An-Najah National University

Faculty of Graduate Studies

Electrochromic Properties of Tungsten Trioxide (WO₃) doped with Titanium (Ti) and Zinc (Zn) atoms

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Dedication

To my Parents

IV Acknowledgment

After the Almighty Allah, I would like to express my sincere thanks and heartfelt gratitude to my supervisor Dr. Iyad Saadeddin for his guidance, helpful efforts, excellent advices, and encouragement, and to my Co-supervisor Dr. Mohammad Suleiman. Special thanks to the members working in the physics and chemistry departments laboratories for their help and support, especially, Mr. Mohammad Bahjat, and Mr. Nafeth Zakrea. I would also like to take this opportunity to express my deep thankfulness to my family (my father, my mother, my sisters, my brother) for the continuous support and encouragement.

أنا الموقعة أدناه مقدمة الرسالة التي تحمل العنوان:

Electrochromic Properties of WO₃ doped with Ti and Zn atoms

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XI Electrochromic Properties of WO₃ doped with Ti and Zn atoms By Salam Adnan Mahmoud Ghanma Supervisor Dr. Iyad Saadeddin Co-Supervisor Dr. Mohammad Suleiman

Abstract

WO₃ electrochromic thin films doped with Ti and/or co-doped with Zn atoms have been prepared, onto FTO/Glass substrates, by sol-gel technique. WO₃ nominally doped with 0.05% of Ti ($W_{0.95}Ti_{0.05}O_3$) was co doped with Zn nominal molar concentration according to $W_{0.95}Ti_{0.05}$ $_{x}Zn_{x}O_{3}$, where x ranges from 0 - 5 %. For these films, different optical and electrochromic parameters have been studied. Cyclic voltammetry (CV), Chronoamperometry (CA), and transparency during CA experiment was used to study the electrochromic parameters. Best electrochromic properties was observed for co-doped film with nominal composition of all studied $W_{0.95}Ti_{0.04}Zn_{0.01}O_3$. Compared to films. this film $(W_{0.95}Ti_{0.04}Zn_{0.01}O_3)$ showed the highest contrast ratio $(T_b/T_c \approx 1.9)$. Also, this film has highest coloration efficiency (22.2 cm^2/C), which is 1.48 times higher than WO₃ doped with Ti alone ($W_{0.95}Ti_{0.05}O_3$). Moreover, co-doped film has a good switching time and excellent reversibility (Qa/Qc ≈ 0.95), which are almost same as single doped film.

FTO thickness increased by 79 nm for single dipping in the sole-gel and the film thickness increased by other 479 nm when dipped for another time. Moreover, Energy band gap was found to be 3.91 eV, 3.87 eV and 3.83 eV for single layer, double layer and triple layer respectively.

Chapter One Introduction

Chapter One Introduction

1.1 Objectives

The main objective of this work is to enhance the electrochromic properties of WO_3 based thin films by doping these films with Ti and/or Zn atoms using sol-gel technique.

Thin films with different concentration of Ti and/or Zn atoms will be studied and analyzed by Chronoamperometry and Transparency during Chronoamperometry.

1.2 Why WO₃ based thin films?

One of the most popular of electrochromic materials is tungsten oxide, it has been widely studied for its important electrochromic properties such as its fast switching time, high coloration efficiency and relatively low cost [1-3]. Due to these properties these materials are used in several fields, as optical switching devices, memory devices, smart sunroofs, solar energy converters, catalysers, smart windows and rear view mirrors. [4-9].

1.3 Hypothesis

When Tungsten oxide is doped with other substances like Ti and Zn atoms, their physical nature are be modified and hence affect their crystal structure and properties. Electrochromic and optical properties of these materials are to be studied and analyzed.

1.4 Previous Studies

The most common electrochromic material is WO_3 , for that reason the researchers were interested to know more about it. The first electrochromic phenomena was reported by Deb since 47 years ago [10], then several studies on these amorphous thin film followed.

Yanping and his group used to prepare smooth tungsten oxide thin film by spray pyrolysis technique and they found that this method improves the coloration efficiency [11]. Another technique to improve tungsten oxide properties is electrodeposition technique [12].

In a study to enhance the coloration efficiency of tungsten trioxide thin films, the magnetron spattering method succeed in obtaining 79 cm²/C. This coloration efficiency was observed for the first time for films deposited using 150W DC power and pulsing frequency of 25 kHz [13].

The most common technique for tungsten oxide thin film preparation is sol-gel technique, because it is cheap, low temperature technique, and used in several fields as in optics, electronics and medicine [2,3].

Badilescu and Ashirt used sol-gel technique to study the characterization of tungsten oxide films properties and they compare these films with others films fabricated by using other techniques (thermal treatment or solvent extraction) [14]. Catalini and his group used sol-gel method to prepare tungsten oxide films and they studied the effect of temperature the prepared films using scanning electron microscope and X-ray diffraction [15].

Many researchers worked to improve electrochromic properties of WO_3 by doping WO_3 with different types of atoms. Hyo-Jin Ahn and his group investigate the effect of SnO_2 addition to tungsten oxide, they found that the doped films have faster response time and greater coloration efficiency by 14% than tungsten oxide alone [16]. Reich and Tsabba used Na atoms and doped it with tungsten oxide and they studied the change of the films conductivity with temperature[17]. Chang and his group used Zn atoms as a dopant atoms, they found that Zn addition to tungsten oxide improves its properties[18].

Bathe and his group analyze the effect of adding Ti atoms on the electrochromic properties of tungsten oxide and they found that the charge storage capacity and reversibility of these films are improved [19].

There are many studies about the effect of co-doping on based films. Recently, co-doping NiO with Ti and Zn was found to improve the electrochromic properties better than doping with NiO or with Ti alone, such behavior was ascribed to stronger adhesion of co-doped NiO on the FTO substrate [20].

In addition to that, Yang and his groups developed new WO₃-based material for smart window applications and found that co-doping of WO₃ with Li and other atoms is more stable than mono-doping [21]. Furthermore, Junling Zhou and his group prepared NiO based thin film by sol-gel method, co-doped with Li and Ti to enhance electrochromic performances and cycle stability for these thin films. They found that Li–Ti–NiO films exhibit rapid color change within 1 s [22].

