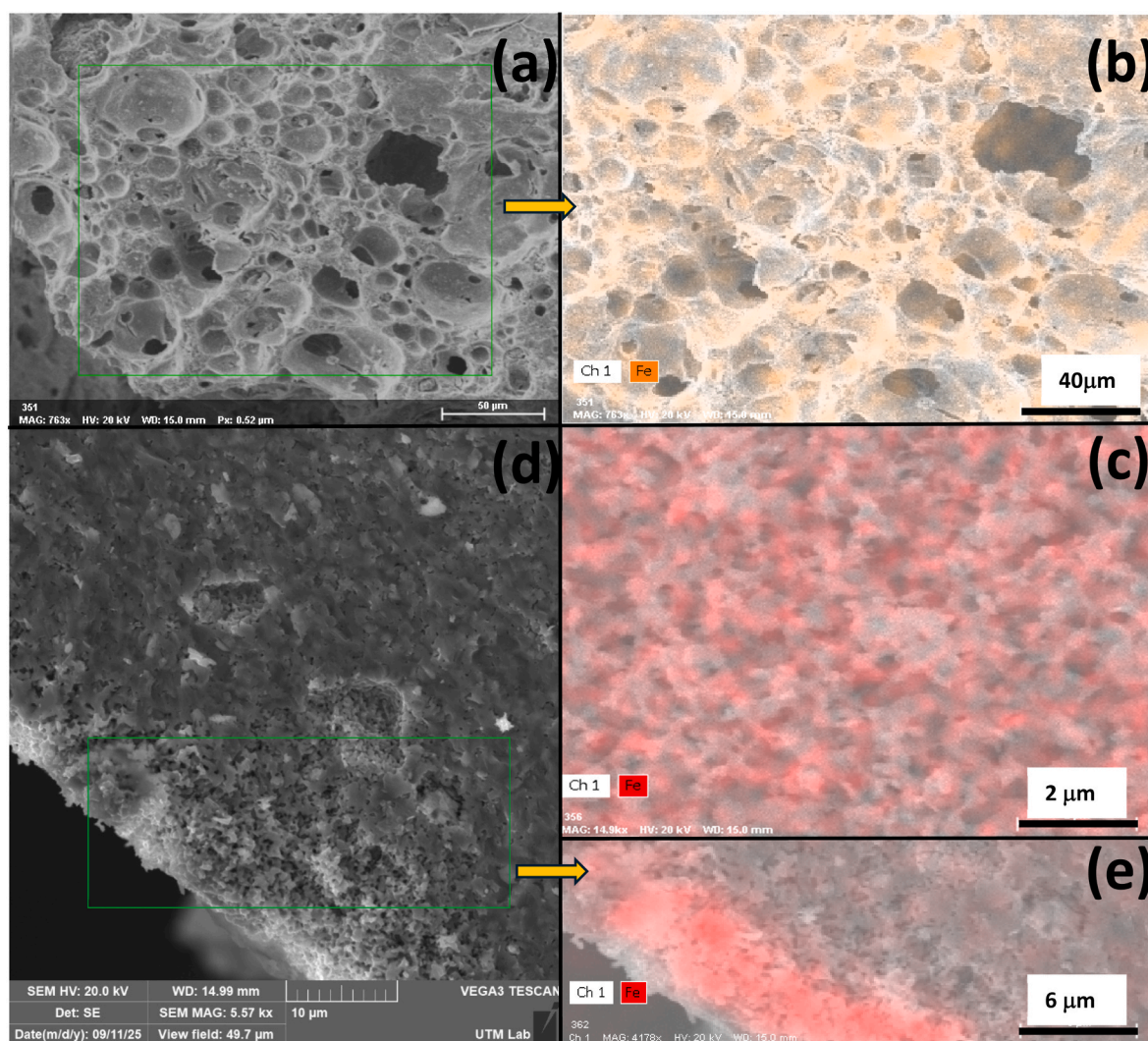


Fig. 5. SEM micrographs and elemental maps of the Fe-containing coating on $\text{Al}_2\text{O}_3\text{-ZnO}$ ceramics prepared from mixtures pressed at (a, b) 370 kPa with Glycix polymer and (c–e) 150 MPa without polymer. Data were collected on the surface (a–c) and in cross-section (d, e) of the samples.

