

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**SYNTHESIS AND ANALYSIS OF TUNGSTEN OXIDE-BASED
CHROMOGENIC SYSTEMS**

M.Sc. THESIS

Amin TABATABAEI MOHSENI

Graduate School of Science Engineering and Technology

Nanoscience & Nanoengineering Program

Thesis Advisor: Assoc. Prof. Dr. Esra ÖZKAN ZAYİM

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*To my parents and professors with love,
who shaped my identity and prepared me for future.*

FOREWORD

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ABBREVIATIONS

ECD	: Electrochromic Devices
PC	: Photochromic
GC	: Gasochromic
PVP	: Polyvinylpyrrolidone
DMF	: Dimethylformamide
AIPTA	: Acetylated Peroxotungstic Acid
SEM	: Scanning Electron Microscope
XRD	: X-Ray Diffraction
FTIR	: Fourier Transform Infrared
XPS	: X-Ray Photoelectron Spectroscopy
EDS	: Energy-dispersive X-ray spectroscopy

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SYNTHESIS AND ANALYSIS OF TUNGSTEN OXIDE- BASED CHROMOGENIC SYSTEMS

SUMMARY

Photochromism (PC, for short) has been described as a reversible change in the color, or darkening of a material caused by absorption of more generally ultraviolet or visible light. The color change is often attributed to alteration in the structure of the compound. Because of high potential applications of photochromic materials such as active elements for various optical devices, data recording and storage, multi-color displays, optical memory and high-speed photonic switches, polarizers and beam splitters for optical communication and image processing and filters, extensive research on these materials still goes on to date.

In principle, both inorganic and organic materials can represent photochromic properties. Tungsten oxide has been regarded as the best candidate for chromogenic applications amongst inorganic materials because of its relatively high stability, durability, multifunctional properties as well as its high color efficiency. In accordance with its superior properties, both photochromic and electrochromic properties of tungsten oxide is well-studied since the original report on the photochromic properties of amorphous- WO_3 by Deb. Traditionally, tungsten oxides can be prepared in various forms by several techniques, such as electrodeposition, vacuum deposition, thermal evaporation, sputtering, sol-gel, molecular beam epitaxy (MBE), physical vapor deposition (PVD), chemical vapor deposition (CVD), casting and so on. Additionally, development of electrospinning and droplet drawing techniques allowed researchers to prepare nanofibers and microfibers of tungsten oxide, respectively.

Whilst electrochromism of tungsten oxide has been studied considerably, its PC properties has not drawn as much as attention as its electrochromism. This is so because tungsten oxide has been well-known to undergo irreversible color change, which largely limits its use as photochromic device. To date, electrochromic systems are preferred because of their ability to reversibly change color. Of course, the fact that electrochromic systems are traditionally made up of seven layers (such as electrode, electrolyte and so forth) and require a power supply renders their structure more complex. Despite of the limitation of irreversibility of tungsten oxides, still photochromic systems are favored over electrochromic systems since fabrication of PC systems, which is typically made up of two layers, is clearly less demanding.

Tungsten oxide films exhibit different electrical and optical properties depending on the used deposition technique and deposition parameters. Therefore, in this study, different deposition techniques were used and deposition parameters were changed in order to compare the structural, optical and chromogenic properties of tungsten oxides films. So far, many precursors such as tungsten hexachloride, metallic tungsten powder, WO_3 powder, tungsten (IV) isopropoxide, tungstic acid powder etc. have been utilized to acquire various forms of tungsten oxides.

In this work, we describe a novel procedure for tungsten oxide from tungsten hexachloride (WCl_6) and tungsten metallic powder (W) as precursors, exhibiting reversible photochromic properties, improved stability and lifetime. In addition, this procedure permits us to fabricate films as either nanofibers or microfibers, displaying photochromic effects. Furthermore, we have prepared thin films and

microfibers of the organic/inorganic blend of tungsten hexachloride and PVP, via electrospinning, spin coating, droplet drawing, casting and writing ink, given that the technique to prepare tungsten oxide is the prime determinant of size of the fibers and formation of the film. Our results indicate that tungsten oxide in the form of films and microfibers has PC properties (it is also worth noting that we have been unable to detect these PC effects with nanofibers so far, which is currently under investigation in our laboratory). Herein, we report that these structures, as photochromic materials, offers numerous advantages such as (i) the color change is relatively rapid, (ii) they have large optical modulation and last (iii) they possess long memory and long life-time. In overall, we believe that this reported procedure is a novel avenue to prepare photochromic materials, with superior properties.

In the first part of the experiment, tungsten oxide films were deposited by electrodeposition technique with WCl_6 , W metal powder and AIPTA precursors. Uniform films were obtained by this technique and thickness of these films can be controlled easily. Optical and structural characterizations of the as-deposited films were analyzed. In the second part of the experiment, the films were deposited by dip coating techniques. Sol-gel deposition technique is simpler, faster and needs less material, so cheaper than the other deposition techniques. Tungsten oxide films (by dip-coating) and tungsten oxide/PVP films (by spin-coating) were prepared in the second part. Finally, nanofibers of tungsten oxide were obtained by electrospinning technique using different precursors such as WCl_6 and W metallic powder besides PVP polymer. Microfiber tungsten oxide were collected with drawing with various thicknesses. Nanofibers and microfiber tungsten oxide were collected on different substrates such as glass, ITO coated glass, papers, metal surfaces.

