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Enhancing the hydrogen photo-production using zinc oxide films doped with iron, tin, and aluminum

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ABSTRACT

Hydrogen is recognized as the most promising renewable energy source and can be efficiently produced through water photo-electrolysis green process. This study investigates the performance of ZnO nanorods doped with Fe, Al, and Sn at a 2 % molar ratio for hydrogen photo-production. The films were prepared using a combination of successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD) methods. X-ray diffraction (XRD) analysis confirmed the hexagonal structure of the doped ZnO films with preferential growth along the (002) orientation, while energy-dispersive X-ray spectroscopy (EDX) confirmed their high purity. The doping with Al maintains the ZnO nanorods morphology while Fe, and Sn doping induced changes to overlapped nanoflakes/nanoflowers morphology. Optical analysis revealed a clear trend in the energy band gap, with Fe-ZnO film exhibiting the lowest value (2.95 eV), followed by Al-ZnO (3.03 eV), Sn-ZnO (3.07 eV), and ZnO (3.11 eV). The Fe-ZnO film also demonstrated the best performance as a photoelectrode for hydrogen generation, achieving optimized incident photon-to-current efficiency (IPCE) and applied bias photon-to-current efficiency (ABPE) values of 1.45 % and 0.20 % respectively, under 500 nm monochromatic illumination, with high reproducibility, and durability. These findings represent one step forward to developing ZnO-doped photoanodes for efficient and sustainable hydrogen green production.

1. Introduction

The global demand for clean and renewable energy sources has prompted extensive research to overcome the limitations associated with fossil fuels, including greenhouse gas emissions and limited availability [1]. In this context, solar cells, piezoelectric materials, wind energy, geothermal energy, hydropower energy, marine energy, bioenergy, and other sources have emerged as key contributors to the renewable energy landscape [2]. Hydrogen green production has gained significant attention as a promising avenue for sustainable energy generation [3], although the predominant method of hydrogen extraction from fossil fuels contributes to global warming and environmental concerns due to the release of greenhouse gases [4].

Photoelectrochemical (PEC) water splitting has emerged as a promising technique for green energy production, particularly in hydrogen generation. By utilizing semiconductors that generate electron-hole pairs upon exposure to light, PEC directly splits water molecules into H₂ and O₂, enabling the direct conversion of sunlight energy into chemical energy [5,6]. Metal oxides such as Fe₂O₃, NiO, WO3, SnO2, Cu2O, Ta2O5, and ZnO have been extensively studied as photocatalysts to enhance the efficiency of PEC water splitting [7–13]. ZnO nanoparticles, in particular, have shown remarkable potential as PEC photocatalysts that find applications in diverse fields such as adsorption, optoelectronics, biosensors, electronics, and photocatalysis [13–15]. ZnO has many desirable properties including environmental compatibility, cost-effectiveness, high electron mobility, and a strong

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exciting binding energy [16,17]. However, pure ZnO suffers from limitations such as poor electrical conductivity, limited UV light absorption due to its wide bandgap, high charge recombination, and inadequate charge separation. Consequently, researchers have explored strategies such as doping with specific elements, surface modification, and morphology control to enhance ZnO's hydrogen generation capabilities [18,19].

Previous studies have investigated the utilization of ZnO nanomaterials in PEC water splitting for hydrogen production. For example, Basu et al. demonstrated enhanced performance by employing Bi₂S₃/ ZnO junctions [20], Rekha et al. achieved notable photocurrent ($J_{\rm ph} =$ 0.39 mA/cm²) using ZnO nanoparticles (NPs) [21], Kim et al. mitigated photo-corrosion through ZnS/ZnO thin films [22], and Hsu et al. improved efficiency with Fe₂O₃/ZnO core–shell structures [23]. However, these studies encountered challenges such as low photocurrent, short carrier lifetime, photo-corrosion, and limited conversion efficiency [24,25].

Doping ZnO involves introducing specific impurities into its crystal lattice to improve its electronic, optical, and electrical properties. These advantages encompass the reduction of the bandgap, enhancement of visible light absorption, improvement of charge separation, and an increase in stability [14,16]. These combined enhancements result in a greater efficiency in converting solar energy into hydrogen. A smaller band gap allows for more photons to be used to excite electrons. The higher absorption of visible light photons boosts the generation of electron-hole pairs. This results in an augmented photocurrent density. Improved charge separation extends the lifespan of charge carriers, allowing more time for electron-hole pairs to engage in the watersplitting reaction. Increased stability results in reduced defect formation and minimizes surface reactions, enhancing the reliability of the photoelectrode for long-term hydrogen production.

Within this context, Indrajit et al enhanced the performance of ZnO nanowires (NWs) in PEC applications by doping them with nitrogen (N), resulting in a 7.5-fold increase in photocurrent density compared to pure ZnO NWs [26]. This improvement was attributed to the suppressed recombination of photogenerated carriers. Another study by Yichao et al involved the preparation of ZnO nanorod arrays doped with V ions for PEC under visible light. The incorporation of V dopants into the ZnO lattice expanded the optical absorption of ZnO from UV into the visible region [27]. This led to an increase in the photocurrent density of pure ZnO NRs from 1.9 μ A/cm² at an applied potential of 0.8 V to 10.5 μ A/cm² for V-doped ZnO.