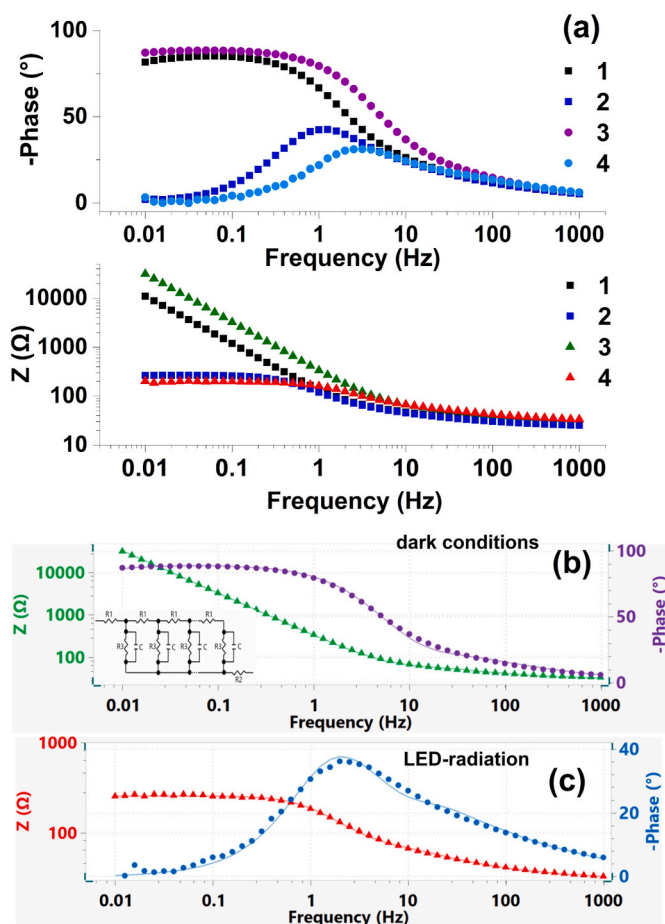


Fig. 6. Bode plots of (a) the experimental EIS data for bare ceramics (curves 1 and 2) and ceramics coated with Fe compounds (curves 3 and 4), together with (b, c) the corresponding fitting results for the coated ceramics. Curves 1 and 3 were recorded under dark conditions, while curves 2 and 4 were recorded under blue LED illumination at 1.1 V vs. RHE in 0.1 M NaOH. The fittings are represented by solid lines in (b, c). The equivalent circuit used (transmission-line model based on Bisquert #3) is shown in (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

distinct differences between the photoelectrode behavior under dark and illuminated conditions become evident at frequencies below 10 Hz (Fig. 6).

The impedance in the high-frequency region is dominated by the series resistor R2, which represents the electrolyte resistance. In the middle-frequency range, where charging of the porous ceramics occurs, the impedance exhibits transmission-line behavior described by the R1 and C elements of the equivalent circuit. At low frequencies, the response is strongly influenced by the R3 resistances, associated with charge-transfer processes, and by the C elements, which represent the interfacial capacitance [51].

Water oxidation is the photoreaction occurring at the interface between the photocatalytic materials and the electrolyte. Under dark

conditions, the charge-transfer resistance R3 is very high for both bare and coated ceramics, but it decreases markedly under illumination (Table 2). This decrease corresponds to the onset of intensive oxygen evolution, initiated when photogenerated holes reach the photoelectrode–electrolyte interface. In contrast, the R3 values calculated from the data recorded under dark conditions for both the bare and coated substrates are very similar (Table 2), indicating that the electrical properties of the Al₂O₃–ZnO substrates are not significantly affected by the 800 °C, 30-min heat treatment used to form the photocatalytic coating. This confirms the robustness of the substrates used. Because the photoelectrodes contain multiple photocatalytic materials (ZnO, ZnFe₂O₄, α-Fe₂O₃) exposed to the electrolyte and possess a highly porous surface, Mott–Schottky analysis for flat-band potential determination was not attempted.

Fig. 7 shows the cyclic voltammograms recorded for the photocatalytic structures based on Al₂O₃–ZnO ceramics prepared with and without the polymer. The photoelectrode formed on ceramics without polymer—whose SEM micrographs are shown in Fig. 4a,e—exhibited a photocurrent density of approximately 7.6 mA cm^{−2} at 1.23 V vs. RHE under chopped blue LED illumination (455 nm, 198 mW cm^{−2}), corresponding to an incident photon-to-current efficiency (IPCE) of 10.4 % at 455 nm (Fig. 7). However, the photoelectrode formed on the more porous substrate prepared with Glycix (Fig. 4b and f) yielded a photocurrent of approximately 5.2 mA cm^{−2} under the same conditions, corresponding to an IPCE of about 7.1 % at 455 nm. The lower performance of this photoelectrode may result from the presence of dome-shaped macropores, whose size and depth hinder the formation of a uniform precursor coating on the pore walls during horizontal chemical vapor deposition. Some of the larger pores remain almost entirely

