

Performances of Dye-Sensitized Solar Cells (DSSCs) Based on Zinc Oxide (ZnO) Photoanode Doped with Tungstic Acid Prepared by the Sol-Gel Method

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<https://doi.org/10.14447/jnmes/v29i2.a05> **ABSTRACT**

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Undoped ZnO and tungstic-acid (H₂WO₄)-doped ZnO photoanodes were synthesized by the sol-gel route and evaluated as photoanodes in dye-sensitized solar cells (DSSCs). Tungstic acid was introduced at concentrations from 0.5x10⁻⁴ M to 5x10⁻⁴ M during synthesis, using zinc acetate dihydrate as precursor. The resulting sol-gels were spin-coated as thin films on fluorine-doped tin oxide (FTO) glass, and platinum counter-electrodes were fabricated by doctor-blade deposition. XRD confirmed the hexagonal wurtzite structure of ZnO in both doped and undoped samples, while SEM showed that tungstic acid doping changes the seed-layer morphology from spherical to polyhedral grains with a higher surface-to-volume ratio. UV-visible/Tauc analysis revealed two distinct optical band gaps in the doped samples (3.26 eV and 3.8 eV), consistent with the formation of a ZnO-WO₃ nanocomposite phase in addition to ZnO. Current-voltage measurements under AM1.5 illumination showed that tungstic-acid doping raised significantly the DSSC power-conversion efficiency of 22.3% relative gain due a 20.8% increase in short-circuit current density and a lower series resistance. This was attributed to a favourable shift in conduction-band alignment and reduced recombination at the ZnO-WO₃ interface.

NOMENCLATURE

<i>A</i>	Absorbance (dimensionless)
<i>d</i>	Film thickness / inter-reticular spacing, nm
<i>E_g</i>	Optical band gap, eV
<i>FF</i>	Fill factor, %
<i>FWHM</i>	Full width at half maximum of the XRD peak, degree
<i>I</i>	Transmitted light intensity, a.u.
<i>I₀</i>	Incident light intensity, a.u.
<i>I_M</i>	Operating (maximum-power point) current, mA
<i>I_{sc}</i>	Short-circuit current density, mA/cm ²
<i>K</i>	Scherrer shape constant (dimensionless)
LUMO	Lowest unoccupied molecular orbital
<i>n</i>	Diffraction order (dimensionless)
<i>P_{inc}</i>	Incident light power density, mW/cm ²
<i>P_m</i>	Operating (maximum) power density, mW/cm ²
<i>R_{ch}</i>	Characteristic resistance, Ω.cm ²
<i>R_s</i>	Series resistance, Ω.cm ²
<i>R_{sh}</i>	Shunt resistance, Ω.cm ²
<i>S</i>	Active area of the photoanode / cell, cm ²
<i>T</i>	Transmittance, %

V_M	Operating (maximum-power point) voltage, V
V_{oc}	Open-circuit voltage, V

Greek symbols

α	Optical absorption coefficient, cm ⁻¹
η	Power conversion efficiency, %
θ	Diffraction / incidence angle, degree
λ	Wavelength, Å (or nm)
τ	Average crystallite size, nm

Subscripts

<i>ch</i>	Characteristic
<i>inc</i>	Incident
<i>M</i>	Operating (maximum power) point
<i>oc</i>	Open circuit
<i>s</i>	Series
<i>sc</i>	Short circuit
<i>sh</i>	Shunt

1. INTRODUCTION

Photosensitized solar cells are photo-electrochemical devices built on photoanodes of titanium oxide (TiO₂), tin oxide (SnO₂), zinc oxide (ZnO) or tungsten oxide (WO₃) onto which a molecular sensitizer is adsorbed [1,2]. Dye-sensitized solar cells (DSSCs) are considered part of the third generation of photovoltaic technology, offering low manufacturing cost, low fabrication-energy consumption, and a thin-film (monolayer) architecture that requires only small quantities of active material. Their operation at low and diffuse light intensity, their conversion efficiency's weak sensitivity to the angle of incidence, and their compatibility with flexible glass or plastic substrates make them attractive for autonomous or mobile power generation - for example, integration into building windows, laptops, bags or clothing.

To date, the highest solar-to-electricity conversion reported for DSSCs (12.3-14%) has been obtained with TiO₂-based photoanodes [3,4,5], a figure since extended to 15.2% through co-sensitization strategies [6]. DSSC efficiency depends, to a first approximation, on the relative energy alignment of the dye and the photoanode: the dye's LUMO (lowest unoccupied molecular orbital) must lie above the conduction band of the n-type semiconductor so that, under illumination, the photoexcited electron can be injected from the LUMO into the conduction band and collected through the external circuit, while the redox couple at the counter-electrode regenerates the dye from a level below the semiconductor conduction band (Section 3.8). The overall photocurrent also depends on the optical properties and active surface area of the photoanode, which is why porous, high-surface-area semiconductors such as TiO₂, ZnO, SnO₂ and Nb₂O₅ are the materials of choice: their band structure allows comparatively efficient electron transfer from the dye LUMO to the semiconductor conduction band and onward to the redox couple [7,8]. Doping or otherwise modifying these semiconductor thin films during sol-gel synthesis is one route to improved photoanode performance.

Among these oxides, ZnO has been widely investigated as a photoanode because of its wide band gap (3.24-3.32 eV), low cost, favourable conduction-band edge (4.3 eV), high optical transparency and near-UV/visible luminescence [9,10]. These properties have also given ZnO applications as an anti-reflective and transparent conductive coating, and in gas sensors, surface acoustic wave devices, photonics and light-emitting diodes [11,12], aided by its high exciton binding energy (60 meV) [13,14]. In a DSSC, the porous structure of ZnO additionally supports dye adsorption, and its morphology - nanorods, nanoparticles, nanowires, nanotubes or nanosheets - can be tuned to improve charge collection [15,16,17,18]. ZnO-based DSSCs have been fabricated by hydrothermal synthesis [19], chemical bath deposition [20], chemical vapour deposition [21,22], physical vapour deposition [23,24] and sol-gel processing, with reported efficiencies of 4-5% using the N719 dye [25,26,27,28].