Chapter Two Fundamentals and theoretical background

Chapter Two

Fundamentals and theoretical background

2.1 Chromism,

The meaning of chromism is color change, the color change is noticed by naked eye because the change is in the visible region of the spectrum (400-800 nm) [23].

The most important kinds of chromism are explained below.

- **Thermochromism** : color change caused by temperature change [24].
- Photochromism : color change which result from illumination by light
 [25].
- Halochromism : color change due to change in pH(potential of hydrogen) [26].
- Piezochromism : color change caused by change in pressure applied[25].
- **Tribochromism** : color change due to mechanical friction.[25].
- ✤ Vapochromism : color change due to vapor /gas contact[26].
- ✤ Humidochromism : color change due to humidity[25].
- ★ **Ionochromism** : color change associated with the addition of ions [27].
- **Electrochromism** : color change due to applied voltage [28].

2.2 Electrochromism

Electrochromism is the phenomenon in which the variation of color is caused by applying voltage or passing a current, the topic of electrochromism dates back to the nineteenth century but in the last of twentieth century the study gained a real attention so the application have amazing success.[29]

2.2.1 Operation and design of electrochromic devices (ECDs)

The standard complete electrochromic device acts as a thin film battery which consists of five layers positioned between two substrates by use of lamination (Fig. 2.1).



Fig. (2. 1): Schematic diagram of the electrochromic device [30].

Generally, the substrates are made from glass and flexible transparent foil. The central part is ion conductor (electrolyte) which is positioned between active electrochromic layer and ion storage (counter electrode). It can be organic or inorganic material, the ions must have small radius in order to move easily in an electric field as a proton (H⁺) and lithium ions (Li⁺). This electrolyte is in contact with tungsten oxide (as an example of electrochromic thin film), and this thin film serving as ions storage, ideally with electrochromic properties complementary to those on the first electrochromic film. These three layers exist between two transparent conductors, the transparent conductive layers are based on F-doped SnO_2 (FTO) or Sn-doped In_2O_3 (ITO) .FTO more available than ITO since and cheaper than ITO.

When a few volts are applied between the transparent electrical conductors, ions are shuttled regularly between the electrochromic film and the ion storage. At the same time, the electrons are extracted from the fifth layer of electrochromic device (transparent conductors). When a voltage is reversed, return back to the original state [30].

2.2.2 Applications of ECDs

There are many various application of ECDs such as electrochromic windows, electrochromic mirrors, electrochromic displays, smart glass, smart sunroofs and filters [31].



Fig. (2.2): Various applications for electrochromic devices.

There are many various application of ECDs such as electrochromic windows, electrochromic mirrors, electrochromic displays, smart glass, smart sunroofs and filters [31].

2.3 Background on tungsten and tungsten oxide

2.3.1 Tungsten

Tungsten is a metallic transition element and it positioned in periodic table in group VI and period VI, with atomic number of 74, average relative atomic mass is 183.85 \pm 0.03 g/mole, atomic radius is 137 pm ,ionization potential is 7.98 eV, electron affinity (M \rightarrow M⁻) is 0.816 \pm 0.008 eV [32,33], and electronic configuration of [Xe] 4f¹⁴ 5d⁴ 6S². The melting and boiling points are about 3422 °C, 5930 °C respectively. Also tungsten has high mass density of 19.3 g/cm³. Tungsten has different oxidation numbers (0, 1⁺, 2⁺, 3⁺, 4⁺, 5⁺, 6⁺) [34]. Tungsten combine with several elements as: Carbon, nitrogen, phosphorous, oxygen, sulfur, Fluorine, Iodine, and Bromine. These composition are used as catalysts, electrochromic devices and ceramic glazes.

2.3.2 Tungsten oxide (WO₃)

WO₃ is a chemical composition consisting from oxygen and tungsten. It has an intermediate band gap (2.7 eV). It has a molar mass of 231.84 g/mole, it appears as ayellow powder, and its density is 7.16 g/cm³. For WO₃, the melting and boiling point are 1473 °C, 1700 °C respectively [33,35]. Robert Oxland was the first scientist who prepared it (in 1841).

(a) Preparation

There are many procedures to prepare tungsten oxide, as it appears from these equations [36] :

- 1) At high temperature
- CaWO₄ + 2 HCl \longrightarrow H₂WO₄ + CaCl₂ H₂WO₄ \longrightarrow WO₃ + H₂O 2) (NH₄)[H₂W₁₂O₄₂].4H₂ \bigoplus 12 WO₃ + 10 NH₃ + 10 H₂O 3) In the presence of air 2 WCl₆ + 3 O₂ \longrightarrow 2WO₃ + 5 Cl₂.

(b)<u>Structure</u>

Tungsten trioxide exhibit a monoclinic crystal structure at room temperature with a unit cell parameters of a =7.30Å, b =7.53Å, c =7.68Å and β =90.54[36,37]. Actually, single crystals of WO₃ has a different structures with different temperature ranges, it is triclinic from (-50 – 17) °C, monoclinic from (17 - 330) °C, orthorhombic from (330 -740) °C, and tetragonal above 740 °C. The stable form of WO₃ is Monoclinic at room temperature .



Fig. (2.3): monoclinic structure of tungsten oxide (WO₃) at room temperature.

(c) <u>Technological applications:</u>

Due to it's electrical, optical, and photocatalytic characteristics, WO₃ became a promising material for technology applications, so it is used in different fields such as in electrochromic devices, photo catalysis, dye-sensitized solar cells, and high temperature super conductor [38]. It is also used to fabricate fireproofing fabrics, pigments in ceramic and paints due to its yellow color, and to manufacture tungstate[39].