The study, we investigate the impact of doping with Sn, Fe, and Al on the nanomorphology and water-splitting efficiency of ZnO. The differences in oxidation state, ionic radii, and electronegativity among Zn, Fe, Al, and Sn play a crucial role in shaping the structural morphology and optical properties of ZnO, ultimately influencing its performance in hydrogen photo-generation applications.

2. Experimental details

2.1. Materials

Zinc acetate dihydrate (Zn(CH₃COOH)·2H₂O, Alfa Aesar), ferric chloride hexahydrate (FeCl₃·6H₂O, Sigma-Aldrich), tin chloride dihydrate (SnCl₂·2H₂O, Sigma-Aldrich), aluminium chloride hexahydrate (AlCl₃·6H₂O, Sigma-Aldrich), anmonia (NH₄OH, ADWIC), zinc sulfate (Zn(SO₄), ADWIC), sulfuric acid (H₂SO₄, Alfa Aesar), acetone (C₃H₆O, Alfa Aesar), sodium hydroxide (NaOH, Alfa Aesar), ethanol (C₂H₆O, Alfa Aesar), and hexamethylene tetra ammine (C₆H₁₂N₄, Alfa Aesar) were obtained from reputable suppliers, as indicated, and used as received.

2.2. Preparation of ZnO thin films

Before the ZnO film deposition process, the glass substrates were thoroughly cleaned by treating them with boiled dilute sulfuric acid (1:15 v/v) for 30 min, followed by a meticulous rinse in acetone, ethanol, and distilled water (DW). Two steps were involved in the deposition of ZnO thin films. Initially, a nanostructured ZnO seed layer was deposited on glass substrates using the successive ionic layer adsorption and reaction (SILAR) method. Subsequently, ZnO nanorods (NRs) were grown by employing the chemical bath deposition (CBD) technique. In this study, the precursor solutions and conditions for SILAR and CBD techniques were carefully selected and optimized after numerous attempts, taking into consideration previous reports [28–32]. The detailed mechanism and chemical reactions for the growth process of ZnO nanorods are explained in Supplementary data (Equations S1-S8).

2.2.1. Preparation of ZnO seed layers by SILAR method

For the fabrication of ZnO seed layers through the SILAR method, a zinc ammonium complex solution was employed as the cationic precursor. The cationic precursor containing 50 mM ZnSO₄, was dissolved in diluted ammonia (1:10 v/v). Hot DW maintained at 85°C served as the anionic precursor. The deposition process involved several steps. Firstly, the glass substrate was immersed vertically in the cationic precursor solution for a controlled duration of 40 s. The excess immersion time led to more weakly bound species, which influenced the quality of the resulting ZnO seed layer. Subsequently, the substrate was rinsed in DW at room temperature for 20 s to eliminate loosely bound zinc hydroxide molecules. Ultrasonic agitation was then applied for 60 s to further remove any remaining loosely bound species. Finally, the substrate was immersed in the anionic precursor for 40 s, resulting in the formation of a well-defined solid ZnO seed layer. To ensure uniformity, multiple deposition cycles were carried out, resulting in the formation of high-quality ZnO seed layer films. In this study, 30 deposition cycles were employed, which yielded excellent ZnO seed layer films with desired properties. Increasing the number of cycles during the deposition process led to a thicker ZnO seed layer film, but excessive cycle numbers resulted in insufficient adhesion and subsequent peeling of the material from the surface.

2.2.2. ZnO thin film growth via CBD method

High-quality ZnO thin films were grown using a carefully prepared chemical bath solution. An equimolar (0.05 M) mixture of zinc acetate dihydrate and hexamethylene tetra ammine (HMTA) was dissolved in 50 mL of DW. It was observed that no precipitation when the compounds were mixed which indicated that the chosen concentration was within the solubility range, allowing both compounds to dissolve effectively in the solution. The low concertation of HMTA suppressed growth along the c-axis and lateral growth occurs on the side walls of nanorods because it works as a capping agent for inducing anisotropic growth along the c-axis [33]. The pH of the solution was maintained at 7 by dropwise addition of 0.1 M sodium hydroxide (NaOH). ZnO seed layers, previously obtained through 30 deposition cycles, were immersed vertically in the chemical and subjected to a temperature of 85°C for 2 h to facilitate controlled growth of the ZnO films [34]. After deposition, the films were thoroughly rinsed with DW and acetone to remove any residual salts, ensuring the preservation of film quality. Before undergoing further characterization and analysis, the films were gently airdried at room temperature. During the air-drying step, the films were placed vertically in a closed box to prevent the risk of external contamination from dust and scratches or smudges.

2.3. Fe, Al, and Sn-doped ZnO films prepared by CBD method

To prepare the Fe, Al, and Sn doped ZnO films, 1 mM of ferric chloride hexahydrate (FeCl₃·6H₂O), aluminium chloride hexahydrate (AlCl₃·6H₂O), and tin chloride dihydrate (SnCl₂·2H₂O), with the doping mole ratio of 2 % were individually incorporated into the chemical bath solution with identical conditions. The ZnO seed layers were subjected to a 2-hour immersion vertically in the chemical bath at 85°C. The



Fig. 1. XRD patterns of pure ZnO, Fe-ZnO, Al-ZnO, and Sn-ZnO nanostructured thin films.

resulting films were labelled as pure ZnO, Fe-ZnO, Al-ZnO, and Sn-ZnO. The obtained films were kept in a desiccator for further analysis and characterization to investigate the influence of doping on the properties of ZnO.