A persistent limitation of ZnO photoanodes is their isoelectric point of pH 8-9 [29], markedly more basic than that of TiO₂ (pH 5.5-6.5) [30]. Because common ruthenium dyes are acidic, they tend to attack the ZnO surface and form Zn²⁺-dye agglomerates that slow electron injection into the conduction band [31]. Doping strategies that passivate or modify this surface chemistry are therefore of particular interest; the W⁶⁺ ion, whose ionic radius closely matches that of Zn²⁺, is well suited to substitute into the ZnO lattice [32]. Photocatalytic properties of tungsten-, oxygen- and hydrogen-based additives have previously been demonstrated in solar cells [33,34,35] and semiconductor electrodes [36,37,38]; Li et al. showed that heteropolyacids (H₃PW₁₂O₄₀, H₄SiW₁₂O₄₀, H₄GeW₁₂O₄₀) incorporated into ZnO photoanodes improve photosensitized-cell performance [38]. More recently, TiO₂-ZnO and other oxide nanocomposite photoanodes combined with tailored gel-polymer electrolytes have continued to demonstrate efficiency gains over single-oxide references [39,40], and co-doping strategies for ZnO photoanodes remain an active area of DSSC research [41], underscoring the continued relevance of oxide-doping approaches such as the one investigated here.

In this work, tungstic acid (H_2WO_4) is used as a sol-gel dopant of ZnO for DSSC photoanode fabrication, and its effect on the semiconductor and on cell performance is investigated. The sensitizer used throughout is N719, selected because it satisfies the recognized criteria for an effective DSSC dye [42,43,44]: fast dye regeneration relative to interfacial recombination; a LUMO level above the semiconductor conduction band and a HOMO level below its valence band; a density of semiconductor electron-acceptor states matched to the injected carriers; an exciton-dissociating molecular structure; stability under irradiation and in the electrolyte; broad solar-spectrum absorption; and an excited-state lifetime long enough to allow charge transfer to the electrode.

The photoanodes of both cells studied here - Cell 1 (undoped ZnO) and Cell 2 (tungstic-acid-doped ZnO) - were fabricated by the sol-gel route from a single zinc acetate dihydrate precursor; the cathode, sensitizer and electrolyte were identical for both cells. The central question addressed is whether the tungstic acid (H_2WO_4) is incorporated intact into the doped

ZnO electrode, or whether it decomposes into WO_3 and/or a ZnO- WO_3 composite phase that facilitates electron injection into the doping element's conduction band and thereby improves the photocurrent. The following sections describe the materials and characterization methods (Section 2), present the structural, morphological, optical and electrical characterization of the samples together with the DSSC performance data (Section 3), and close with conclusions on the mechanism by which tungstic-acid doping improves ZnO-based DSSC performance (Section 4).

2. MATERIALS ELABORATION AND METHODS OF ELECTRODE CHARACTERIZATION

2.1 DSSC structure, materials and chemicals

The DSSC structure used in this work is a stack of FTO / semiconductor (undoped or tungstic-acid-doped ZnO) / dye / electrolyte / platinum / FTO, schematized in Figure 1.

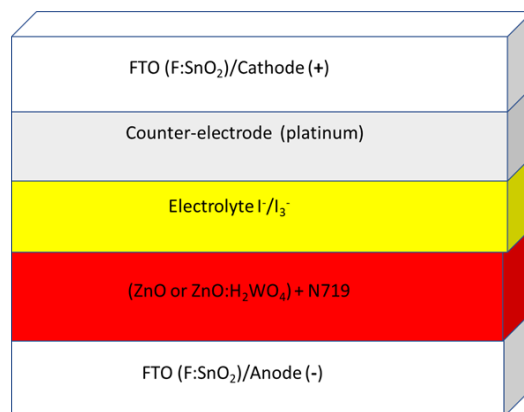


Figure 1. Schematic of the structure of the undoped or doped ZnO-based DSSC.

The FTO substrate ($\text{SnO}_2\text{:F}$ -coated glass, Sigma-Aldrich) used for both photoanode and cathode had a visible transmittance of 80-82%, a sheet resistance of $7 \Omega/\text{sq}$ stable up to 500°C (the maximum sol-gel processing temperature), and was cut to $2 \text{ cm} \times 2 \text{ cm}$ with a 1 cm^2 active deposition area.

Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 98.0-101.0%, Sigma-Aldrich) was used as the ZnO precursor, with ethanol (95.0%), methanol or isopropanol as solvent, NaOH (>97%, Sigma-Aldrich), HCl (15%) or KOH as catalyst, and monoethanolamine ($\text{HOCH}_2\text{CH}_2\text{NH}_2$, 99.95%, Fisher Chemical), diethanolamine, tetramethylammonium hydroxide or ethylenediaminetetraacetate as stabilizer; all reagents were used as received. Tungstic acid was added to the sol-gel at a W/Zn molar ratio of 0.5×10^{-4} to 1.5×10^{-4} , and the mixture stirred for about 7 minutes until a homogeneous, colourless solution was obtained. Thin films were deposited with a KW-4A spin-coater (up to 8500 rpm) and an automatic MSK-AFA-III doctor-blade system, dried in a Thelco laboratory oven, and annealed in a VULCAN 3-550 programmable furnace.

The N719 dye (Solaronix) was used as sensitizer for both undoped and doped ZnO photoanodes. The electrolyte was the commercial iodolyte Z-150 (Solaronix), containing the I^-/I_3^- redox couple in a 3-methoxypropionitrile solvent with an alkylbenzimidazole additive at 150 mM redox concentration.

The two electrodes were sealed with a 25 μm Dupont Surlyn gasket (Solaronix) that confines the electrolyte between them, as shown in Figure 1.

2.2 Synthesis of undoped and tungstic-acid-doped ZnO photoanodes

ZnO thin films were synthesized following the method of Alias and Mohamad [45]. Zinc acetate (4.4 g) was dissolved in 100 mL of ethanol and stirred at 60°C for 15 minutes to give a clear solution. Tungstic acid was then added at $0.5 \times 10^{-4} \text{ M}$ to $1.5 \times 10^{-4} \text{ M}$, followed by dropwise addition of monoethanolamine (MEA, 1.2216 g) under continued magnetic stirring at 60°C for 120 minutes. The electrolyte pH was adjusted to 9.5-10 by further dropwise addition of MEA to ensure complete dissolution of the tungstic acid and successful ZnO synthesis, following the same procedure reported previously [45]; the solution was then left for 24 h at room temperature, reaching a final pH of about 7.5.