2.4 Coloration process in tungsten oxide-based thin films

Electrochromic and optical properties of tungsten oxide based thin film have been studied in alkaline electrolyte (H_2SO_4). When potential is applied, the electrochromic reaction take place, so the color switches from transparent state to color state (blue)[9,6,40-44]. This change in color is due to injection of protons and electrons into the thin film. This injection will switches transparent case into dark blue color in accordance with the reaction [44] :

$$2WO_{3} (transparent) + 2M^{+} + 2e^{-} \langle \longrightarrow W_{2}O_{5} (blue) + M_{2}O \qquad (2.1)$$
$$W^{+6} \qquad W^{+5}$$

Where (M = H, Li, Na, etc.).

This operation can be described obviously in Fig. (2.4).



Fig. (2.4): The reduction of W^{+6} in WO₃ to a W^{+5} state and the oxidation of M^+ to form M₂O [44].

2.5 Optical properties

2.5.1 Coloration effeciency

The most important parameter of electrochromic device is the color change. The contrast ratio is expressed in equation below:

$$CR = \frac{T_b}{T_c}$$
(2.2)

Where:

T_b represents the light transparency in bleached states.

T_c represents the light transparency in colored states.

Higher CR indicates larger difference in transmittance and hence higher coloration efficiency.

For a given of electrochromic device, CR and absorbance (A), could evaluated together, where A is equal to change of optical density Δ OD (λ),

$$A = \Delta OD(\lambda) = \log \frac{T_b}{T_c}$$
(2.3)

Optical density change, $\Delta OD(\lambda)$, can also be expressed by [45],

$$\Delta OD (\lambda) = \eta Q = CE Q \qquad (2.4)$$

Where:

Q is the injected electronic charge per unit area to switch the electrochromic thin film from the colored to the transparency state. η or CE indicates the coloration efficiency and its measured in (cm²/C).

It appears from Eq. (2.4) that the coloration effecience is proportional to $\triangle OD$ and inversely proportional to the injected charge per unit area.

$$CE = \frac{\Delta OD(\lambda)}{Q}$$
(2.5)

High coloration efficiency means large difference in transmittance with a little amount of electric charge. [46].

2.5.2 Film thickness

Transmission spectra of the thin films is an important feature to determine the thickness of transparent thin films. Considering a thin film of refractive index (n) deposited on a transparent substrate of refractive index (n_1) (figure 2.5). the refractive index of the substrate can be calculated using equation below: [47]

$$n_{1} = \frac{1}{T_{s}} + \left(\frac{1}{T_{s}^{2}} - 1\right)^{1/2}$$
(2.6)

where Ts is the interference-free transmission of the substrate.

	R
<i>n</i> ₀ = 1	T ₀ = 1
Film d	n
Substrate	<i>n</i> 1
$n_0 = 1$	т

Fig. (2.5): System made of an absorbing thin film on a thick finite transparent substrate [47].

In the UV-visible range, two region can be distinguished, the first one is a strong absorption region and the other is interference transmission region fig.(2.6).



Fig. (2.6): Typical transmission spectrum for a uniform TCO thin film [48]. $T_{max} (\lambda)$ and $T_{min}(\lambda)$ illustrated in fig.(2.6) occur for

$$2nd = m\lambda \tag{2.7}$$

Where: m=integer of maxima or half integer of minima, d is equal thin films thickness.

The real part of the complex refractive index equal:

$$n = \left[F + \left(F^{2} - n_{0}^{2}n_{1}^{2}\right)^{1/2}\right]^{1/2}$$
(2.8)

And

$$F = \frac{n_0^2 + n_1^2}{2} + 2n_0n_1\frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{max}}T_{\text{min}}}$$
(2.9)

Where n_0 is the real part of refractive index of the air and n_1 for the substrate. Real part of refractive index is determined from T_{max} , T_{min} with n_1 and n_0 are known, after calculating *n*, one can find the film

thickness, which can be calculated from the two successive maxima or

minima using the relation (2.8 and 2.9), and this equation

$$d = \frac{\lambda_1 \lambda_2}{2[n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1]}$$
(2.10)

where λ_1 and λ_2 are the wavelengths of two successive maxima or minima.

2.5.3 Energy band gap

There are three main kinds of energy bands:

- 1. The conduction band (CB): the set of electron orbitals , in this band the electrons are free to move, so the electrons here contribute to the electrical conductivity.
- 2. The valence band (VB): this band is filled with electrons and these electrons do not contribute to the electrical conductivity.
- 3. Energy gap: It is a forbidden gap which separate top of the conduction band and bottom of the valence bands[50,51].

The sorting of materials to the physical states (conductor, semiconductor or insulator according to the size of band gap.

- Insulator : large gap between valence band and conduction band , so large amount of energy is needed for electrons to shift from valence to conduction band and energy gap ranges between (4-12 eV)[51].
- 2. Semiconductor: small gap between conduction and valence band, the gap is less than 4eV.
- 3. Conductor : The valence band is partially filled with electrons which are exist in the conduction band so the current easy to flow.



Fig 2.7 :The conduction and the valence bands in conductor, semiconductor and insulator [51].

Because the conduction and valence bands are overlapping in conductors, the conductivity is very large as a result of valence electrons easy jump to the conduction band. In insulators, the gap is very wide, so the electrons in valence band can not be raised to the conduction band and the conductivity is absent for this material. Even at room temperature, the energy gap is small in semiconductors, so any electron exist in valence band can absorb the amount of energy that is the same of energy gap and then can release from valence band to conduction band.

When electrons release from valance band they leave holes, also these holes can also contribute in the electrical conduction as shown in figure (2.8).



Fig 2.8: In direct band gap. (a) Electrons (solid dots) occupy the (V.B), (b) electrons leave holes in (V.B) when they are excited to (C.B) [52].

2.5.4 Absorption coefficient (α):

Absorption coefficient is a quantity that measure how much materials absorb the light. It can be measured by knowing the film thickness and transparency spectra as shown in Eq.(2.11) below [53].

$$\alpha = -\frac{1}{d}\ln(T) \tag{2.11}$$

Where: d is the film thickness and T is the transparency spectra.