This study covers the applications of the following techniques for the analysis of tungsten oxide structures: Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, X-Ray Diffraction (XRD) and X-Ray Photoelectron (XPS) are also used as complementary methods. Crystallinity, structural and chemical composition of the tungsten oxide structures were probed with these methods. FTIR and XPS are two methods used to extract information on the surface of the tungsten oxide. One of our aims is to find out the chemical and physical structure of thin films regarding the photochromic phenomenon. As on the most interesting chromogenic systems, photochromism is the main function of our thin layers and microfibers. We expose the films to a UV light source to check out the responses. The expected response can be a color change in visible electromagnetic spectrum range or only a change in chemical structure. Therefore, we need to characterize each film or fiber separately, once before applying UV light (as prepared form) and then after UV irradiation with UV-Vis. spectrophotometry and optical microscopy.

TUNGSTEN OKSİT BAZLI KROMOJENİK SİSTEMLERİNİN ÜRETİMİ VE ANALİZİ

ÖZET

Fotokromizm (PC) geri dönüşümlü renk değişimi olarak tanımlanır, ya da daha genel olarak morötesi veya görünür ışığın soğurulmasının bir sonucu olarak malzemenin renginin değişmesidir. Fotokromizm, optik cihazların aktif elmanı olarak, veri kaydı ve saklama işlemlerinde, çok renkli ekranlarda, optik bellek ve yüksek hızlı fotonik anahtarlarda, optik iletişim için polarizasyon cihazlarında ve ışık bölücülerde, görüntü işleme ve filtrelerde yüksek kullanım potansiyeline sahiptir. Bu nedenle bu tip malzemeler üzerindeki araştırmalar halen yoğun olarak devam etmektedir.

Prensip olarak, hem inorganik hem de organik maddeler fotokromik özellik gösterebilir. Tungsten oksit, nispeten yüksek stabilitesi, dayanıklılığı, çok fonksiyonlu özelliklerinin yanı sıra yüksek renk verimliliği nedeniyle inorganik maddeler arasında kromojenik uygulamalar için en iyi aday olarak kabul edilmiştir. Üstün özelliklerinden ötürü tungsten oksidin hem fotokromik özellikleri hem de elektrokromik özellikleri Deb'in amorf WO₃'ün fotokromik özelliklerini ile ilgili çalışmasından bu yana detaylı olarak incelenmiştir. Geleneksel olarak tungsten oksit, elektrodpozisyon, vakum biriktirme, termal buharlaştırma, püskürtme, sol-jel, moleküler ışın epitaksi (MBE), fiziksel buhar biriktirme (PVD), kimyasal buhar biriktirme (CVD) gibi çeşitli tekniklerle farklı şekillerde hazırlanabilir. Buna ek olarak, elektrospin ve damlacık çekme tekniklerinin gelişmesi, araştırmacılara sırasıyla tungsten oksit nanolifler ve mikrofiberler hazırlama imkânını sunmuştur.

Tungsten oksit filmler (WO₃) bugüne kadar üzerinde en çok çalışılan elektrokromik malzeme olmuştur. Tungsten oksit filmler gerilim uygulandığında tersinir olarak saydam halden mavi hale dönerler. Deb tarafından 1969'da ilk defa tungsten oksitin elektrokromik özellikleri rapor edildiğinden bu yana pek çok farklı elektrokromik malzeme farklı kaplama yöntemleri ile kaplanmıştır. Renklenme mekanizmasının esaslarını anlamak için tungsten oksit filmler en ideal malzemelerdir, çünkü; tungsten oksit filmler; termokromizm, fotokromizm ve elektrokromizm gibi çeşitli tiplerde renklenme özellikleri gösterirler; diğer elektrokromik malzemelerden çok daha detaylı çalışılmışlardır; bugüne kadar çalışılan çoğu elektrokromik cihazda en uygun optik fonksiyon gösteren tabaka olmuştur. Elektrokromik özellik gösteren diğer metal oksitlerin pek çoğunun fizik ve kimyası oldukça benzerdir; bu nedenlerle tungsten oksit filmler, optik olarak aktif tabakaların ana özelliklerini açıklayabilmek için güvenilir bir modeldir. Bütün bu nedenlerden ötürü tungsten oksit filmlere olan ilgi hala sürmektedir. Tungsten oksidin elektrokromik özellikleri önemli ölçüde çalışılmasına rağmen, fotokromik özellikleri elektrokromizm kadar dikkat çekmemiştir. Bunun sebebi tungsten oksidin ışığın etkisi ile renk değişiminin tersinirliğinin uzun ömürlü olmamasıdır ve bu nedenle tungsten oksidin fotokromik alanında kullanımı sınırlıdır. Genel olarak, tungsten oksit tersinir renk değiştirme özelliğinden ötürü elektrokromik sistemler tercih edilmiştir. Elektrokromik sistemlerin en yaygın tasarımı yedi katmanlı olan yapısıdır (elektrot, elektrolit ve diğerleri). Ayrıca güç kaynağı gereksinimi bulunmaktadır. Geri dönüşü olmayan renk değişimine rağmen fotokromik sistemler daha az zahmetli olan iki katmanlı üretim şekilleri sebebiyle elektrokromik sistemlere göre daha uygun bulunmaktadır ve güç kaynağı gereksinimi bulunmamaktadır.