FTO-glass substrates were cleaned by ultrasonication in acetone, then isopropanol (or ethanol), rinsed in deionized water and dried under ozone; the edges were masked with Teflon tape before the sol-gel solution was deposited by spin coating (3000 rpm, 20 s), giving a uniform film. Each sample was dried at 150°C for 10 min, and the deposition-drying

cycle was repeated three times to build up the film. Samples were then annealed at 450 °C for 120 min and cooled to 25

°C at 10 °C/min, yielding a thin, adherent layer of undoped or tungstic-acid-doped ZnO. The full sequence is summarized in Figure 2a. Photoanodes were sensitized by immersion in 3x10⁻⁴ M N719 for 30 min, then dried at 60 °C for 1 h (Figure 2b).

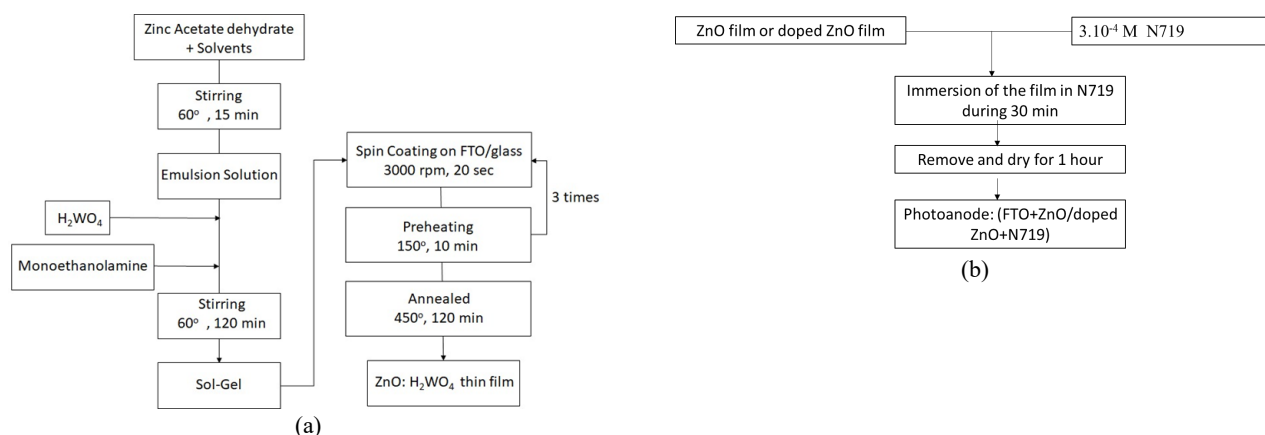


Figure 2. (a) Summary of the synthesis steps for tungstic-acid-doped ZnO thin films. (b) Flowchart for dye sensitization of the photoanode.

The counter-electrode was prepared by doctor-blade deposition of Platisol T/SP solution (Solaronix) onto FTO glass (Figure 3), followed by heating from 25 to 450 °C at 10

°C/min, a 10 min hold, and cooling back to 25 °C at 10 °C/min.

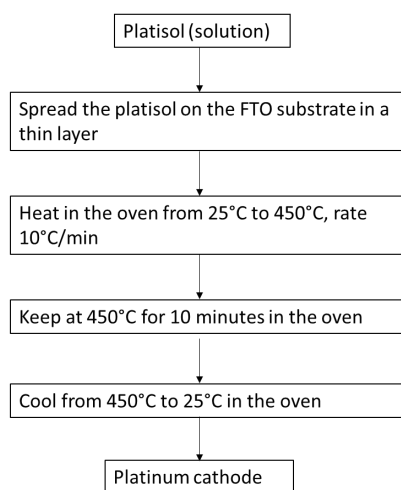


Figure 3. Steps in the fabrication of the platinum counter-electrode from the Platisol solution.

The two electrodes were assembled into a complete DSSC with the I⁻/I₃⁻ electrolyte sandwiched between the photoanode and the platinum cathode, sealed with the 25 µm Dupont Surlyn gasket; the electrolyte was introduced between the electrodes by capillary action.

2.3 Characterization methods

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE diffractometer (Cu-K alpha radiation, lambda = 1.5418 Å, 40 kV, 40 mA), with the diffracted intensity recorded as a function of diffraction angle and interpreted through Bragg's law [46]:

$$2d_{hkl}\sin\theta_{hkl} = n\lambda \quad (1)$$

where (h,k,l) is the Miller index, d the inter-reticular spacing, n the diffraction order, lambda the wavelength and theta the incidence angle.

Surface morphology and elemental composition were examined by field-emission SEM/EDS (JEOL JSM-7600F with an Oxford Instruments EDS detector, 10 kV accelerating voltage, 100,000x and 220,000x magnification). Film thickness was measured with a Dektak XT Bruker stylus profilometer (diamond-tipped stylus, sub-nanometre vertical resolution, 4 Å repeatability at 0.1 mm).

UV-visible transmittance spectra (250-1200 nm, +/-2%) were recorded on a PerkinElmer LAMBDA 1050 UV-vis/NIR spectrometer to obtain the absorption coefficient alpha and, via Tauc's relation, the optical band gap. For a beam of wavelength

lambda passing through a film of thickness d, the transmittance T [47] and absorbance A are:

$$T = \frac{I}{I_0} = e^{-\alpha d} \quad (2)$$

$$A = -\log(T) = \log\left(\frac{I_0}{I}\right) = \alpha d \quad (3)$$

and the direct optical band gap E_g follows from Tauc's equation:

$$\alpha h\nu = B(h\nu - E_g)^{\frac{1}{2}} \quad (4)$$

where B is a constant and $h\nu$ the photon energy.

Chemical bonding was probed by FTIR spectroscopy (PerkinElmer FTIR 65 ATR spectrometer), and sheet resistance was measured with a non-contact, non-destructive Delcom Instruments 737 conductance monitor (99.9% accuracy). Current-voltage characteristics of the assembled DSSCs were recorded with a Model 273A potentiostat/galvanostat under AM1.5, 25 °C, 1 atm, using a Xenon lamp (XQ-500 W) at incident power densities of 50 and 100 mW/cm².