2.4. Materials characterizations

The fabricated ZnO thin films and the doped samples were subjected to comprehensive characterization using various analytical techniques. X-ray diffractometry (XRD) analysis using a Bruker/Siemens D5000 instrument (Karlsruhe, Germany) to determine the molecular structure of the nanostructured thin films. Scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray (EDX) unit, specifically the Auriga Zeiss FIB instrument (Munich, Germany), was utilized for morphology investigations and the chemical composition analysis of the fabricated samples, respectively. The X-ray diffractometer used for the measurement operated at a voltage of 40 keV and a current of 35 mA. It utilized a copper source (CuK_{\alpha1}) with a wavelength (λ) of 1.54 Å. The XRD measurement was performed with a step size of 0.05° in the range from 5° to 70°. The optical properties of the films were assessed using a double-beam spectrophotometer (Perkin Elmer, Lamba 950, Waltham, USA).

2.5. Photoelectrochemical measurements

Photoelectrochemical (PEC) water-splitting studies were conducted using an OrigaFlex potentiostat (OrigaLys ElectroChem., OGF01A, Rillieux, France) equipped with a three-electrode configuration system at room temperature. The electrolyte consisted of a Pyrex cell reactor containing 0.1 M sodium thiosulfate (Na₂S₂O₃) aqueous solution in 50 mL distilled water (DW) with a pH of 7.0. The working electrodes employed were the fabricated pure ZnO and doped ZnO films. The active surface area of the film is about 1x1 cm². A platinum sheet (>99 %, Sigma-Aldrich) served as the counter electrode. Photocurrent versus voltage (J_{ph}-V) characteristics were recorded by scanning the potential from -1 V to +1 V versus Hg/Hg₂Cl₂ reference electrode (Hanna Instruments, HI5412) at a scan rate of 100 mV/Sec. The measured potentials vs. Hg/Hg₂Cl₂ were converted to the reversible hydrogen electrode (RHE) using the Nernst equation [35]

$$E_{RHE} = E_{Hg/Hg_2Cl_2} + 0.059 \, pH + E^o_{Hg/Hg_3Cl_2} \tag{1}$$

where E_{RHE} is the converted potential vs. RHE, $E^o_{Hg/Hg_2Cl_2}=0.2412$ V at 25 °C, and E_{Hg/Hg_2Cl_2} is the experimentally measured potential against Hg/Hg_2Cl_2 reference electrode.

A solar simulator comprising a Xenon lamp (Newport) with a power intensity of 100 mW/cm² coupled with monochromator optical filters from 390 to 636 nm (Oriel) was used for illumination. Figure S1(supplementary data) shows the emission spectrum of the Xenon lamp. The power intensity of the Xe lamp at various monochromatic lights is illustrated in Table S1 (Supplementary data).

3. Results and discussion

3.1. Structure and morphology characterizations

The X-ray diffraction (XRD) patterns shown in Fig. 1 demonstrate the characteristics of the crystal structure of pristine ZnO thin films as well as Fe, Al, and Sn-doped ZnO thin films with a 2.0 % molar doping ratio. All films exhibited a hexagonal wurtzite structure of ZnO with a space group of P63mc (186), as confirmed by the standard card JCPDS 96–901-1663 [28]. The diffraction peaks observed at 20 angles of 31.83°, 34.48°, 36.32°, 47.59°, 56.64°, 62.91° and 67.99° corresponded to the (100), (002), (101), (102), (110), (103), and (200) crystallographic planes, respectively [36,37]. Notably, the (002) plane appeared as the dominant peak in all films, indicating a highly c-axis-oriented structure and the preferential orientation of ZnO nanocrystallites, which is consistent with prior studies on ZnO films [38,39]. Importantly, no new peaks were observed after doping, affirming the successful incorporation of Fe²⁺, Al⁺³, and Sn²⁺ ions into the ZnO lattice without the presence of impurities like Zn, Zn(OH)₂, or ZnCl₂. Moreover, the XRD patterns displayed intense and well-defined diffraction peaks, indicating the nanocrystalline nature and high-quality deposition of both pure and doped ZnO films [40,41].

Metal doping with Fe, Al, and Sn in the ZnO matrix significantly influences the crystalline quality of ZnO thin films. The inclusion of these elements leads to a reduction in the intensity of prominent peaks along the (002) plane, concurrently enhancing the peak intensity along the (100) and (101) planes. Furthermore, the XRD patterns, illustrated in Figure S2 (Supplementary data), exhibit slight peak shifts, particularly observed in the Fe-doped film. These observations can be attributed to the disparity in ionic radii between the doping elements (Sn⁺²: 1.18 Å, Al⁺³: 0.57 Å, Fe⁺²: 0.63 Å) and the ionic radius of Zn⁺² (0.74 Å).