Tungsten oksit filmler kaplama yöntemine ve kaplama parametrelerine bağı olarak çok farklı elektriksel ve optik özellikler sergilemektedir. Bundan ötürü bu çalışmada farklı yöntemlerle filmler kaplanmış ve kaplama parametreleri değiştirilip tungsten oksit filmlerin yapısal, optik ve elektrokromik özellikleri araştırılmıştır. Deneysel kısmın ilk kısmında, tungsten oksit ince filmler WCl_6 , W metal tozu ve AIPTA olmak üzere farklı başlangıç malzemeleri kullanılarak elektrodpozisyon yöntemi ile ITO kaplı camlar üzerine kaplanmıştır. Filmlerin kalınlıkları mümkün olduğunda aynı tutulmaya çalışılmıştır. Elektrodpozisyon yöntemiyle elde edilen tungsten oksit filmlerin optik ve yapısal analizleri yapılmıştır. WCl_6 başlangıç malzemesi ile tungsten oksit filmler hızlı, zahmetsiz ve az malzeme israfı ile düzgün şekilde kaplanmıştır. WCl_6 başlangıç malzemesi ile tungsten oksit filmler çalışmanın ikinci bölümünde sol-jel yöntemiyle kaplanmıştır.

Deneysel kısmı ikinci aşamasında filmler sol-jel yöntemlerinden olan daldırma yöntemi ile WCl_6 başlangıç malzemesi ile Corning cam taşıyıcılar üzerine kaplanmıştır. Bu aşamada literatürde çok yaygın olarak kullanılan WCl_6 ve etanol ile hazırlanan reçete kullanılmış ve SEM, XRD, EDS ve UV-Vis. Spektrofotometresi alınarak filmlerin optik, yapısal ve kimyasal analizleri yapılmıştır. Sol-jel yöntemi diğer kaplama yöntemlerine kıyasla daha basit, hızlı ve daha az malzeme kullanıldığı için ekonomiktir. Sol-jel yöntemi ile metal oksitleri ya da organik molekülleri birbirine karıştırarak kaplama yapmak mümkündür. Daha gözenekli filmler de kolaylıkla elde edilmektedir. Bu avantajlarından ötürü sol-jel yöntemi ile tungsten oksit filmler hem daldırma hem de döndürme yöntemleri ile kaplanmış ve karakterizasyonları yapılmıştır. Şimdiye kadar, tungsten oksit yapılar tungsten hekzaklorür, metalik tungsten tozu, WO_3 tozu, tungsten (IV) izopropoksit, tungstik asit tozu, W metali gibi birçok farklı başlangıç malzemeleri kullanılarak sol-jel, elektrodpozisyon, vakum buharlaştırma, sıçratma vb gibi farklı kaplama yöntemleri ile elde edilmişlerdir.

WCl_6 başlangıç malzemesi kullanılarak hem elektrodpozisyonla hem de sol-jel yöntemi ile tungsten oksit filmler hazırlanmış ve detaylı olarak optik, yapısal karakterizasyonları yapılmıştır. Çalışmanın üçüncü aşamasında, tungsten hekzaklorür (WCl_6) ve polivinilpirrolidon (PVP) organik/inorganik moleküllerin karışımı ile ince film ve mikroyapılar elde edilmiştir. Bu reçete literatürde daha önce bilinen yöntemler üzerine çeşitli avantajlar sağladığı gözlenmiştir. Bunlar şu şekilde özetlenebilir: İlk olarak, tersinir renk değişikliği gösteren filmler ve mikroyapıların elde edilmesine imkân vermektedir. İkincisi, ince filmde, mikro ve nanoliflere kadar farklı boyutlarda tungsten oksit yapıları elde etme imkânı vermektedir. Nanolifler, mikrolifler ve ince filmler farklı metotlar kullanılarak elde edilmiştir (elektrodpozisyon, döndürme ve daldırma kaplama, damlacık çizim ve elektrodöndürme gibi). Bu yapılar kağıt, cam, metal gibi pek çok farklı yüzeye uygulanabilmiştir. Bu reçete ile hazırlanan tungsten oksit yapıların optik ve elektrokimyasal analizleri, bu filmlerin ve liflerin büyük optik modülasyona ve yüksek tersinirliğe sahip olduğunu göstermiştir. Sonuç olarak, bu reçete ile hazırlanan tungsten oksit filmler ve mikrolifler tersinir fotokromik özellikler sergilemişlerdir.

Deneysel bölümün son kısmında, tungsten oksit nanolifler ve mikrolifler, WCl_6 ve W metal tozu başlangıç malzemesi kullanılarak metal, cam, ITO kaplı cam taşıyıcılar üzerine elektrodöndürme yöntemiyle toplanmıştır. AIPTA başlangıç malzeme kullanılarak mikro ve nanolifler elde edilememiştir. Tungsten oksit mikro ve nanolif oluşturma parametreleri optimize edilmiştir. Daha sonra bu tungsten oksit liflerin

altlıklara tuturulması ısıtıl işlem ile iyileştirilmiştir. Tungsten oksit lifleri elde etmek için 500°C’de kalsinasyon işlemi uygulanmış ve ortamdaki polimer uzaklaştırılmıştır. SEM, XRD, FTIR, XPS, UV-Vis. Spektrofotometre cihazları kullanılarak bu tungsten oksit yapıların, mikroyapısal, optik ve kimyasal analizleri detaylı olarak yapılmıştır. Özellikle WCl₆ başlangıç malzemesi ile elde edilen tungsten oksit/PVP mikrolifler ve filmler üstün fotokromik özellikler sergilemiştir. UV aydınlatmaya maruz bırakılan bu tungsten oksit yapılardan, tersinir ve yüksek ömre sahip PC sistemler elde edilmiştir.