2.5.5 Energy band gap determination:

Determination of the band gap of any materials is important in the semiconductor, solar industries and nanomaterial. It can be found by many techniques such as it is measured from the reflection and absorption spectra by spectroscopy and from the thermal activation energies in electrical conductivity measurement, or from photoconductivity measurement [50]. In both direct transition and indirect transition, the transition may be

In both direct transition and indirect transition, the transition may be allowed or not allowed due to the transition probability, and it is independent of energy. The optical absorption coefficient (α) is given by following equation [54].

$$\alpha = \frac{B\left(E - E_{s}\right)^{p}}{E}$$
 (2.12)

Where:

B: constant related to the transition probability

 E_g : energy band gap.

P: index which is depending on the optical absorption type and it take several values such as 2 for indirect allowed, 3 for indirect forbidden, 1/2 for direct allowed or 3/2 for direct forbidden transitions.

 α is larger than 10⁴ cm⁻¹ in the high absorption region , and in low absorption region is less than 10⁴ cm⁻¹.

When α is plotted versus *E*, it will be seen that at the absorption coefficient edge α increases rapidly above background, so the energy gap can be measured by extrapolating the linear part of absorption to the value of absorption coefficient which is assumed to represent background [50,55].

2.6 Electrochromic properties

2.6.1 Chronoamperometry (CA)

In a chronoamperometry measurements the current measured as a function of time as a result of potential pulse. When the experiment started, the potential of the working electrode at t = 0 is equal *Ei*. Then the

potential is varied to *E1* instantaneously, so corresponding current time response is recorded as illustrated in Fig. 2.7.b.



Fig. (2.9) The chronoamperometric experiment. **a**) The potential-time profile applied during experiment. **b**) The corresponding response of the current [56].

The anodic and cathodic charge density Q_a and Q_c respectively are calculated by integration the (current density – time) graph, where Q_a is associated with positive current density (+J) and Q_c is associated with negative current density (-J). For reversible reaction, the ratio between Q_a and Q_c is equal one.



Fig. 2.10: Chronoamperometry curve showing current () response with applied potential (---) [56].

2.7 Electrochemical properties

2.7.1 Cyclic voltammetry (CV)

Cyclic voltammetry is a method which is applying continuous cyclic potential to working electrode [57]. So the voltage is swept periodically and linearly between (V_1, V_2) at given potential scan rate. V_1 and V_2 are called the switching potentials because the voltage reaches V_2 , then is inverted to its original value V_2 .



Fig. (2.11): Voltage swept during CV experiments.

Cyclic voltammograms has several properties .firstly, the positions of peak voltage is changed, and the peak currents increases as the scan rate increases. As shown in Fig. (2.12.b), the ratio between the anodic peak current (i_{pa}) and the cathodic peak current (i_{pc}) is equal to one. And the peak currents are proportional to the square root of the scan rate [58].



Fig. 2.12: A typical cyclic voltammograms recorded for a reversible single electrode transfer reaction a) at one scan rate b) at different scan rate [58]. For reversible case, the peak current is represented by the Ranndles-Sevcik equation which is:

$$i_{n} = (2.69 \times 10^{5}) n^{\frac{3}{2}} AD^{\frac{1}{2}} C v^{\frac{1}{2}}$$
(2.13)

where:

i_p: the peak current.

n: number of electrons used in the redox event.

A: electrode area.

D: diffusion coefficient.

C: concentration of active metal ion in the electrolyte.

v : scan rate.

If the current peak increased, the diffusion coefficient increased too as seen from equation (2.13).

2.8 Dip Coating

Dip coating technique is a method where the pre-cleaned substrate is immersed in a solution and then withdrawn with a constant withdrawal

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speed at temperature and atmospheric conditions [59]. Fig.(2.17) represents the dip coating technique .



Fig (2. 13): Schematic presentation of the stages of the dip coating process [59]. This technique can be divided into three steps :

• Immersion: The pre-cleaned substrate is dropped in solution at a constant speed.

• Wet layer formation: The substrate has kept in the solution for several minutes. When the substrate is leaving the prepared solution, thin layer precipitate on this substrate. Then, the substrate is withdrawn at fixed speed so that any extra liquid will drain from the surface.

• Evaporation: The solvent vaporize and thin layer forms .

Chapter Three Experimental Work
Chapter Three

Experimental Work

3.1 Materials and film preparation

3.1.1 Chemical materials :

Chemical materials which are used for film preparation are purchased in its pure form, from different companies, which is listed below:

- 1) Tungsten chloride (WCl₆) and Titanium Chloride (TiCl₂) were bought from Sigma-Aldrich (99.99%).
- 2) Zinc Chloride (ZnCl₂) was bought from Chem. Samuel.
- 3) Sulfuric acid (H_2SO_4) was prepared in Biolab.
- 4) Ethanol, methanol, acetate, glycerol a hydrochloric acid (HCl) are selfpacking locally.
- 5) Florine-doped tin dioxide on glass (FTO/ glass) samples was bought from Sigma-Aldrich.

3.1.2 Preparation of WO₃ based films using sol-gel technique

a) Substrate Cleaning Process

FTO/glass substrate which has dimensions of $5 \times 1 \text{ cm}^2$ was used to settle WO₃-based electrochromic films. The FTO/glass substrate was cleaned using the following steps:

- 1) Cleaning FTO with acetate to remove any attachments on it.
- 2) Washing it with soap to clean any dusts or attachments.
- 3) Washing it with deionized water to remove soap remains.
- 4) Dipping it with methanol to dissolve any oily attachments.

5) Dipping it in HCl (10% concentration) for 5 seconds to melt any uncleaned attaches.