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction analysis

The XRD patterns of undoped and tungstic-acid-doped ZnO deposited on FTO (Figure 4) are superpositions of the ZnO and FTO substrate signals. Doping with tungstic acid did not change the ZnO crystal structure but reduced peak intensity and, correspondingly, crystallite size.

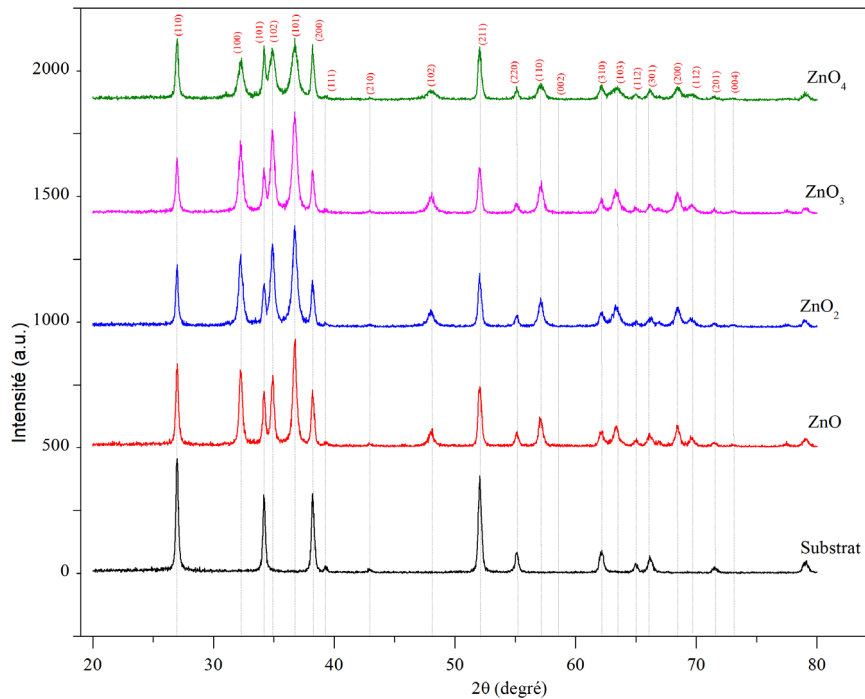


Figure 4. XRD patterns of the FTO substrate (black), reference pure ZnO (red), undoped ZnO on FTO (blue), 5×10^{-5} M tungstic-acid-doped ZnO on FTO (pink) and 10^{-3} M tungstic-acid-doped ZnO on FTO (green).

The average crystallite size tau was obtained from the broadening of the (101) peak ($2\theta = 36$ degrees) using the Scherrer equation:

$$\tau = \frac{180}{\pi} \frac{k\lambda}{\cos \theta \sqrt{FWHM^2 + s^2}} \quad (5)$$

with $K = 0.89$ (Scherrer constant), $\lambda = 1.5406$ Å (CuK α), and $FWHM = 0.264$ degrees for the (101) reflection, giving an average grain size of 21.5 nm - in good agreement with the 23.8 nm seed size observed by SEM (Figure 6a) and confirming a good-purity ZnO synthesis. Table 1 summarizes the (101) peak position, FWHM and crystallite size as a function of tungstic-acid content; the additive systematically reduces ZnO particle size during doping.

Table 1. XRD data and ZnO crystallite size as a function of H₂WO₄ doping content

H ₂ WO ₄ in ZnO (%)	(101) FWHM	Peak position 2 θ (deg)	Crystallite size (nm)
0	0.339	36.73	27.42
0.00005	0.44	36.72	21.11
0.0001	0.543	36.74	17.14
0.00015	0.448	36.73	20.4

3.2 Film thickness

Thickness profiles of the doped and undoped ZnO films, measured by stylus profilometry over a 7 mm scan length, showed non-uniform thickness varying from 40 nm to 14 μ m,

with an average of 10 μ m (Figure 5); this variation reflects the roughness of the underlying substrate rather than the deposition process itself. This average thickness is consistent with values reported elsewhere for ZnO-based DSSC photoanodes [48,49].

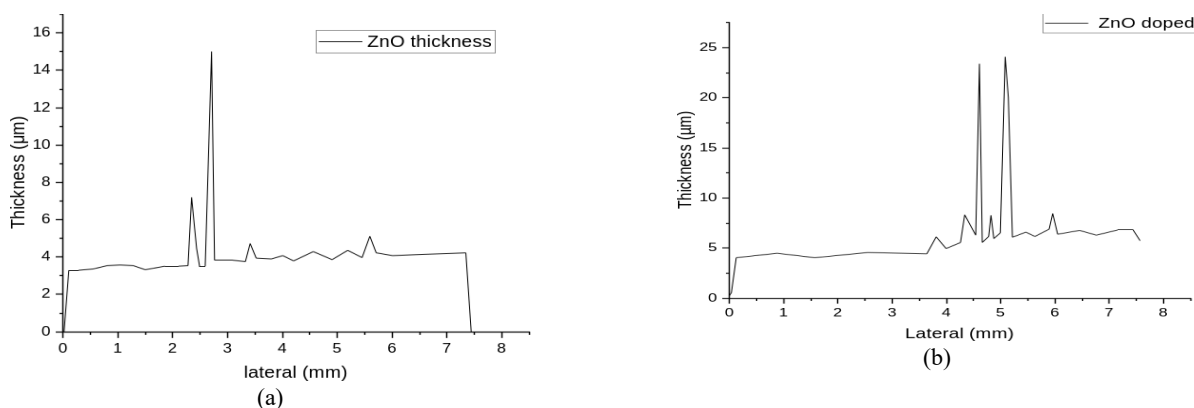


Figure 5. Stylus-profilometer thickness profiles of (a) undoped ZnO and (b) tungstic-acid-doped ZnO thin films.