1. INTRODUCTION

Thin-film technology is one of the oldest arts and one of the newest sciences at the same time [1]. A thin film is a layer of material that its thickness varies from few nanometers to several micrometers. The act of applying a thin film to a surface is called thin-film deposition. Depending on whether the process is primarily chemical or physical, deposition techniques fall into two main categories, which are introduced in section 1.1. Many applications benefit from thin-film construction such as electronic semiconductor devices and optical coatings [2]. Materials that respond to external excitations with spectral changes, especially coloration in the visible range, are electrochromic, thermochromic, piezochromic or photochromic respectively. Reversible transitions in molecular structure, symmetry and energy banding are very common in solids and liquids. The transitions are induced electrically, thermally, with pressure or by exposure to UV-visible radiation [3]. Materials in these classes may be prepared as thin films, nanofibers and microfibers. Photochromic effect of these materials are under investigation recently and they have a great role in this work.

In the following section, a general introduction to applicable fabrication techniques of thin layers will be provided (see, 1.1). After that, chromogenic films are described (see, 1.2) and the materials used for this aim are introduced briefly (see, 1.3). In the end, measurement techniques related to thin films - that are utilized in this work - are listed (see, 1.4).

1.1 Thin layers Fabrication Techniques

There are many applicable techniques for thin films modification and nanofibers and microfibers production. Many alternatives are available for making thin films of chromogenic oxides.

Table 1.1 lists the major methods categorized into physical, chemical and electrochemical ones and further subdivided into varieties [4]. The chromogenic property of different materials is extremely related to the method of preparation, i.e.

it is affected by structure, stoichiometry, binding condition and water content in the films.

Table 1.1: Major technologies for making thin films of chromogenic oxides.

Category	Method	Variety
Physical	Evaporation	Vacuum
		Reactive (O_2 , N_2 , H_2O)
	Sputtering	Non-reactive (Ar)
		Reactive (Ar + O_2)
		Chemical (O_2+CF_4)
Electrochemical	Electrodeposition	
	Anodization	
Chemical	Vapor deposition	Atmospheric pressure
		Low pressure
		Plasma enhanced
	Sol-gel	Dipping
		Spin-coating
		Spraying
	Spray pyrolysis	
	Decomposition reaction	
	Thermal oxidation	

Polymeric nanofibers can be processed by a number of techniques such as Drawing, Template Synthesis, Phase Separation, Self-Assembly and Electrospinning.

1.1.1. Electrodeposition

Inorganic chromogenic films can be produced by electrodeposition technique [5, 6]. Electrodeposition is a process for film growth, which contributes to the formation of a metallic coating onto a base material by electrochemical reduction of metal ions from an electrolyte (an ionic conductor) [7]. Large area films can easily be prepared and besides, this technique is the most economic deposition technique. Interest in the deposition of metal oxides by electrodeposition technique is increasing recently. Because, by using this technique not only it can be possible to use different kinds of materials such as basic phosphates and basic nitrates in dual metal oxide systems but also the quality of the deposited material is increased.

The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be plated on the cathode. Both components are dipped in a solution called an electrolyte, which contains one or more dissolved metal salts as well as other ions that permit the flow of electricity. A power supply provides a direct current to the anode, oxidizing the metal atoms that comprise it and allowing them to dissolve in the solution. At the cathode, the dissolved metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode, such that they "plate out" onto the cathode. The rate at which the anode is dissolved is equal to the rate at which the cathode is plated. In this manner, the anode continuously replenishes the ions in the electrolyte bath.

1.1.2. Electrospinning Technique

Electrospinning is one of the most widely used processes for the production of nanofibers. This technique of producing nanofibers employs electrostatic forces for stretching the viscoelastic fluid [8]. Electrostatic generation of ultrafine fibers or “electrospinning” has been known since the 1930s [9].

The main components of the electrospinning process can be classified as [10]:

- Syringe (or pipette)
- High voltage power supply
- Counter electrode or substrate.

Our electrospinning setup that have the mentioned components above is shown in Figure 1.1.



Figure 1.1: A basic handmade electrospinning apparatus.

A high electric field is generated between a polymer fluid contained in a syringe with a capillary tip and a metallic collection target. When the voltage reaches a critical value, the electric field strength overcomes the surface tension of the deformed droplet of the suspended polymer solution formed on the tip of the syringe, and a jet is produced. The electric field is concentrated at the tip of the needle that contains a pendant droplet of the solution held by its surface tension. Accordingly, charges are induced on the surface of the drop. Then a stretching process is accompanied by the rapid evaporation of the solvent molecules that reduces the diameter of the jet, in a cone-shaped volume called the “envelope cone” [9]. The dry fibers are accumulated on the surface of the collection screen resulting in a nonwoven random fiber mesh of nano- to micron diameter fibers. Once the jet comes into the atmosphere, the low boiling point solvent evaporates, leaving behind only the charged polymer strands. The process can be adjusted to control the fiber diameter by varying the electric field strength and polymer solution concentration [11]. For continuous production of nanofibers, the solution should be pushed at a constant flow rate. Generally, a syringe pump serves this purpose.