The various structural parameters, including crystallite size (D), dislocation density (δ), microstrain (ϵ), and texture coefficient (TC), were calculated and analyzed with the doping elements using the following equations [42,43]:

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$
(2)

$$\delta = \frac{1}{D^2}$$
(3)

$$\varepsilon = \frac{\beta \cot \theta}{4} \tag{4}$$

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{(N^{-1}) \left[\sum_{l_0(hkl)}^{I(hkl)}\right]}$$
(5)

where β represents the full width at half maximum, λ denotes the X-ray wavelength used for recording diffractograms, θ stands for the angle of diffraction, I(hkl) corresponds to the measured intensity of diffraction peaks, I₀(hkl) represents the standard intensity of diffraction peaks from JCDPS card, and N represents the number of diffraction peaks observed in the XRD pattern. The obtained XRD structural parameters are summarized in Table S2 (Supplementary data).

The peak values in Table S2 indicate that there is a very small shift in the peak positions of the doped films compared to the pure film. This is due to well-dispersed and homogeneously distributed dopant atoms preserving the structural integrity of the ZnO film. A limited quantity of dopant atoms (2 % molar ratio) are incorporated into the ZnO lattice,



Fig. 2. The SEM micrographs of (a) pure ZnO, (b) Fe-ZnO, (c) Sn-ZnO, and (d) Al-ZnO films.

resulting in minimum crystal structural disturbance. The dopant atoms are injected interstitially or substitutionally into the ZnO crystal with small changes in the lattice properties. As a result, small shifts in peak shifts occur in the XRD patterns. In addition to the peak shifts, there are noticeable changes in the intensity and broadening of the peaks in the doped films compared to the pure film. This is due to the presence of the dopant atoms, which affect X-ray scattering and bring strain or disorder into the crystal lattice.

The average crystallite sizes of pure ZnO were determined to be ~85.5 nm. Notably, the inclusion of the doping elements into the ZnO system led to distinct changes in crystallite size, resulting in values of ~70.65, 86.79, and 65.28 nm for Fe, Al, and Sn doping, respectively. These variations in crystallite size can be attributed to the differences in ionic radii and the observed shift in peak location, as depicted in Figure S3 (Supplementary data) is consistent with work reported in the literature [44]. In addition, the dislocation density, a crucial parameter influenced by crystal quality and structure, behaves in opposition to the crystallite size [45,46]. Moreover, the defect concentration significantly impacts the morphological and optical properties of thin films [47,48]. The dislocation density of pure ZnO was initially measured at approximately 0.14×10^{-3} and increased for all doped samples as shown in Table S2 (Supplementary data). The rise in dislocation density restricts the surface atomic motion, retards crystallite growth, and confirms the low defect density in the fabricated films.

Moreover, microstrain is directly linked to the broadening of XRD peaks [49] and the positive microstrain value (ε) indicates the presence of tensile residual stress within the fabricated thin films. Besides, this broadening effect arises from non-uniform displacements of unit cell atoms with their positions in the lattice orientation [50,51].

The texture coefficients (TC) of the materials determine the preferred growth along specific crystallographic planes (*hkl*) and quantify the degree of preferential orientation growth which can be calculated using Eq. (4). Notably, the (002) peak exhibits the highest TC value, surpassing 1, for all films, indicating a strong preferential orientation as shown in Table S2(supplementary data).

Fig. 2(a) shows the SEM micrograph of pure ZnO, revealing the presence of highly oriented and multilinked hexagonal nanorod-like nanostructures. The nanorod arrays exhibit a high density and perpendicular growth on the substrate surface, with an average diameter of 450 nm. Figure S3 (Supplementary data) displayed the cross-sectional SEM image of the ZnO nanorods film. The thickness of the ZnO film was measured to be around 612 nm. In the case of Fe-ZnO, the SEM image shown in Fig. 2(b) reveals the morphology appears as fragmented nanoflakes, likely resulting from the etching of ZnO nanorods. The nanoflakes aggregate to form mesoporous pores and voids, creating a three-dimensional mesoporous framework with a high surface area. The morphology of Al-ZnO nanorods shown in Fig. 2(c) resembles that of pure ZnO nanorods but with a lower density and more random distribution. The average length and diameter of the Al-ZnO nanorods reach about 1020 and 300 nm, respectively. On the other hand, the Sn-ZnO film exhibits nanoflower structures as depicted in Fig. 2(d). These nanoflowers consist of interconnected small-size ZnO nanoflakes, forming a network-like structure. Such morphological feature changes are observed in ZnO films and could be attributed to the doping effect of the Fe, Al, and Sn ions. For instance, the substitutional incorporation of gallium (Ga) ions into the ZnO host lattice can tune the morphology from urchin-like to rose-like structures [52]. Similarly, the morphology of ZnO nanowires can change to nanoflakes and nanoflowers by doping

Table 1

EDX composition elemental analysis of the pure ZnO, Fe-ZnO, Al-ZnO, and Sn-ZnO film.