3.3 Scanning electron microscopy of undoped and doped ZnO

SEM images of the undoped ZnO seed layer (Figure 6a) show a relatively uniform distribution of spherical grains 20–40 nm in diameter on the FTO substrate. Doping with 10⁻⁴ M H₂WO₄ (Figure 6b) changes this relief into smaller, more uniform polyhedral seeds with a higher surface-to-volume

ratio and better interparticle interconnection; a more voluminous, sub-bright phase attributable to tungsten is also visible within the ZnO matrix. Similar morphological changes have been reported for Cu-doped ZnO [48], and for Cd-doped ZnO, where a 6 wt% Cd doping raised solar-cell efficiency from 0.1% (undoped) to 0.5% [50] - reinforcing the broader observation that dopant-induced morphology changes are frequently a significant contributor to ZnO-based DSSC performance gains.

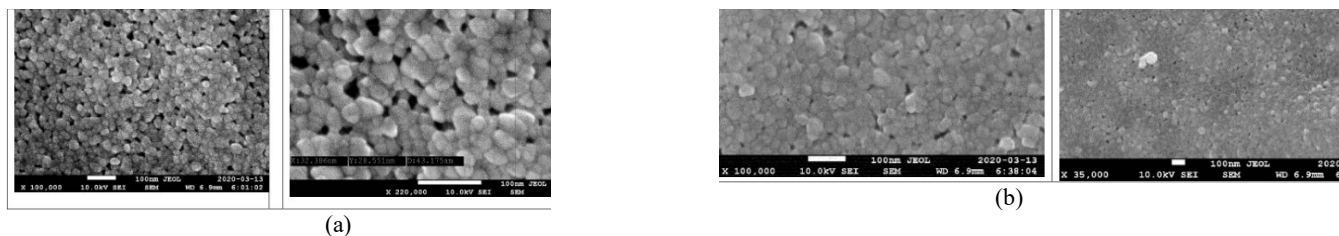


Figure 6. SEM micrographs of (a) the undoped ZnO seed layer and (b) ZnO doped with H₂WO₄, both deposited on FTO/glass by spin coating.

3.4 Chemical analysis by EDS

EDS analysis of the ZnO seed layer (Figure 7, Table 2) gave a chemical composition of 20.3 mass% oxygen and 79.7

mass% zinc (50.86 and 49.14 atomic%, respectively; standard deviation 0.3%), in good agreement with the expected stoichiometric composition of ZnO.

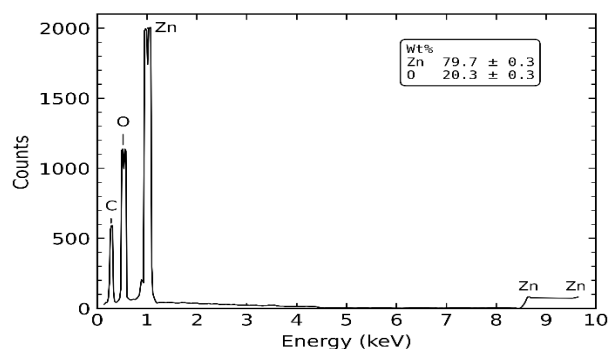


Figure 7. EDS spectrum and semi-quantitative chemical composition of the ZnO seed layer (see Table 2).

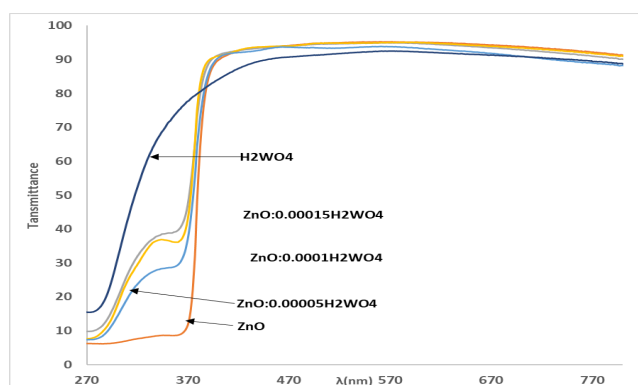
Table 2. Chemical composition of the ZnO seed layer (mass and atomic percentage) by EDS

Element	Theoretical mass %	Theoretical atomic %	EDS mass %	EDS atomic %
O	19.66	50	20.3	50.86
Zn	80.34	50	79.7	49.14

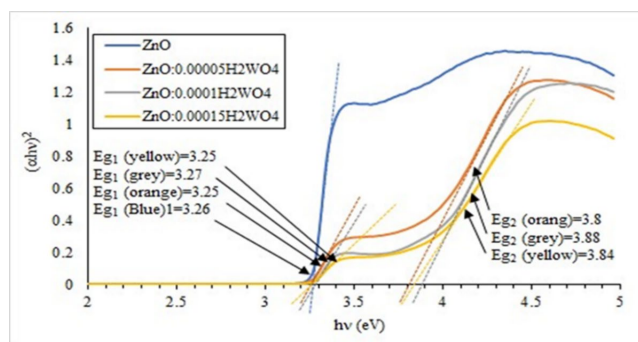
3.5 UV-visible spectroscopy and band-gap determination

Transmittance measurements show absorption between 375 and 750 nm for undoped ZnO, extending down to 250 nm for H₂WO₄-doped ZnO. Applying Tauc's relation (Eq. 4) to the

absorption data (Figure 8) gives straight-line $(\alpha \cdot h\nu)^2$ vs $h\nu$ plots, confirming that both doped and undoped ZnO are direct-band-gap semiconductors. For the doped samples, two distinct linear regions are observed, indicating two coexisting band gaps.



(a)



(b)

Figure 8. UV-visible spectroscopy of ZnO doped with various H₂WO₄ concentrations: (a) transmittance spectra; (b) Tauc plot for band-gap estimation - blue: undoped ZnO; red: 0.5x10⁻⁴ M H₂WO₄; grey: 10⁻⁴ M H₂WO₄; yellow: 1.5x10⁻⁴ M H₂WO₄.

Extrapolating the linear regions to the x-axis gives a first band gap $E_{g1} = 3.26$ eV, consistent with ZnO itself [9,10], and a second band gap $E_{g2} = 3.8$ eV that cannot be attributed to ZnO (3.24-3.32 eV [9,10,11,12,13,14]) nor to WO_3 , whose reported band gap lies between about 2.6 and 3.0 eV [51,52]. We attribute the 3.8 eV feature to a new ZnO- WO_3 nanocomposite phase formed during doping; the donor atoms introduced by the dopant likely shift the Fermi level toward the conduction band, widening the apparent gap. Although WO_3

itself is not directly resolved in the Tauc plots - its absorption signature being too weak against the ZnO background - the

presence of tungsten-oxygen bonding is independently confirmed by FTIR (Section 3.7).