A schematic drawing of the Electrospinning process and the random and aligned nanofibers is shown in Figure 1.2.

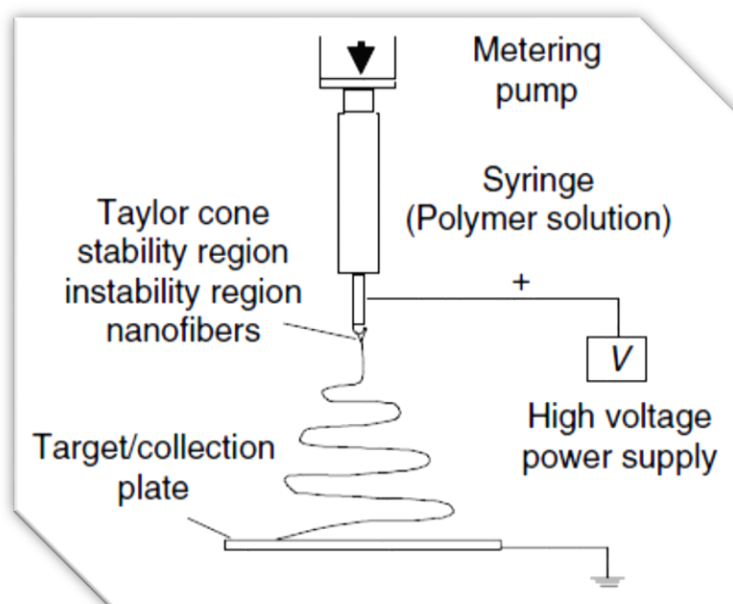


Figure 1.2: Electrospinning process and the random nanofibers.

1.1.3. Drawing

Drawing is the simplest method for generating fibers in nano, micro or macro scales. The solution should be very viscous to be able to be drawn. As illustrated in Figure 1.3, a micropipette or a syringe needle with a diameter of a few micrometers is dipped into the millimetric droplet of the viscous solution on the surface of glass or silicon wafer near the contact line using a micromanipulator. The thicknesses that can be cast on a substrate range all the way from a single monolayer of molecules (adhesion promotion) to tens of micrometers [12].

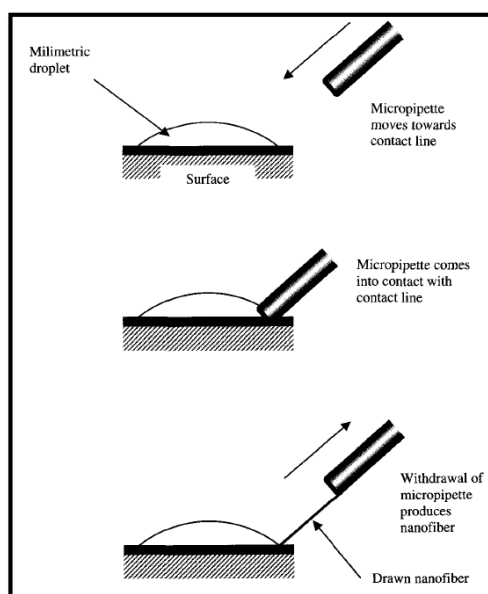


Figure 1.3: Schematic illustration of drawing technique.

1.1.4. Sol-gel theory

The surface of solid bodies such as glasses or plastics is a simple target for the application of functional coatings. This is much easier to accomplish than to design new bulk materials for specific application.

Sols are dispersions of colloidal particles in a liquid. *Colloids* are solid particles with diameters of 1-100 nm. A *gel* is an interconnected, rigid network with pores of sub-micrometer dimensions and either polymeric chains whose average length is greater than micrometer or aggregation of particles [13].

The sol-gel process of thin films includes the following steps:

- Preparation of a sol- gelling the sol on a substrate
- Drying and densification by sintering.

Various products may be obtained via sol-gel process as illustrated in Figure 1.4.

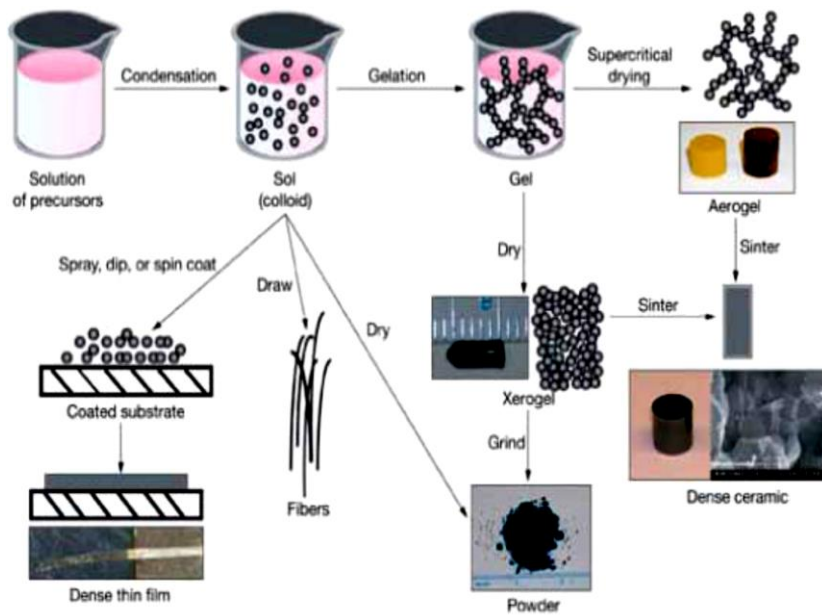


Figure 1.4: Schematic of different Sol-Gel processes and its results.