Thin film	ZnO	Fe-ZnO	Al-ZnO	Sn-ZnO
Zn (wt. %, At. %) O (wt. %, At. %) dopant (wt. %, At. %)	64.82, 31.08 35.18, 68.92 -	59.62, 27.17 38.6, 71.88 Fe 1.78, 0.95	58.37, 37.79 36.95, 61.22 Al 0.71, 0.81	6.16, 29.72 36.13, 69.47 Sn 4.41, 0.99

with indium (In) ions [53]. The introduction of dopants can perturb the crystal lattice, surface energy, and growth mechanism of ZnO, leading to the preferential formation of different crystal planes and resulting in diverse morphologies. Furthermore, the concentration of hydroxyl ions (OH⁻) plays a crucial role in controlling the morphology of ZnO nanostructures prepared by the CBD method [34,54]. The growth process and morphological evolution depend on the OH⁻ to Zn²⁺ ratio. Initially, ZnO growth occurs through Zn(OH)₂, and the presence of impurities in the precursor solution can influence the OH⁻ ions, leading to morphological changes in the resulting material. Studies have observed that high pH environments can induce the etching of nanorods due to the attachment of hydroxide ions on ZnO [55].

The elemental composition analysis of the ZnO, Fe-ZnO, Al-ZnO, and

Sn-ZnO films was performed using energy-dispersive X-ray spectroscopy (EDX) as shown in Figure S4 (Supplementary data) and the corresponding quantitative elemental analysis results are shown in Table 1. The analysis of pure ZnO film reveals the presence of zinc and oxygen, with atomic ratios of 31.08 and 68.92 %, respectively. Fig. S4(a) shows three characteristic peaks of zinc located at 1.10, 8.62, and 9.54 keV, confirming the high purity of the prepared ZnO, consistent with the XRD findings. Additionally, the EDX analysis demonstrates the presence of the doped elements in the impure films, as observed in Figure S4(b-d). The atomic ratios of Fe, Sn, and Al were determined to be 0.95 %, 0.99 %, and 0.81 %, respectively.

3.2. Optical characterization of the doped ZnO films

Fig. 3(a) illustrates a comparative study of the absorbance patterns of pure ZnO nanorods and Fe, Al, and Sn-doped ZnO nanorods using the UV–visible (UV–Vis) spectrum. A wide absorption band ranging from 300 nm to 380 nm is observed, resulting from the transfer of electrons from the valance band to the conduction band of ZnO [4].

Doping of ZnO films with Fe induces a shift in the absorption band towards visible wavelengths compared to the other films, and the absorbance of Fe-ZnO is higher than that of pure ZnO, Al-ZnO, and Sn-ZnO films. Dopants in ZnO crystals create localized energy levels within



Fig. 3. Optical characteristics of Sn, Al, and Fe-doped ZnO nanostructure thin films (a) UV–Vis spectra demonstrating the absorbance patterns, (b) Corresponding energy bandgap (E_g) using Tauc equation, (c) Energy bandgap (E_g) values of the nanostructured films, and (d) Extinction coefficient variation with the wavelength in ZnO films.



Fig. 4. (a) linear sweep voltammetry (LSV) at 100 mV/s under dark and white light illumination of the Fe, Al, and Sn doped ZnO photoanode in 0.1 M $Na_2S_2O_3$ solution, and (b) comparison of the photocurrent density at 1.23 V vs. RHE of the pure ZnO, Fe-ZnO, Al-ZnO photoelectrode.

the bandgap, which can trap electrons or holes and modify the electronic and optical properties of ZnO [56,57]. Furthermore, the surface morphologies of ZnO nanofilms can affect light absorption, and the complex structure of Fe-ZnO contributes to its high absorbance due to lighttrapping effects [38,58].

The Tauc equation is employed to determine the energy bandgap of ZnO nanostructured thin films [59]:

$$(\alpha h\nu)^2 = H_0(h\nu - E_g) \tag{6}$$

where, α , ν , h, and H₀ describe the absorption coefficient, frequency of incident photon energy, Planck's constant, and a constant value, respectively. Here, E_g defines the direct energy bandgap of ZnO between the valance and conduction bands. This parameter can be simply equivalent to the intersecting value when we plot $(\alpha h\nu)^2$ versus h ν (h $\nu = E_g$, when $\alpha = 0$) [60].

Fig. 3(b) shows the energy bandgap of nanostructured doped ZnO films decreases in the order of ZnO (3.11 eV) > Sn-ZnO (3.07 eV) > Al-ZnO (3.03 eV) > Fe-ZnO (2.95 eV). Notably, the reduction in bandgap values (E_g) from 3.11 eV to 2.95 eV upon the doping of ZnO with Fe may be attributed to the difference in electronegativity between Zn and the doping materials [61,62], which generates defect sites and decreases the energy bandgap between the valence and conduction bands [62,63]. The energy bandgap (E_g) of the Fe-ZnO film is shifted towards longer wavelengths within the visible region, making it suitable for the PEC reactions.

Fig. 3(c) provides the correlation between the energy bandgap values resulting from the ZnO doped with Fe, Al, and Sn ions. Additionally, Fig. 3(d) illustrates the role of the doping process on the extinction coefficient (k) of the nanostructured doped films. The maximum values of the extinction coefficients are observed in the UV region (300 nm to 380 nm). Furthermore, upon the doping of Sn, Al, and Fe into ZnO films, slight increases in the values of the extinction coefficients, consequently, the absorption values are expected to increase with the doping process, as demonstrated in Fig. 3(a). In conclusion, the doping of ZnO films with Sn, Al, and Fe significantly affects the absorption values and energy bandgap.