6) Washing it again with deionized water

7) The substrate was dried and packed with lenses papers to be utilized in sol-gel /dip- coating process.

b) Sol-gel solution preparation

 WO_3 electrochromic thin films doped with Ti and/or co-doped with Zn atoms have been prepared, onto FTO/Glass substrates by sol-gel solutions.

c) Sol-gel solution for WO₃ co-doped with Ti and Zn (WO₃:Ti:Zn) films

In a previous study, the best sample of WO₃ doped with Ti alone was $(W_{0.95}Ti_{0.05} O_3)[66]$. For the WO₃ co-doped with Ti and Zn, we will keep the same W molar concentration ratio to 0.95, Zinc atoms were added to compensate 0.05 of Ti atoms in the WO₃ amorphous structure. The empirical formula is assumed to be "W_{0.95}Ti_{0.05-y}Zn_y O₃" after annealing the films .In order to prepare 0.4 M sol-gel solution of W_{0.95}Ti_{0.05-y}Zn_y O₃. ZnCl₂ ,TiCl₂ and WCl₆, with a suitable molar concentration (see table) were dissolved in 10 mL of ethanol and 1.0 mL of glycerol (binding material in sol-gel solution). This solution was stirred continually with repeated sonificating and stirring for 2h. As noticed, The color of the solution changes from yellow to dark blue . Table (3.1) : List of nominal composition, Titanium (II) Chloride mass, and Zinc (II) chloride mass used in the sol-gel preparation. All sol-gel solutions contain 1.658 gm of Tungsten (VI) chloride.

Sample number	Composition	Titanium (II) Chloride (gm)	Zinc (II) Chloride (gm)
1	W _{0.95} Ti _{0.05} O ₃	0.026	0
2	$W_{0.95}Ti_{0.04}Zn_{0.01}O_3$	0.021	0.006
3	W _{0.95} Ti _{0.03} Zn _{0.02} O ₃	0.016	0.012
4	W _{0.95} Ti _{0.02} Zn _{0.03} O ₃	0.011	0.018
5	W _{0.95} Ti _{0.01} Zn _{0.04} O ₃	0.005	0.024
6	W _{0.95} Zn _{0.05} O ₃	0	0.030



Fig. (3.1): Steps of preparing sol-gel solution: (a) weighting, (b) stirring, (c) sonificating, (d) the color change of the solution from yellow to blue.

c) Dip-Coating Process

Using dip coating process to deposite the sol-gel solution on the pre-cleaned FTO/Glass substrate [59].



Fig (3.2): Procedure of WO₃-based films deposition by dip coating process.

Dipping was done using dip coater which was designed at physics department by Dr.Iyad Saadeddin and Mr.Mohammad Bahjat, is shown in figure (3.2).

The steps of dip coating process are abbreviated below:

- 1) A beaker which has a prepared sol-gel was put under the motor (see figure (3.2).
- 2) To get one thin layer on FTO side of the film, the glass substrate was coated by Adhesive tape.
- 3) The cleaned FTO/glass substrate was immersed in the sol-gel solution with a speed of 9.43×10^{-4} m/s. This slow speed to obtain sufficiently

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thin film. The upper part of the substrate was not dipping in the prepared solution in order to hold it easyly.

- 4) The FTO/glass substrate was immersed for 10 minutes to obtain good exposure of the substrate film.
- 5) Drawing the Film/FTO/Glass with the same speed mentioned above.
- 6) The coated film was kept above the beaker for 10 min to evaporate the solvent.
- The coated film was left for one day to dry under atmospheric pressure.
- B) Grown films were immediately annealed at 350 °C under air into the oven for 1.5 hours.

The steps for preparing the two layers on FTO/glass substrate:

- 1) Repeat the previous steps from 1-6.
- 2) The coated film was dried under 100 °C for 15 minutes.
- 3) Redeposit it another time using the same technique.
- 4) The new film was dried under 100 °C for 15 minutes.
- 5) Grown film was annealed at 350 °C under air into the oven for 1.5 hour.

3.2 Measurements

3.2.1 Cyclic voltammetry (CV)

The cyclic voltammetry measurements was achieved by using three electrodes electrochemical cell that is containing $0.125 \text{ M H}_2\text{SO}_4$ as an electrolyte. CV measurements were obtained at room temperature by using the PGZ402 Universal Potentiostat. The potential steps between ±800 mV,

against reference electrode (Ag/AgCl), at a scan rate of 100 mV/s. For all thin film, 20 cycles have been taken.

3.2.2 Transparency during Chronoamperometry

Transparency during Chronoamperometry measurements were achieved, at room temperature, using Shimadzu UV-3101PC UV-Vis-NIR scanning spectrophotometer connected with the PGZ402 Universal Potentiostat. The measurements were done in the three electrode electrochemical cell, the potential was varied between -800 mV and +800mV against Ag/AgCl reference electrode, in 0.125 M H₂SO₄ solution at $\lambda = 633$ nm.



Fig (3.3): Transparency during Chronoamperometry measurements

3.2.3 Transmittance

The transmission of light using single wavelength was done by using Shimadzu UV-3101PC UV-Vis-NIR scanning spectrophotometer and recorded against time in the wavelength range from 300 to 1000 nm, The results are analyzed for determining the thickness and energy band gap.

Chapter Four Results and Discussion

Chapter Four

Result and Discussion

Impurities and imperfections drastically affect the optical and electrical properties of materials. As for example, the addition of Ti and Zn atoms to WO_3 is reported to change the conductivity, and most of other electrical properties. As a result here in this work, electrochromic thin films of WO_3 nanoparticles, doped with 5% of Ti molar concentration and co-doped with different molar concentrations of Zn atom, have been prepared and studied involving different measuring techniques.

4.1 X-Ray diffraction (XRD):

The structural tests of all thin films were done by XRD method. The XRD patterns for $W_{0.95}Ti_{0.05-x}Zn_xO_3$ are shown in fig. (4.1). As seen no intensive patterns were observed. The non intensive X-ray reflections indicate the amorphous nature structure. This result is acceptable as compared with literature data which indicates the existence of some polycrystalline grains inside an amorphous. Seen of grains consistent with literature data [62].



Fig. (4.1): XRD patterns of Ti and Zn doped WO_3 .

4.2 Optical properties:

4.2.1 Film thickness :

The transmission spectra for FTO/glass substrate, single and double layer of $W_{0.95}Ti_{0.01}Zn_{0.04}O_3$ were scanned versus air (reference) at wavelength varied between (300-1000) nm and against a reference cell which contains (0.125 M H₂SO₄) which was experimentally determined as an appropriate ratio.

The transmission of FTO/glass (ref.) relative to the air is represented in figure (4.2.a) and it reached 62%, the transparency of single layer of $W_{0.95}Ti_{0.01}Zn_{0.04}O_3$ film is roughly half of the reference transparency 28% (figure 4.2.b), also the transparency of double layer film is about half of the single layer and it's equal 14% as shown in figure (4.2.c).