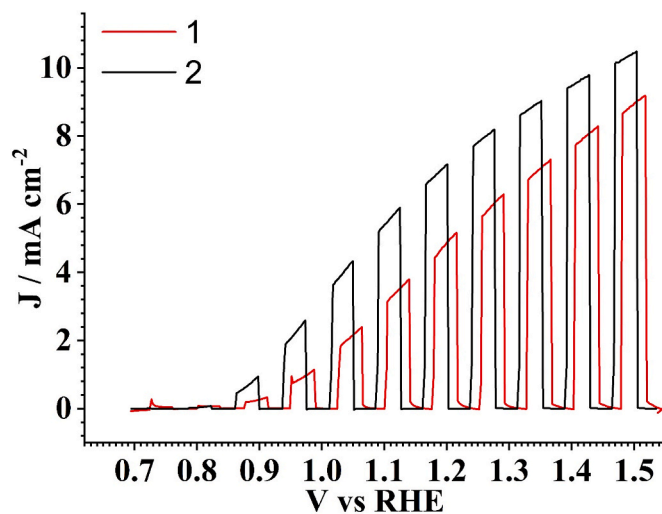


Fig. 7. Cyclic voltammetry (scan rate: 2.5 mV s^{−1}; 0.1 M NaOH) of photoelectrodes formed on Al₂O₃–ZnO ceramic substrates prepared with Glycix polymer (curve 1) and without polymer (curve 2). The measurements were performed under chopped blue LED illumination (455 nm, 198 mW cm^{−2}) during the forward potential sweep. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2

Fitting results of the EIS data for the photoelectrodes measured in 0.1 M NaOH under dark conditions and blue LED illumination (frequency range: 0.01 Hz–1 kHz; AC amplitude: 10 mV; applied potential: 1.1 V vs. RHE). Fitting errors are shown in parentheses as percentages.

Photoelectrode	Dark conditions				Under LED radiation			
	R1/Ohm	R2/Ohm	R3/kOhm	C _{total} /mF	R1/Ohm	R2/Ohm	R3/Ohm	C _{total} /mF
Bare ceramics	79.7 (3.6 %)	23.5 (1.46 %)	63.5 (13.38 %)	1.33 (0.90 %)	78.1 (2.43 %)	23.4 (0.74 %)	216.7 (0.69 %)	1.58 (1.33 %)
Ceramics with coating	79.8 (3.2 %)	28.7 (1.31 %)	54.7 (33.2 %)	0.49 (0.64 %)	110.5 (3.64 %)	29.5 (1.05 %)	192.97 (0.99 %)	0.84 (2.45 %)

uncoated, resulting in a smaller total surface area covered by Fe compounds (Fig. 5b) compared with materials without such pores (Fig. 5c). Vertical chemical vapor deposition may be more effective for forming coatings inside these pores.

It should be noted that bare Al_2O_3 -ZnO ceramics, used as free-standing substrates to host $\alpha\text{-Fe}_2\text{O}_3$ and ZnFe_2O_4 coatings, also exhibit intrinsic photocatalytic properties. The cyclic voltammograms recorded for the bare ceramics show a photocurrent density of 0.79 mA cm^{-2} at 1.23 V vs. RHE under LED illumination (Fig. S5). This PEC performance corresponds to about 10 % of that achieved by ceramics coated with hematite and zinc ferrite. Thus, the Al_2O_3 -ZnO ceramic substrate contributes to the overall photoelectrode performance alongside the $\alpha\text{-Fe}_2\text{O}_3$ and ZnFe_2O_4 coatings. Moreover, the photocatalytic performance of these photoelectrodes can be further improved by engineering the ceramic substrate prior to coating. This advantage distinguishes such substrates from conventional FTO or ITO electrodes, which merely act as conductive supports and cannot be readily modified during fabrication.

Fig. 8 shows the photocurrent–time response recorded at 1.23 V vs. RHE under chopped-light illumination using an AM1.5G solar simulator (350–1100 nm; 79.1 mW cm^{-2}). The photocurrent density initially reaches 0.32 mA cm^{-2} under 1 sun illumination and then gradually decreases over 10 min to 97 % of its initial value (0.31 mA cm^{-2}). During a subsequent 10-min rest period in the dark, the photocurrent density drops to $\sim 5 \times 10^{-4} \text{ mA cm}^{-2}$, but it recovers to 0.31 mA cm^{-2} once the AM1.5G light is switched on again. This photocurrent behavior is reproducible over subsequent cycles without noticeable degradation (Fig. 8). In addition, the photocurrent–time response of the photoelectrode was recorded over a longer period (3.2 h) in 0.1 M NaOH under chopped blue LED illumination (Fig. S6). For the photoelectrode grown on the porous Al_2O_3 -ZnO substrate prepared using the Glycix polymer, the photocurrent density initially reaches 5.35 mA cm^{-2} and gradually decreases to 95 % of its initial value (5.08 mA cm^{-2}) after 3.2 h. Thus, although a slight decrease in photocurrent is observed over time, the photoelectrochemical performance of the obtained photoelectrodes remains sufficiently stable.