3.3. Photoelectrochemical (PEC) characterisation

The comparison of photocurrent and dark current densities presents a preliminary indication of the photoelectrode efficiency towards the PEC hydrogen production process. Fig. 4(a) showed the photocurrent density as a function of the applied potential (V vs. RHE) for ZnO (red line), Sn-ZnO (blue line), Al-ZnO (green line), and Fe-ZnO (magenta line) under the illumination of 100 mW/cm² Xenon arc lamp. In addition, the dark current density for ZnO (black line) is illustrated for comparison.

For pure ZnO photoelectrode at 1.23 V vs. RHE, the photocurrent

density is higher under light $(0.25 \ \mu A/cm^2)$ than under dark illumination $(0.18 \ mA/cm^2)$. In the absence of light, the current density is very low and can be negligible due to the absence of photogenerated electronhole pairs (e-h). The high photocurrent density reflects the efficient redox reactions that occur at the interface between the photoelectrode and electrolyte. The incorporation of Fe, Al, and Sn into the ZnO crystal affects the photoelectrode properties. At 1.23 V vs. RHE, the photocurrent density reaches 0.56, 0.23, and 0.06 mA/cm² for Fe-ZnO, Al-ZnO, and Sn-ZnO, respectively as seen in Fig. 4(b). The higher photocurrent density for Fe-ZnO compared to other studied electrodes indicates that Fe doping enhanced the hydrogen production of ZnO film.

In the LSV data (Fig. 4), the photocurrent density reaches saturation for Al-ZnO and Sn-ZnO, indicating that the electrochemical reaction on their surfaces is reaching its maximum rate limited by factors such as mass transport or the availability of active sites. However, the Fe-ZnO sample does not reach saturation in the same voltage range, suggesting that the PEC reaction on its surface is not reaching its maximum efficiency. This behaviour can be attributed to various factors, including the presence of surface defects, high surface area, and the availability of active sites of Fe-ZnO film [19,64]. Surface defects can modify the electronic properties of the material and induce intrinsic intermediate gap states. These defect-induced states can facilitate charge transfer processes and enhance the photo-interaction between light and the electrolyte. Additionally, the presence of active sites on the Fe-ZnO electrode promotes efficient charge migration and electron extraction. The high surface area indicates Fe-ZnO electrode has a higher capacity for charge extraction. These factors improved charge distribution and transfer dynamics on the Fe-ZnO electrode, resulting in fast PEC kinetics. Hence, the photocurrent density of Fe-ZnO continues to increase within the tested voltage range without reaching saturation compared to Al-ZnO and Sn-ZnO.

Furthermore, the Fe-ZnO film exhibits a J_{ph} (25 μ A/cm²) even with zero voltage applied. This shows that the Fe-ZnO film can generate hydrogen from incident light without the applied external bias voltage. This behaviour is known as self-biasing. It is very desirable for PEC electrodes because it can improve process efficiency and reduce overall energy consumption [65].

The Fe-ZnO photoactivity enhancement can be correlated with the surface morphology and optical properties of films where the Fe doping enhances the absorption of visible light and reduces the band gap of the ZnO thin film to 2.95 eV. Hence, the Fe-ZnO photoelectrode is capable of absorbing visible light and converting it into charge carriers which significantly benefits the PEC activity. Moreover, the morphology of Fe-ZnO film offers a large surface area with more light absorption and active sites for reactions and reactant adsorption [66,67]. The interconnected nanoflakes also provide a pathway for efficient surface charge transport resulting in faster reaction kinetics at the electrode/electrolyte interface. In addition, it can trap and confine charge carriers, which



Fig. 5. (a) Photocurrent density–voltage characteristics of the Fe-ZnO film under white light illumination. (b) Comparison chopping mode (on/off) analysis for pure ZnO and Fe-ZnO.



Fig. 6. Photocurrent characteristics and performance parameters of the Fe-ZnO film. (a) photocurrent density vs applied potential under monochromatic light with different wavelengths, (b) photocurrent density vs incident wavelengths, (c) incident photo-to-current efficiency (IPCE, %), and (d) absolute photocurrent-to-photon energy efficiency (APBE, %).

avoids the recombination rate of electrons and holes.

3.4. Reproducibility, stability, and durability of Fe-ZnO photoelectrode

The reproducibility, stability, and durability of the photoelectrodes are critical factors that need to be ensured for consistent and efficient hydrogen production in PEC water splitting. Reproducibility can be evaluated by repeatedly testing the photoelectrode's photocurrentvoltage (J_{ph} -V) characteristics under operating conditions. Fig. 5(a) shows the J_{ph} -V characteristics of Fe-ZnO photoelectrode repeated for 6 runs under 100 mW/cm² illumination. The results show that the photocurrent retains about 72 % of the original value (decreased from 0.60 to 0.43 mA/cm²) at an applied voltage of 1.23 V vs. RHE and after the sixth run as shown inset Fig. 5(a). This confirms the good stability of the Fe-ZnO film against surface degradation.