Fig.(4.2): Transparency spectra for a)FTO/glass substrate, b) one layer/FTO/glass substrate, c) two layers/FTO/glass substrate.

As shown in these figures, transparency decreased as a number of layer increased and the thickness of layer is increased too .To calculate the film thickness from the previous figures, T_{max} and T_{min} were taken from each

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graph to find the refractive index using (eq.2.8 and 2.9) by substitute $n_0=1$ for air and $n_1=1.55$ for glass and to calculate the film thickness calculated by using (eq.2.10).

At first FTO/glass substrate thickness was calculated then the thickness of single layer film /FTO/glass substrate, and the second one substract from the first one to obtain the thickness of single layer alone. By using the same technique, the thickness of double layer is evaluated and the result is detailed in table (4.1)

ay	vers film	S.						
	Sampl e	n (λ ₁)	$n(\lambda_2)$	T_{max} % (λ_1)	T_{max} % (λ_2)	$T_{min}\% \ (\lambda_1)$	$T_{min}\% \ (\lambda_2)$	Thickne ss (nm)
	FTO/g lass	2.16	1.86	59.93	66.15	51.08	61.19	343
	One layer/ FTO/g lass	2.04	1.85	28.31	30.00	26.67	28.98	422
	Two layers/ FTO/g	1.87	1.91	13.40	14.22	13.18	13.93	901

lass

Table (4.1): Thickness in (nm) and refractive index for 1, 2 and 3layers films.

As shown in the table, the thickness of the 1st layer was 79 nm ,the thickness of second dipping in the sol-gel was increased by 479 nm and the thickness of three layers was expected to be 1037 (increment by 479 nm)[61].

These result are explained by the types of materials which are deposited on the substrate, the single layer is deposited onto FTO/glass which are two different materials (weakly adhesioned), but the 2^{nd} layer was deposited on the one layer of $W_{0.95}Ti_{0.01}Zn_{0.04}O_3$ which are the same material (more adhesion) due to existence of dangling bonds which are attached to other molecules, also the 3^{rd} one is deposited on the second layer which are the same material, so we expect the same increment for the 3^{rd} layer (479 nm), higher thickness is obtained due to more and more adhesion interface [61].

4.2.2 Energy band gap:

The electrons in crystal are arranged in energy bands separated by regions in energy for which no wavelike electron orbitals exist. Such forbidden regions are called energy gaps, and results from the interaction of the conduction electron waves with the ion cores of the crystal.

Energy gap was calculated by plotting $(\alpha h \upsilon)^2$ vs $(h \upsilon)$ through considering the direct allowed electronic transitions type of the band gap [62].

Where α is absorption coefficient, h is planck constant and υ is the frequency, and it's calculated by eq.(2.11)



Fig. (4.3): The plot of $(\alpha E)^2$ as a function of (E) for 1layer/FTO/glass substrate, two layers/FTO/glass substrate and three layers/FTO/glass substrate.

The E_g is determined and registered in table (4.2).

Table (4.2): energy gap in (eV) for one, two and three layers of $W_{0.95}Ti_{0.01}Zn_{0.04}O_3$

Sample	E _g (eV)		
Dip1	3.91		
Dip 2	3.87		
Dip 3	3.83		

As it's seen from this table the energy band gaps are close to each others. This is due to transparent property of the film because it's prepared in the transparent state in these measurements. It is observed that the band gap is decreasing with the increasing of film thickness, which is due to increase in the number of electrons as a result of reduction process[61].

The energy band gap for $W_{0.95}Ti_{0.05-x}Zn_xO_3$ thin films also measured using the same technique and they are expected to have large energy band gaps in the range 3 to 4 eV, which correspond to photon wave length range of about 300-400 nm. While they are absorbed, these photons induce electronic transitions from the valence band to the empty energy states in the conduction band.



Fig. (4.4): The plot of $(\alpha E)^2$ as a function of (E) for WO₃, W_{0.95}Ti_{0.05}O₃, W_{0.95}Ti_{0.04}Zn_{0.01}O₃, W_{0.95}Ti_{0.02}Zn_{0.03}O₃, W_{0.95}Zn_{0.05}O₃.

As shown from figure (4.4), the energy gap of WO_3 is observed about 3.27 eV and 3.28 eV after doping with 5% of Ti.

The energy band gap is equal 3.37, 3.39 and 3.4 for $W_{0.95}Ti_{0.04}Zn_{0.01}O_3$, $W_{0.95}Ti_{0.02}Zn_{0.03}O_3$, $W_{0.95}Zn_{0.05}O_3$ respectively.

The observed slight increase of E_g as the percentage of doping is increased, and this due to slight increase of carrier concentration.

4.3 Electrochromic properties

4.3.1Coloration efficiency:

Coloration efficiency is the most important parameter in electrochromic device, transparency during chronoamperometry for 1000 cycles was carried out for all prepared thin films to calculate the coloration efficiency.











Fig. (4.5): Transmission spectra up to 1000 cycle for (a) WO_3 b) $W_{0.95}Ti_{0.05}O_3$, (c) $W_{0.95}Ti_{0.04}Zn_{0.01}O_3$, (d) $W_{0.95}Ti_{0.03}Zn_{0.02}O_3$, (e) $W_{0.95}Ti_{0.02}Zn_{0.03}O_3$, (f) $W_{0.95}Ti_{0.01}Zn_{0.04}O_3$, (g) $W_{0.95}Zn_{0.05}O_3$.

The more transmittance in bleach state (T_b) and the less transmittance in color state (T_c) is needed to obtain high coloration efficiency and efficient electrochromic device. As shown from these previous figures, the $W_{0.95}Ti_{0.04}Zn_{0.01}O_3$ has more transparency in bleach state (77.4%) and less transparency in color state (40.7%). Cathodic charge Q_c evaluated by integration the cathodic current with respect to time and coloration efficiency was calculated by using equation (2.4) and (2.5) for WO_3 , $W_{0.95}Ti_{0.05}O_3$, $W_{0.95}Ti_{0.04}Zn_{0.01}O_3$, $W_{0.95}Ti_{0.03}Zn_{0.02}O_3$, $W_{0.95}Ti_{0.02}Zn_{0.03}O_3$, $W_{0.95}Ti_{0.01}Zn_{0.04}O_3$ and $W_{0.95}Zn_{0.05}O_3$ for the cycle number 100, 500 and 1000 are registered in the table (4.3).