3.6 Sheet resistance measurements

Sheet resistance, measured as a function of doping level (Table 3), reaches a minimum at 10^{-4} M H_2WO_4 , lower than that of undoped ZnO. This trend is consistent with the higher power density subsequently observed for H_2WO_4 -doped ZnO-based DSSCs (Section 3.8).

Table 3. Sheet resistance of undoped ZnO and tungstic-acid-doped ZnO

Sample	Sheet resistance (Ω/sq)
ZnO (undoped)	2.29
ZnO : H_2WO_4 (0.5×10^{-4} M)	1.81
ZnO : H_2WO_4 (10^{-4} M)	1.45
ZnO : H_2WO_4 (1.5×10^{-4} M)	1.95
ZnO : H_2WO_4 (5×10^{-4} M)	2.00

3.7 Chemical composition by FTIR spectroscopy

The FTIR spectrum of the ZnO seed layer on FTO (Figure 9) shows Sn-O and Sn-O-Sn peaks from the FTO substrate between 450 and 700 cm^{-1} , overlapping the Zn-O elongation

vibrations expected at 425-560 cm^{-1} [49,53], in agreement with the ZnO bond assignments of Kooti and Sedeh (436 cm^{-1}) [54], Nagaraju et al. and Kleinwechter et al. (425-560 cm^{-1}) [55,56], and Dhanalakshmi et al. (450 cm^{-1} , confirming the wurtzite structure) [57].

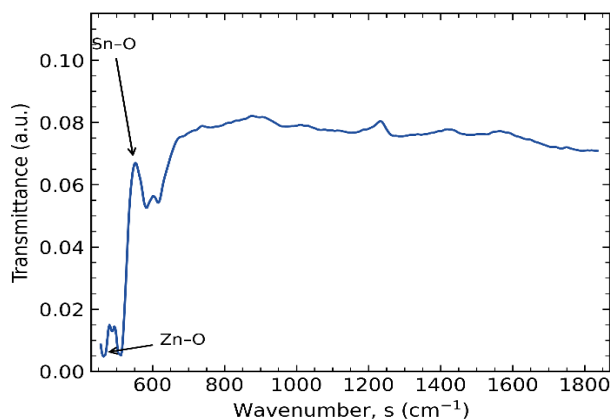


Figure 9. FTIR transmittance spectrum of the ZnO layer deposited on FTO.

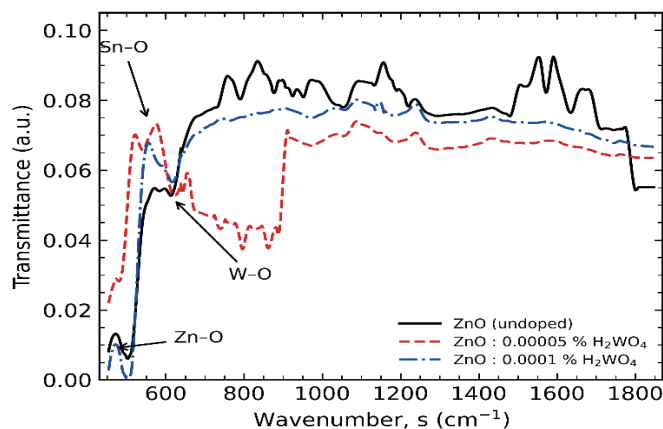


Figure 10. FTIR transmittance spectra of ZnO (blue), ZnO doped with 5×10^{-4} M H_2WO_4 (brown) and ZnO doped with 10^{-4} M H_2WO_4 (grey).

Comparing FTO, undoped ZnO and ZnO doped with 5×10^{-4} M to 10^{-4} M H_2WO_4 (Figure 10), a stronger absorption appears between 2700 and 4000 cm^{-1} as the dopant concentration increases, consistent with observations for other ZnO dopants [56]. At lower wavenumbers (620–2700 cm^{-1}), transmittance decreases as doping increases. W-O, Zn-O and Sn-O absorption bands overlap between 500 and 900 cm^{-1} , with a small shift from 536 cm^{-1} (undoped ZnO) to 550 cm^{-1} (doped ZnO), and a lower transmittance amplitude for the doped samples between 450 and 600 cm^{-1} - consistent with W-O vibrations being weaker than Zn-O because of the larger atomic radius of W relative to Zn. The generally higher

absorbance of the doped samples between 450 and 2700 cm^{-1} supports the presence of a ZnO- WO_3 -type nanocomposite rather than separate ZnO and WO_3 phases.

The FTIR spectrum of tungstic acid itself (Figure 11) shows W-O peaks at 550–950 cm^{-1} and O-H peaks at 1641 and 3494 cm^{-1} ; the broad 3494 cm^{-1} band reflects O-H elongation vibrations of water of hydration in $\text{H}_2\text{O} \cdot \text{WO}_3$ [57], the 1641 cm^{-1} band is a further O-H mode [54], and the 550–950 cm^{-1} W-O bands are consistent with those reported by Nogueira et al. [58] and Kustova et al. [59].

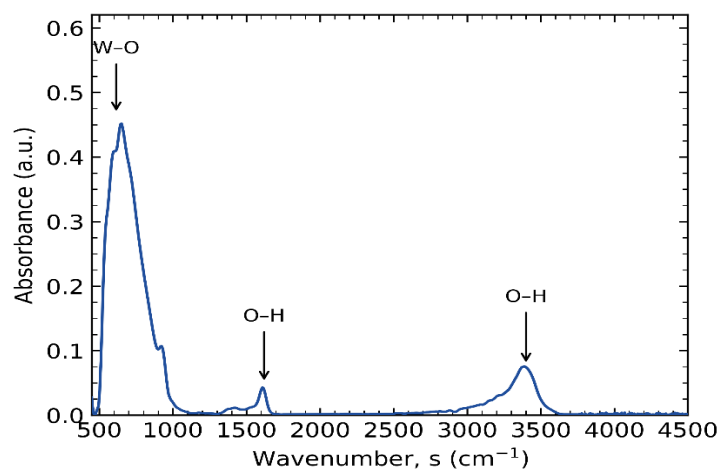


Figure 11. FTIR transmittance spectrum of tungstic acid (H_2WO_4).