Two well-known techniques of sol-gel process are spin-coating and dip-coating which are explained in the following [14].

The advantage of this process include the purity of reagents, the control of the degree of homogeneity of mixing of the precursors, the potential control of the phase evolution and microstructure, and the opportunity for fabrication of materials into useful non-traditional shapes (fibers, thin films, spheres, optical elements, patterned surfaces, etc.)

1.1.4.1 Spin-coating

Spin-coating is a procedure used to apply uniform thin films to flat substrates. It has been used for several decades. A typical process involves depositing a small puddle of a fluid resin onto the center of a substrate and then spinning the substrate at high speed (typically around 3000 rpm).

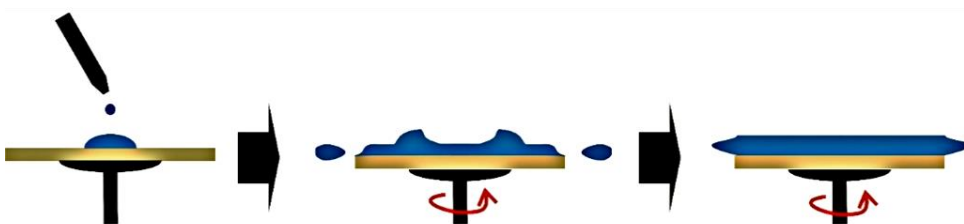


Figure 1.5: Schematic of spin-coating process.

As depicted in Figure 1.5, centripetal acceleration will cause the resin to spread to the edge of the substrate leaving a thin film of resin on the surface [15]. The physics behind spin coating involve a balance between centrifugal forces controlled by spin speed and viscous forces that are determined by solvent viscosity.

The spin coating technique consists of four basic stages [16]:

1. The polymer is dispensed onto the wafer
2. The polymer is spread across the wafer (by spinning at ~ 500 rpm)
3. The wafer is then spun at a higher speed (2000-4000 rpm)
4. The "edge bead" is removed using a backside wash cycle that causes solvent to curl back over the lip of the wafer and wash off the "bead" that is created due to the surface tension at the edge of the wafer.

Some variable process parameters involved in spin coating are:

- Solution viscosity
- Solid content
- Angular speed
- Spin Time

The film-forming process is primarily driven by two independent parameters – viscosity and spin speed. The range of film thicknesses easily achieved by spin coating is 1-200 μm . For thicker films, high material viscosity, low spin speed, and a short spin time are needed. However, these parameters can affect the uniformity of the coat. Multiple coatings are preferred for a film thickness greater than 15 μm [17].

1.1.4.2 Dip-Coating

Dip-coating is a procedure to apply uniform thin films to flat substrates. The whole dip-coating process can be divided to five stages: Immersion, start-up, deposition, draining and evaporation [18]. Figure 1.6 shows the procedure which starts by immersing a clean substrate into a coating solution where it stays for a defined period. It should be long enough to guarantee a heat equilibrium and settle down the turbulence caused by the immersion of the substrate in solution. The substrate is withdrawn then from the solution at moderate speed and stopped adequate distance

above the solution bath to unhindered the drying, this is called the steady state of the process. After drying the deposited film, a curing is needed in order to obtain the desired film material. This is usually done by heating the system in an oven.

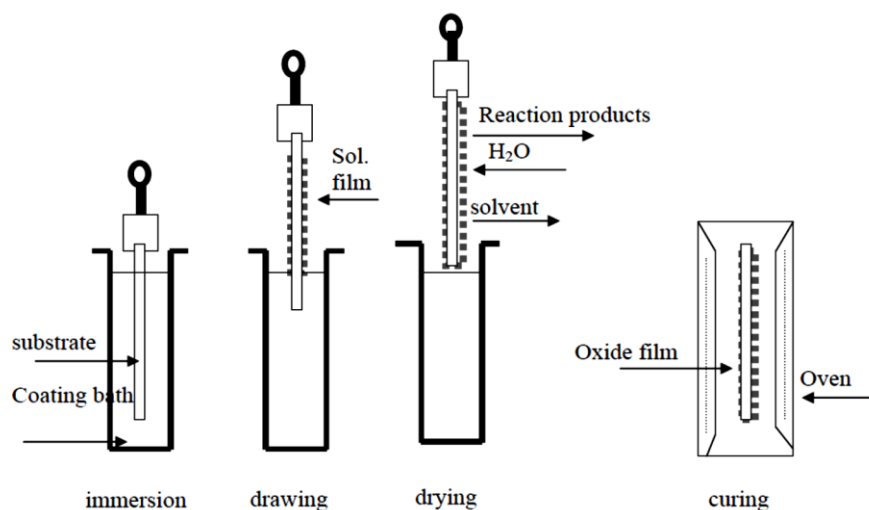


Figure 1.6: Steps of sol-gel oxide film deposition by dip-coating process.