Table (4.3): coloration efficiency for thin film doped with Ti 5% andco-doped with different molar concentration of Zn atom.

Sample	C.E(cm ² /C)	C.E(cm ² /C)	$C.E(cm^2/C)$	
	(cycle number	(cycle number	(cycle number	
	100)	500)	1000)	
WO ₃	1.16	1.04	1.31	
W _{0.95} Ti _{0.05} O ₃	14.31	14.52	15.04	
W _{0.95} Ti _{0.04} Zn _{0.01} O ₃	19.16	21.58	22.20	
W _{0.95} Ti _{0.03} Zn _{0.02} O ₃	8.18	7.52	0.81	
W _{0.95} Ti _{0.02} Zn _{0.03} O ₃	12.02	11.66	8.22	
W _{0.95} Ti _{0.01} Zn _{0.04} O ₃	0.94	0.05	0.26	
W _{0.95} Zn _{0.05} O ₃	7.71	6.21	4.68	

As noticed from the table (4.3), the higher coloration efficiency obtained after co-doped thin film in Zn atom with 1% percentage and means that the larger surface area are exposed to reaction may be as a result to less grain size, after doping with 5% Ti and co-doping 1% Zn, the electrochromic materials are improved due to improve in C.E.

It's worth notifying that there is abnormal values of C.E for $W_{0.95}Ti_{0.03}Zn_{0.02}O_3$ and $W_{0.95}Ti_{0.01}Zn_{0.04}O_3$ and this related to film degrades and it's material appears in solution.

The anodic and cathodic charge density Q_a and Q_c respectively were calculated by integration the (current density – time) graph , where Q_a is associated with +J and Q_c is associated with –J. For reversible reaction, the ratio between Q_a and Q_c must be one unit.

Sample	Q _a (mC/cm ²)	Q _c (mC/cm ²)	Q _a /Q _c	t _b (s)	t _c (s)				
WO ₃	26.517	28.165	0.940	2.4	3.0				
W _{0.95} Ti _{0.05} O ₃	15.386	16.390	0.930	1.8	3.0				
$W_{0.95}Ti_{0.04}Zn_{0.01}O_3$	13.761	14.565	0.950	1.2	2.4				
$W_{0.95}Ti_{0.03}Zn_{0.02}O_3$	22.436	23.641	0.940	2.4	3.0				

24.905

10.911

26.171

23.652

9.654

24.831

0.950

0.880

0.940

2.4

1.8

1.8

3.0

2.4

3.0

W_{0.95}Ti_{0.02}Zn_{0.03}O₃

 $W_{0.95}Ti_{0.01}Zn_{0.04}O_3$

 $W_{0.95}Zn_{0.05}O_3$

Table (4.4): the ratio between Q_a and Q_c and response time for all films and for cycle number 100.

Table (4.4) shows that Q_a is less than Q_c due to quasi reversible reaction which result from slow electron exchange of the redox species with the working electrode. It seems that all co-doped film except for $W_{0.95}Ti_{0.01}Zn_{0.04}O_3$ represent a good quasi reversible process [60]. It is worth noting that Zn has electronic configuration that [Ar]3d¹⁰4s² and ionic radius is 134pm and this ionic radius is less than tungsten (137 pm), it means that there should be some additional separation which reduces the atomic stress leading to a relaxation process that changes the lattice constant, so changing the lattice constant will change all the physical parameters[63].

4.3.2: Switching time

The response time for coloring and bleaching were calculated from (J-t) graph under chronoamperometry measurements which are shown in Fig.(4.6) and it offers fast switching time. It's worth notifying that the response time for bleaching is less than in coloring, so the bleaching process is faster than the coloration in all films.





Fig. (4.6): Current density with time for WO₃:Ti:Zn WO₃, $W_{0.95}Ti_{0.05}O_3$, $W_{0.95}Ti_{0.04}Zn_{0.01}O_3$, $W_{0.95}Ti_{0.03}Zn_{0.02}O_3$, $W_{0.95}Ti_{0.02}Zn_{0.03}O_3$, $W_{0.95}Ti_{0.01}Zn_{0.04}O_3$, $W_{0.95}Zn_{0.05}O_3$. Experiment was performed at a scan rate 100 mV/s.

4.3.3: Stability

To examine the stability and to know how long the cycle life was for the films.The transparency during chronoamperometry was tested for all doped and co-doped thin films.

C.E was measured for cycle number 2, 100, 200,...., 900 and 999 for all prepared films and illustration in figure (4.7) below.



cycle number

Fig. (4.7): C.E vs cycle number for WO₃, $W_{0.95}Ti_{0.05}O_3$, $W_{0.95}Ti_{0.04}Zn_{0.01}O_3$, $W_{0.95}Ti_{0.03}Zn_{0.02}O_3$, $W_{0.95}Ti_{0.02}Zn_{0.03}O_3$, $W_{0.95}Ti_{0.01}Zn_{0.04}O_3$ and $W_{0.95}Zn_{0.05}O_3$.

As the figure (4.7) indicates, owing to the most stability, largest contrast ratio and the largest C.E values, the $W_{0.95}Ti_{0.04}Zn_{0.01}O_3$ film can be regarded as the most stable. This film has less response time as shown in table (4.4), so it's the fastest during bleaching and coloring process.

As a complementery work, the stability was checked for a high number of cycle, WO₃, $W_{0.95}Ti_{0.05}O_3$, $W_{0.95}Ti_{0.04}Zn_{0.01}O_3$ and $W_{0.95}Zn_{0.05}O_3$ are chosen for this purpose, and transparency during chronoamperometry was measured up to~ 5000 cycle and the coloration efficiency was calculated and illustrated in fig. (4.8) as a function of cycle number.