Chopping mode is a useful technique for investigating the kinetics of the charge transfer process as well as the stability of photocatalysts. Fig. 5(b) presented the photocurrent response of the Fe-ZnO photoelectrode during the chopping mode (light turned on and off) over multiple cycles under Xe Lamp light irradiation at an applied potential of 1.23 V vs. RHE 100 mM $Na_2S_2O_3$ solution. For all cycles, the Fe-ZnO photoanode exhibits a fast and high photocurrent response that

implies that most of the photogenerated electrons could be transferred to the back contact across the material to produce photocurrent responses upon light irradiation and confirm the durability of the Fe-ZnO electrode.

The J_{ph}-t curve of the photoelectrode under continuous irradiation is useful to assess the photoelectrode's stability for long-term watersplitting applications. Figure S5 (Supplementary data) shows the J_{ph}-t curve of the Fe-ZnO photoanode under 100 mW/cm² visible light continuous illumination at an applied potential of 1.23 V vs. RHE using the chronoamperometry technique. The high value of photocurrent at the beginning of the experiment is due to the capacitive effect. The photocurrent decreased to 0.1 mA/cm² during the first 30 min and then stayed constant indicating very stable photoeaction and fast collection of the ionic charges at the Fe-ZnO photoanode surface.

The linear sweep voltammetry (LSV) response of the Fe-ZnO photoelectrode illuminated with monochromatic light at different wavelengths (from 390 to 636 nm) is shown in Fig. 6(a). The results indicated that the Fe-ZnO photoanode responses are changed according to the applied light wavelengths. The values of J_{ph} at 1.23 V vs. RHE at different monochromatic light wavelengths are shown in Fig. 6(b).

The highest response was observed at 500 nm and the J_{ph} values decreased from 0.58 mA/cm² at 500 nm to 0.23 at 390 nm. The high J_{ph} value at 500 nm is due to the proximity of the wavelength to the energy band gap of the Fe-ZnO photoanode (2.95 eV). Since photons at 500 nm have sufficient energy to drive electrons across the band gap, electronhole pairs are produced. Consequently, the Fe-ZnO photoelectrode exhibits high photoconversion efficiency at this wavelength. The spectral response can provide insights into the photoconversion efficiency of photoelectrode and the strong response at wavelength 500 nm suggests that the Fe-ZnO photoelectrode has a high photoconversion efficiency at this wavelength (visible region).

The incident photon-to-current efficiency (IPCE) measures the efficiency of photoelectrode material for converting incident photons into electrical current. It can be calculated by measuring the photocurrent generated by a photoelectrode to the number of incident photons (light intensity) at a specific wavelength using the following equation [68]:

IPCE (%) =
$$\frac{J_{ph} (mA/cm^2)}{P (mW/cm^2)} \times \frac{1240}{\lambda (nm)} \times 100$$
 (7)

where $J_{ph}~(mA/cm^2)$ is photocurrent taken at a certain wavelength of incident light; $\lambda~(nm)$ is the wavelength of the radiating monochromatic photon, and P (mW/cm^2) is the illuminating light power density.

Fig. 6(c) shows the correlation of the IPCE (%) with the wavelength of the monochromatic light for the Fe-ZnO photoanode. The highest IPCE (%) value observed was 1.45 % at a wavelength of 500 nm, corresponding to the high visible region absorption. The applied bias photon-to-current efficiency (ABPE) is a metric for evaluating the performance of a photoelectrode material in converting light to electrical energy for hydrogen generation at various applied bias voltages. ABPE values can vary depending on the applied bias voltage. Measuring the ABPE value helps in determining the optimum bias voltage to achieve maximum efficiency and it can be calculated by the following equation [69]:

ABPE (%) =
$$\frac{J_{ph} (mA/cm^2)}{P (mW/cm^2)} \times (1.23 - V_{app}) \times 100$$
 (8)

Fig. 6(d) shows how the ABPE varies as a function of applied voltage at different wavelengths (390–636 nm) and the highest ABPE % value of 0.2 % at an applied bias voltage of 0.8 V vs. RHE under monochromatic illumination12 of 500 nm was obtained. Both IPCE (%) and ABPE (%) exhibit the highest values at 500 nm which is associated with enhanced light absorption and a significant increase in charge generation in the visible region.

Finally, the assessment of large-scale hydrogen generation systems



Fig. 7. Hydrogen evolution rate (mol/s) as a function of exposure time for pure ZnO and Fe-ZnO photoanode under white light illumination at an applied potential of 1.23 V vs. RHE 0.1 M Na₂S₂O₃ solution.

Table 2

Comparison of the Fe-ZnO PEC performance with photo-catalysts previously published in literature.

-				
Electrode Materials	Efficiency	J _{ph} (mA/ cm ²)	Condition	Reference
V/ZnO	_	0.018	1 V vs. Ag/AgCl	[26]
ZnO/ZnS	-	0.53	1.2 V vs. Ag/AgCl	[70]
Si/ZnO/Au	$\mathrm{IPCE}=1.20~\%$	0.45	1.5 V vs. Pt counter electrode	[71]
ZnO/Au/	IPCE = 0.70 %	0.55	1.5 V vs. Ag/AgCl	[72]
Al ₂ O ₃				
ZnO	IPCE = 0.10 %	0.44	1.2 V vs. Ag/AgCl	[73]
Al-ZnO	ABPE = 0.02 %	0.15	1.2 V vs. Ag/AgCl	[74]
Si/ZnO	ABPE = 0.035 %	0.5	2 V vs. SCE	[75]
Fe-ZnO	IPCE = 1.45 %, ABPE = 0.20 %	0.56	1.23 V vs RHE	This work

hinges on the determination of the number of hydrogen moles produced during the PEC reaction. By applying Faraday's law, it is possible to determine the number of hydrogen moles from the photocurrent density and the quantity of electric charge transmitted during the PEC reaction is proportional to this photocurrent. The amount of charge required to produce one mole of hydrogen gas is given by the Faraday constant (F = 96485C/mol) and the electrolysis law of Faraday is given by using the following equation [68]:

$$H_2 \text{ (moles)} = \frac{1}{F} \int_0^t J_{\text{ph}} dt$$
(9)