1.2 Chromism Types

Optically active thin film coatings can change their optical properties as a function of external stimuli. These substances, recently named ‘chromogenics’, include both inorganic and organic materials. Chromogenic property of films may fall into four different categories: Electrochromic, thermochromic, photochromic and gaschromic. Materials with controllable light absorbance, transmittance or reflectance possess a great technical relevant, because of their high potential applications. In the near future, optically active films may be utilized to regulate the throughput radiation energy for windows in the buildings and cars, to maintain comfortable lighting and temperature, in sunglasses, as an optically active filter, or in systems with variable reflectance, as automobile rear-view mirrors, in sensors, in detectors, in displays, as road signs, and so forth. Chromogenism has been well documented for oxides of the elements indicated in namely transition metals as shown in Figure 1.7 [19].

Ti	V	Cr	Mn	Fe	Co	Ni
	Nb	Mo			Rh	
	Ta	W			Ir	

Figure 1.7: Transition metals of period.

As seen in Table 1.2, all of these elements belong to the transition series. Cathodic coloration is found in oxides of Ti, Nb, Mo, Ta, and W with tungsten oxide being by far the most extensively studied one [20]. Anodic coloration is found in oxides of Cr, Mn, Fe, Co, Ni, Rh, and Ir, with nickel oxide and iridium oxide being the ones investigated in most detail. Vanadium is exceptional in that the pentoxide (with V^{5+}) exhibits anodic and cathodic electrochromism within different wavelength ranges, while the dioxide (with V^{4+}) has anodic electrochromism. Among these materials, tungsten is chosen in our work because of dominant chromic properties.

Table 1.2: Oxidation of transition metals.

Metal	Oxidised form ^a of oxide	Reduced form ^a of oxide
Tin	SnO ₂ Colourless	Li _x SnO ₂ Blue-grey
Titanium	TiO ₂ Colourless	M _x TiO ₂ Blue-grey
Tungsten	WO ₃ Very pale yellow	M _x WO ₃ Intense blue
Vanadium	V ₂ O ₅ Brown-yellow	M _x V ₂ O ₅ Very pale blue

^a The counter cation M is lithium unless stated otherwise.

1.2.4 Gasochromism

Gasochromic film, which consists of an electrochromic layer and a thin catalyst coating, can reversibly react with hydrogen in air while exhibiting significant changes in their optical properties [21]. Transition metal oxides (e.g. WO₃, MoO₃ and Nb₂O₅) are well known electrochromic materials that show cathodic coloration with H⁺ and Li⁺ ion insertion [22-24]. Overlying Pd and Pt thin films can be used as catalyst materials that facilitate the reaction with hydrogen. Hydrogen gas is dissociated on the catalyst into H atom, which diffuses into and colors the underlying transition metal oxide film. The current interest in gasochromic devices arises from applications concerned with gasochromic windows and optically based hydrogen sensors [25].

1.2.5 Thermochromism

Thermochromic films change their optical properties as a function of substance temperature. The films alter optical data reversibly when heated, and return to their original properties when cooled to the starting temperature [26]. Thermochromism is now observed in polymer, organic materials, compounds containing metals and, last

but not least, inorganic materials. Certain transition metal oxides and related compounds are candidates for such behavior. They transform from semiconducting to metallic state when a certain “critical” temperature is exceeded [27].

Thermochromism of the different types of materials is based on a very different mechanism. The thermal behavior of the different materials may be divided into two categories. One exhibits thermochromism over a wide temperature range, the other exhibits a sharp change in optical properties at a definite temperature. A different class of thermochromic materials are the transition metal oxides which exhibit a dielectric-to-semiconductor transition. The transition temperature in such compounds is reduced (10 to 18°C). The most common inorganic thermochromic thin film materials, in terms of how much they have been investigated, are crystalline transition metal compounds, especially the different oxides of vanadium. VO₂ exhibits a sharp semiconductor-metal transition at $\approx 68^\circ\text{C}$ [28].

1.2.6 Photochromism

Photochromism is simply defined as the light induced reversible change of color. It is the reversible phototransformation of a chemical species between two forms having different absorption spectra [29, 30]. During the phototransformation not only the absorption spectra but also various physicochemical properties change, such as the refractive index, dielectric constant, oxidation/reduction potential, and geometrical structure. The property changes can be applied to photonic equipment such as erasable memory media, photo-optical switch components, and display devices [31]. The field has developed rapidly during the past decade as a result of attempts to improve the established materials and to discover new devices for applications. Photochromism is derived from the Greek words: phos (light) and chroma (color) [32].

In other words photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two forms of a chemical species, A and B, having different absorption spectra. A and B represent energy states of the respective material and $h\nu$ is the energy of electromagnetic radiation [33].

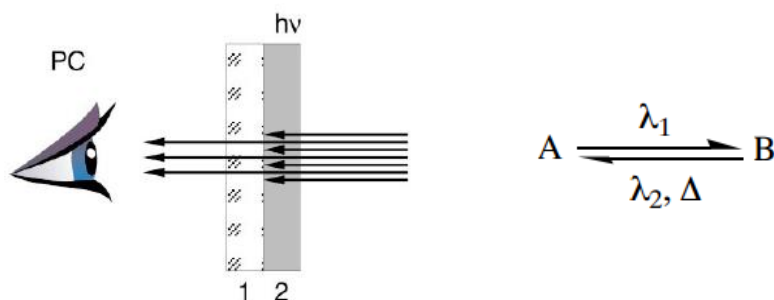


Figure 1.8: Photochromic Effect principle.