Fig. (4.8): C.E as a function of cycle number up to ~5000 cycles for a) WO₃, b) $W_{0.95}Ti_{0.05}O_3$, c) $W_{0.95}Ti_{0.04}Zn_{0.01}O_3$, d) $W_{0.95}Zn_{0.05}O_3$.

As it is showed in figure (4.8), the $W_{0.95}Ti_{0.04}Zn_{0.01}O_3$ film is the most stable sample because it has the most C.E up to ~5000 cycles , so it is the best electrochromic thin film.

4.4 Electrochemical properties

4.4.1 Cyclic voltammetry:

Cyclic voltammetry measurements were taken for $W_{0.95}Ti_{0.05-x}Zn_xO_3$ thin film, where x ranges from 1-5%, the potential was cycled between ±0.8V in 0.125 M H₂SO₄ against reference electrode (Ag/AgCl) at 100mV/s scan rate.



Fig. (4.9): Cyclic voltammetry measurements of the $W_{0.95}Ti_{0.05-x}Zn_x$ with x changes from 0-5 % at the scan rate of 100 mV/s.

As shown in figure (4.9), the scan start from left to right side of the plot and it reaches a peak before dropping down, also there is a change in the peaks position and these may be related to the formal potential of the redox process and the size of the diffusion layer.

The value of i_p for H⁺ ions is used to calculate the diffusion coefficient by using eq. (2.13).

Sample	Peak	Current	Density	Diffusion	Coefficient	
	(mA/c	2) cm ²)		(cm^2/s)		
W _{0.95} Ti _{0.05} O ₃	5.490			40.15×10 ⁻¹⁰		
W _{0.95} Ti _{0.04} Zn _{0.01} O ₃		5.725		42.43×10 ⁻¹⁰		
W _{0.95} Ti _{0.03} Zn _{0.02} O ₃	4.041			21.74×10 ⁻¹⁰		
$W_{0.95}Ti_{0.02}Zn_{0.03}O_3$	4.646		28.76×10 ⁻¹⁰			
$W_{0.95}Ti_{0.01}Zn_{0.04}O_3$	3.753			18.76×10 ⁻¹⁰		
$W_{0.95}Zn_{0.05}O_3$	4.840			31.21×10 ⁻¹⁰		

Table (4.5) : Calculation of diffusion coefficient using Randles-Sevcik equation.

It is clear that diffusion coefficient increases as anodic peak current increases due to the size of the diffusion layer that arises from difference in material defects arising different dopant.

4.5 General Conclusions:

Doping WO3:Ti with Zn was found to improve the electrochromic

properties of the prepared thin films.

Hence, higher contrast ratio and higher coloration efficiency will be obtained after co-doping films, good reversibility and fast switching time are obtained after co-doping it. Moreover, $W_{0.95}Ti_{0.04}Zn_{0.01}O_3$ represent good stability (up to ~5000 cycle).

Furthermore, higher thickness is obtained due to more and more adhesion interface as number of layer is increased.

Suggestions for Further Works

The author suggest the following for the new electrochromic electrode WO₃:Ti:Zn for future work:

1) Doing more analysis for the films as: XRD, PL, SEM, TEM,

AFM, etc.

2) Preparing WO₃ thin films using different techniques.

3) Studying the electrochromic properties when the films annealing with different temperatures.

4) Studying the previous films characteristics with different electrolytes and different electrolyte concentrations.

5) Doping with different materials such as: Sn, F, Li, etc.

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كلية الدراسات العليا

خصائص التلوين الكهربائي لأكسيد التنجستون المطعم بالتيتانيوم والخارصين

قدمت هذه الأطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في الفيزياء بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس – فلسطين.

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خصائص التلوين الكهربائى لأكسيد التنجستون المطعم بالتيتانيوم والخارصين

الملخص

في هذا البحث تم تحضير أفلام WO₃ الرقيقة النانوية على شرائح من الزجاج الموصل (FTO/glass) باستخدام طريقة السول-جل (الطلاء بالغمس). طعمت هذه الأفلام بمركبات عنصري التيتانيوم (Ti) والزنك (Zn) بتركيز 5% للعنصر الأول ومن 1%-5% للعنصر الثاني. تم دراسة خصائص عدة لتلك الشرائح بهدف المقارنة بينها، منها: سلوك التلوين الكهربائي واقتران الفولتية الدوري و أطياف النفاذية. تم دراسة الية التلوين أثناء التجارب المختلفة في المحلول الكهرلي 20.00 مولار من حمض الكبريتيك، وحسبت كذلك كمية الشحنة الداخلة والخارجة من الطبقة خلال عملية التلوين بالاضافة الى فعالية التلوين. تم فحص استقرار العينات في حمض الكبريتيك، وحسبت كذلك كمية الشحنة الداخلة والخارجة من الطبقة خلال عملية التلوين بالاضافة الى فعالية التلوين. تم فحص استقرار العينات في حمض الكبريتيك ل 5000 دورة على الأكثر. وتم حساب سمك الفلم وفجوة الطاقة و كل النتائج في حمض الكبريتيك ل 5000 دورة على الأكثر. وتم حساب سمك الفلم وفجوة الطاقة و كل النتائج الشارت الى أن تطعيم مادة أكسيد التنجستون بالتيتانيوم والزنك معا بتراكيز معينة يحسن من التلوين الكهربائي الكهربائي والمحارت الى أنها المحلوين العملية التلوين. تم فحص استقرار العينات المحلول الكبريتيك ل 5000 دورة على الأكثر. وتم حساب سمك الفلم وفجوة الطاقة و كل النتائج في حمض الكبريتيك ل 5000 دورة على الأكثر. وتم حساب سمك الفلم وفجوة الطاقة و كل النتائج في حمض الكبريتيك ل 5000 دورة على الأكثر. وتم حساب سمك الفلم وفجوة الطاقة و كل النتائج أشارت الى أن تطعيم مادة أكسيد التنجستون بالتيتانيوم والزنك معا بتراكيز معينة يحسن من التلوين