Fig. 7 shows the equivalent number of H_2 moles as a function of the generation time obtained from the corresponding photocurrent-time curve shown in Figure S5 (Supplementary data) during the PEC process. The accumulated number of the generated hydrogen moles reaches 0.85 mmol/ cm² as obtained by integrating the photocurrent-time curve.

Finally, Table 2 summarises a comparison between the photo performance of the Fe-ZnO photoanode with some photo-catalysts previously published in literature. The results show that the Fe-ZnO electrode has high efficiency for the PEC process, making it a significant advantage over other electrodes.



Fig. 8. Schematic depiction of the photoelectrochemical (PEC) mechanism on the Fe-ZnO photoelectrode.

3.5. Mechanism of the Fe-ZnO photo-performance

A plausible catalytic mechanism for iron-doped ZnO is depicted in Schematic Fig. 8. In undoped ZnO, when irradiated, electrons (e⁻) in the valence band (VB) are excited to the conduction band (CB), leaving holes in the VB of ZnO through the following reaction

$$ZnO + h\nu \rightarrow ZnO(h_{VB}^{+} + e_{CB}^{-})$$
(10)

However, the high recombination rate of these photogenerated electron-hole pairs in ZnO diminishes the PEC efficiency. With the introduction of Fe(3d) ions into ZnO, defects are generated in the crystal structure [76]. The presence of Fe ions introduces two discrete energy levels within the Fe-ZnO band gap [77,78]. This is because the redox potentials of Fe are positioned between the CB and VB of the ZnO crystal [79,80]. The Fe ions act as surface traps for the photogenerated charges. Fe³⁺ ions can react as an electron acceptor, forming Fe²⁺, and they can also act as a hole acceptor, forming Fe⁴⁺. The reactions of Fe³⁺ ions with electrons and holes can be described by the following chemical equations

$$\mathrm{Fe}^{3+} \rightarrow \mathrm{e}_{\mathrm{CB}}^{-} + \mathrm{Fe}^{2+} \tag{11}$$

$$Fe^{3+} \rightarrow h_{VB}^+ + Fe^{4+} \tag{12}$$

The Fe²⁺ and Fe⁴⁺ ions are relatively unstable compared to Fe³⁺ ions. To regain stability, these ions react with water adsorbed onto the catalytic surface, producing H₂ gas. Consequently, the doping levels serve as separation centres for the photogenerated e^-/h^+ pairs, preventing or reducing electron-hole recombination. The presence of Fe states increases the density of states (DOS) near the Fermi level, resulting in a narrower band gap and improved visible light absorption [81]. As a result, more photogenerated electrons and holes can be excited and participate in the PEC reaction. Thereby, improving activity by Fe-ZnO photocatalyst.

4. Conclusion

In summary, this study presents the synthesis and characterization of Sn, Fe, and Al-doped ZnO films for efficient hydrogen production through water splitting. The films were analyzed using SEM, EDX, and XRD techniques. Doping with 2.0 % Fe resulted in a decrease in the crystallite size (D) of the ZnO film from 85.5 nm to 70.1 nm. The energy band gaps of the nanostructured films (ZnO, 2 %Sn-ZnO, 2 %Al-ZnO, and 2 %Fe-ZnO) were measured as 3.11, 3.07, 3.03, and 2.95 eV, respectively. The incorporation of Sn, Fe, and Al significantly influenced the morphology of the CuO thin films. Notably, the 2 %Fe-ZnO film

exhibited superior photoelectrochemical (PEC) performance, displaying higher photocurrent and favourable optical properties. The hydrogen production rate measured for this film was 0.85 mmol/h cm². Furthermore, the 2 %Fe-ZnO photoelectrode demonstrated excellent stability and reproducibility, as confirmed by on/off chopped photocurrent analysis. These findings highlight the potential of Fe-doped ZnO films as highly efficient photoelectrodes for sustainable hydrogen generation via water splitting.

CRediT authorship contribution statement

Mohamed Zayed: Methodology, Formal analysis, Writing – review & editing. Mohamed A. Ghanem: Writing – review & editing, Funding acquisition, Resources. Mariam Taha: Methodology, Investigation, Software. Hussein A. Elsayed: Investigation, Validation, Data curation. Ahmed Mehaney: Investigation, Data curation, Visualization. Mohamed Shaban: Writing – review & editing, Methodology, Resources. Khaled M.H. Mohammed: Investigation, Validation. Ashour M. Ahmed: Supervision, Writing – review & editing, Conceptualization.

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

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