It is worth noting that, although modified hematite photoanodes incorporating dopants and co-catalysts have achieved significantly higher photocurrents (e.g., 4.21 mA cm^{-2} at 1.23 V vs. RHE under AM 1.5G illumination [46]), to the best of our knowledge, the highest reported photocurrent for a pristine (unmodified) hematite photoelectrode under the same conditions is approximately 1.23 mA cm^{-2} [47]. Moreover, in general, the photocurrent density reported in the literature for hematite photoelectrodes that are not modified with dopants or co-catalysts usually does not exceed 1 mA cm^{-2} at 1.23 V vs. RHE under 1-sun illumination [48–50]. Thus, the performance of the photocatalytic structures reported herein (0.31 mA cm^{-2} at 1.23 V vs. RHE under AM 1.5G illumination) is comparable to those reported for unmodified hematite photoelectrodes. However, the main interest in the photoelectrodes presented here lies in their robust and porous ZnO-based ceramic substrate, which enables their use in filtration systems (e.g., for wastewater treatment or the removal of pharmaceutical residues from water), can withstand high-temperature annealing, and allows further engineering for specific applications, including the enhancement of their intrinsic photocatalytic properties. These advantages are limited or unavailable when using conventional ITO- or FTO-coated glass substrates, positioning the conductive and porous ceramic substrates reported herein as promising platforms for hosting photocatalytic coatings.

4. Conclusion

Photocatalytic structures of ZnFe_2O_4 and $\alpha\text{-Fe}_2\text{O}_3$ grown on Al_2O_3 -ZnO ceramics by MO-CVD exhibit a relatively high photocurrent (0.31 mA cm^{-2} at 1.23 V vs. RHE under AM1.5G illumination in 0.1 M NaOH) and stable photoelectrochemical performance, making them suitable for use in photoelectrode applications. Al_2O_3 -ZnO ceramics

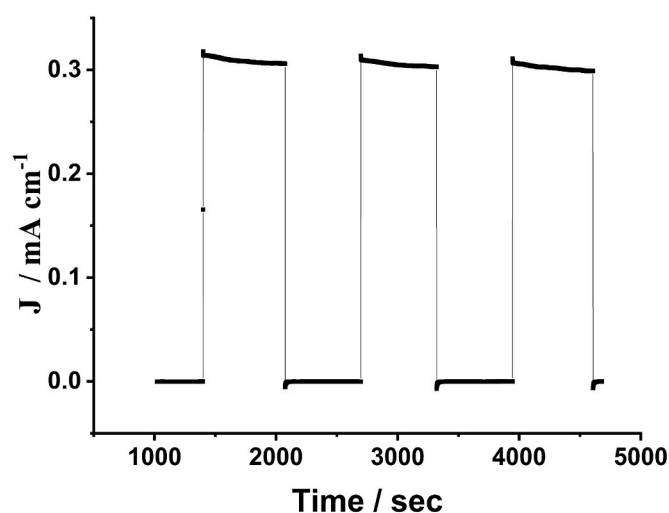


Fig. 8. Photocurrent–time dependence of the photoelectrode recorded at 1.23 V vs. RHE in 0.1 M NaOH under chopped-light illumination (AM 1.5G, 79.1 mW cm^{-2}).

synthesized with Glycix polymer under vacuum exhibit high porosity, consisting of a network of small pores ($<400 \text{ nm}$) and dome-shaped macropores reaching several tens of micrometers. The Glycix polymer functions both as a foaming agent, to generate macropores, and as a binder, ensuring close contact between precursor particles during synthesis, and can be successfully used to produce porous oxide ceramics. A high conductivity of Al_2O_3 -ZnO ceramics (1.91 S cm^{-1}) sintered in vacuum at 1100°C for 30 min is primarily attributed to ionized oxygen vacancies acting as donor impurities. Overall, the obtained porous ceramic materials exhibit promising potential for further development in photoelectrode applications and wastewater treatment under visible-light solar irradiation.

CRediT authorship contribution statement

Luis Á. Arellanes-Mendoza: Writing – review & editing, Methodology, Investigation. **Alexander N. Bondarchuk:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Iván Corrales-Mendoza:** Writing – review & editing, Methodology, Investigation. **Sergio A. Tomás:** Writing – review & editing, Methodology, Investigation. **Ulises M. García-Pérez:** Writing – review & editing, Methodology, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2025.153174>.

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