3.8 Effect of tungstic-acid doping on DSSC performance

Figure 12 shows the illuminated current-voltage curves (50 and 100 mW/cm^2) for the DSSC based on undoped ZnO (Cell 1) and on ZnO doped with 10^{-4} M H_2WO_4 (Cell 2), both with 1 cm^2 active area, recorded with a potentiostat/galvanostat under standard AM1.5, 25 $^\circ\text{C}$ laboratory conditions. In the

dark, both cells behave as simple diodes with similarly low current density, indicating that tungstic-acid doping has no effect on the dark current-voltage characteristics; under illumination, however, both the short-circuit current and open-circuit voltage increase markedly, and more so for Cell 2. The undoped-ZnO cell parameters obtained here are consistent with values reported elsewhere for ZnO-based DSSCs [60,61,62].

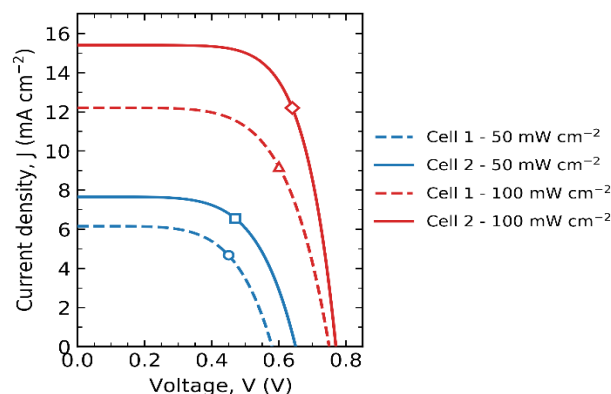


Figure 12. Current-voltage curves of DSSCs based on undoped ZnO (Cell 1) and tungstic-acid-doped ZnO (Cell 2) under 50 mW/cm² and 100 mW/cm² illumination. Photoanode thickness in each case is approximately 10 μ m.

Table 4 summarizes the short-circuit current (I_{sc}), open-circuit voltage (V_{oc}), operating current (I_M) and potential

(VM), efficiency (η) and fill factor (FF) at 50 and 100 mW/cm² ($P_{inc} = 50$ and 100 mW for a 1 cm² active area).

Table 4. Electrical performance of the DSSCs based on undoped ZnO (Cell 1) and tungstic-acid-doped ZnO (Cell 2) under 50 and 100 mW/cm² illumination (1 cm² active area)

DSSC	I_{sc} (mA/cm ²)	V_{oc} (V)	I_M (mA)	VM (V)	η (%)	FF (%)
Cell 1	6.15 / 12.2	0.58 / 0.75	4.67 / 9.2	0.45 / 0.60	4.2 / 5.52	60.0 / 60.3
Cell 2	7.65 / 15.4	0.65 / 0.77	6.55 / 12.2	0.47 / 0.64	6.1 / 7.1	62.0 / 65.8
Increase (%)	19.6 / 20.8	10.8 / 2.6	21.6 / 24.6	4.3 / 6.25	31.0 / 22.25	3.2 / 8.4

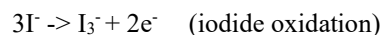
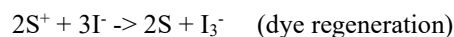
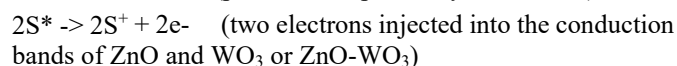
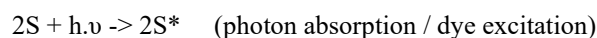
Values shown as (at 50 mW/cm²) / (at 100 mW/cm²).

The tungstic-acid doping raises DSSC efficiency by 31% at 50 mW/cm² and by 22.3% at 100 mW/cm², showing that a properly doped ZnO photoanode can markedly outperform the undoped baseline, particularly under high illumination. We attribute this improvement to a favourable shift in the relative band-edge alignment upon coupling ZnO to a WO₃ or ZnO-WO₃ nanocomposite phase (Section 3.5); if such a composite is indeed responsible, its valence band would need to lie at or below about -8.3 eV to keep its conduction band below that of ZnO. First-principles calculations of the ZnO-WO₃ band-edge positions, and systematic studies correlating band-edge shift, recombination rate and tungstic-acid doping level, would help to confirm this picture. This interpretation is consistent with earlier reports of V_{oc} improvement in TiO₂-based DSSCs doped with ZnO and Au nanoparticles [49,63], and is broadly in line with the continued gains reported for other oxide-nanocomposite photoanode/electrolyte combinations [39,40].

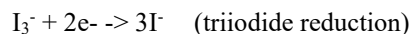
The short-circuit current gain, $(I_{sc,2} - I_{sc,1})/I_{sc,1}$, reaches 20.8% at 100 mW/cm², and the largest single improvement (24.6%) is on the operating current density. We attribute this

to a lower density of intrinsic recombination centres and/or to the addition of the WO₃ (or ZnO-WO₃) conduction-band edge to that of ZnO (Figure 13): because the WO₃ conduction band lies below that of ZnO, carrier injection from the dye's excited LUMO into WO₃ is more favourable than injection into the ZnO conduction band alone, so that up to two electrons per excited dye molecule can, in principle, be injected - one into WO₃ (or the ZnO-WO₃ composite) and one into ZnO - enhancing overall device performance. The relevant photo-electrochemical steps are:

At the anode:



At the cathode:



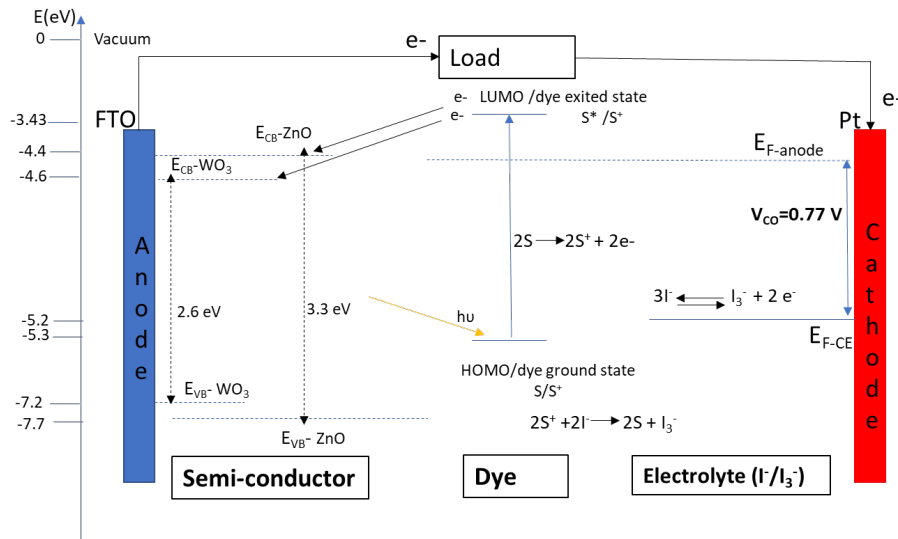


Figure 13. Energy-band diagram showing the relative positions of the dye HOMO/LUMO levels, the I_3^-/I^- redox potential, and the valence- and conduction-band edges of ZnO and WO_3 .

This picture is consistent with reports that doping level and illumination intensity strongly affect ZnO-based DSSC performance [62,64]. If, however, doping produces two coexisting photoanode phases - ZnO and a ZnO- WO_3 nanocomposite with its own band gap, potentially wider than that of either parent oxide and with a deeper valence band - injection efficiency could instead be limited, in which case the relative density of intrinsic traps may play the dominant role in the observed current increase. This tungsten-oxide-mediated mechanism is supported by our earlier work on other semiconductors doped with silicotungstic acid [33,34,35], though it differs from the interpretation of Li et al., who reported doping of ZnO with intact heteropolyacid molecules without decomposition to WO_3 or a ZnO- WO_3 phase [38]. In the present work, we instead attribute the performance gain to the presence of a ZnO- WO_3 phase.

A further possible contribution is an increase in active surface area upon doping: the greater interpenetration of dye within the larger-volume doped ZnO lattice, together with the improved interparticle connectivity observed by SEM (Figure 6), would be expected to increase photocurrent, potentially aided by additional reaction interface area between ZnO and WO_3 nanoparticles. Further work is needed to establish the

relative contribution of each of these mechanisms - band-edge alignment, trap density and surface-area effects - to the observed performance gain.

3.9 Series and shunt resistance

Tungstic-acid doping may also affect the series resistance (R_s , dominated by ohmic losses in the material and at the semiconductor/metal contacts) and shunt resistance (R_{sh} , dominated by manufacturing defects) of the cell. Neither resistance affects V_{oc} or I_{sc} directly, but a high R_s reduces the operating current and potential (and hence the fill factor), while a low R_{sh} is most detrimental at low current density. The optimum power with series or shunt resistance is respectively $P_m' = P_m(1 - R_s/R_{ch})$ and $P_m' = P_m(1 - R_s/R_{sh})$, where $R_{ch} = V_M/I_M$ is the characteristic resistance of an ideal cell; R_s and R_{sh} are obtained from the inverse slope of the illuminated I-V curve at, respectively, V_{oc} and I_{sc} .

Table 5 reports R_s and R_{sh} for both cells at 100 mW/cm² illumination. The shunt resistance of the doped-ZnO cell is higher than that of the undoped cell, suggesting more defects are introduced by doping, while its series resistance is lower - consistent with the higher operating power (P_m) of Cell 2 relative to Cell 1 (Table 4).

Table 5. Shunt (R_{sh}) and series (R_s) resistance of the DSSCs, from the I-V curves of Figure 12 at V_{oc} and I_{sc} respectively (100 mW/cm² illumination)

Cell	R_{sh} ($\Omega \cdot \text{cm}^2$)	R_s ($\Omega \cdot \text{cm}^2$)	R_{ch} ($\Omega \cdot \text{cm}^2$)	P_m (mW/cm ²)
Cell 1 (ZnO undoped)	250	8.19	0.065	5.52
Cell 2 (ZnO : H_2WO_4)	310	5.55	0.053	8.81

The R_s and R_{sh} values obtained here are about an order of magnitude lower than those reported by Hongsih et al. for RF-sputtered ZnO nanobelt DSSCs with various buffer layers [60], likely reflecting the difference in fabrication method: our ZnO photoanodes were prepared by sol-gel synthesis without any buffer layer between ZnO and FTO, consistent with the steeper

I-V slopes we observe at both V_{oc} and I_{sc} relative to that earlier, buffered, sputtered device.

4. CONCLUSION

The sol-gel method was successfully used to synthesize undoped ZnO and ZnO doped with H_2WO_4 , deposited by spin coating with platinum counter-electrodes fabricated by doctor blading, and assembled into complete DSSCs. XRD confirmed a hexagonal wurtzite structure ($a = 0.325 \text{ nm}$, $c = 0.521 \text{ nm}$) unaffected by doping, while SEM showed a morphology change from spherical seeds (undoped) to smaller, higher-surface-area polyhedral seeds (doped).

Current-voltage measurements under standard test conditions showed that tungstic-acid doping raised the short-circuit current by 19.6% and the operating current by 20.8%, together with improved series and shunt resistance, and an overall power-conversion efficiency gain from 5.52% (undoped ZnO) to 7.1% (H_2WO_4 -doped ZnO) at 100 mW/cm^2 . We propose that this improvement reflects a two-semiconductor mechanism, in which tungstic-acid doping introduces WO_3 or a ZnO-WO_3 nanocomposite phase alongside ZnO, favourably shifting band-edge alignment and reducing recombination.

This 7.1% efficiency is a substantial gain over those of the undoped-ZnO baseline and is obtained through a simple, low-cost, single-precursor sol-gel modification.

Future work should combine first-principles calculations of the ZnO-WO_3 band-edge positions with systematic studies correlating doping level, recombination rate and band-edge shift. This will help to establish more precisely which of the mechanisms discussed on band alignment, trap density, or surface-area effects are responsible in the observed performance gain. We should also test whether combining tungstic-acid doping with the co-sensitization or alternative-electrolyte strategies now being reported elsewhere can push ZnO-based DSSC efficiency further still.

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DATA AVAILABILITY STATEMENT

The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request.

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