Many materials and compounds exhibit a change in optical properties when exposed to a certain type of irradiation, but regain their original properties when placed in the dark distinct, different absorption spectra, and a reversible change is induced in at least one direction by the action of electromagnetic radiation. The photochromic phenomenon has been observed in various organic and inorganic substances in solid form and/or solution [34]. The energy of the electromagnetic irradiation $h\nu$, which induces the formation of the colored (activated) species, is usually situated in the blue region and/or in the UV range of the spectrum. The colored state of the substances typically absorbs in the visible region, with few exceptions, which absorb in the near-infrared.

Although, the photochromism was first observed in inorganic materials, subsequent developmental work has proliferated the number of organic materials considerably [34]. Photochromism is also observed in amorphous transition metal oxide films known to be electrochromic. So, for example, in a-MoO₃ and a-WO₃ films a blue coloration is reported when the films are irradiated with light ($h\nu > 3.4$ eV) for several hours. Blue color develops gradually and grows more intense with prolonged exposure [35, 36]. It is believed that the photochromism in the amorphous films is produced by the high energy radiation which results in a photodecomposition.

1.2.7 Electrochromism

Electrochromism is a unique property of thin films and thin film systems to change color, due to an applied potential, and change back to the original state by a potential reversal [37]. From a technological point of view, thin electrochromic films are best investigated, and they are the most promising candidates for various applications in the proximate future.

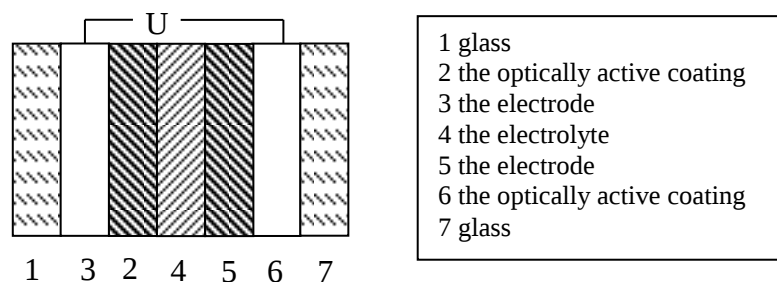


Figure 1.9: Schematic representation of optically active thin films.

Some metal oxides such as WO_3 , MoO_3 , V_2O_5 , NiO , Nb_2O_5 show electrochromic properties [38-40]. Over three decades, electrochromism in a-WO_{3-x} (amorphous tungsten oxide), a persistent and reversible color change induced by an applied electric field, has been broadly studied since it was discovered by S. Deb [41, 42]. Up to now EC devices are still offset by the unsolved problems. One of the most desired applications of EC systems is their use in so-called “smart windows”. In the near future, optically active films may be utilized to regulate the throughput radiation energy for windows in the buildings and cars, to maintain comfortable lighting and temperature, in sun glasses, as an optically active filter, or in systems with variable reflectance, as automobile rear-view mirrors, in sensors, in detectors, in displays, as road signs, and so forth [43]. Compared with other window/glass constructions, up to 50% of the energy costs for heating and cooling buildings can be saved with “smart windows”.

A simple electrochromic device consists of 7 layers as illustrated in Figure 1.9. The 1st and the 7th layers are glasses. The 2nd and the 6th layers are conductive layers (ITO – Indium Tin Oxide – $\text{In}_2\text{O}_3:\text{Sn}$) coated on the glass. The 3rd layer is ion storage layer and the 4th layer is ion conductive layer. Materials showing electrochromic properties are coated as the 5th layer [44-48]. The ability of changing the color of the electrochromic device is due to the reaction in the electrochromic layer. Therefore, the optical and electrochromic properties of electrochromic layer should be controlled. The efficiency of the electrochromic device depends mostly on the properties of the electrochromic layer. It also depends on the number of coloring and bleaching (life time), response time (the time required for being fully bleached in the fully colored state), inserted and extracted charge densities etc.

Tungsten oxide films are by far the most extensively studied electrochromic materials [20]. They switch from transparent to blue upon application of a voltage. After Deb's report of electrochromic properties of tungsten oxide, various electrochromic materials have been produced from different deposition techniques. Especially during recent years, many efforts have been done to improve the deposition techniques of electrochromic tungsten oxide films. Homogenous deposition for large area applications are an important application area in the study of tungsten oxide films. Electrochromic tungsten oxide films may be utilized to regulate the throughput of radiation energy for windows in buildings and cars, to maintain comfortable lighting and temperature, in sun glasses, as an optically active filter, or in systems with variable reflectance (as automotive rear-view mirrors), in displays, in sensors, detectors, as road signs, etc. [19]. Tungsten oxide films exhibit different electrical and optical properties depending upon deposition technique and deposition parameters. Consequently, different deposition techniques were used and deposition parameters were varied in order to compare the structural, optical and electrochromic properties of tungsten oxides films. Table 1.3 summarizes some properties of the sol-gel deposited chromogenic layers [48].

Table 1.3: Summary of key features for the main EC oxides, showing oxide type, whether the coloration is cathodic C or anodic A.

Material	Color (bleached)	Color (colored)	Stability (cyclic)
WO ₃ (C)	No color	Blue	10 ⁴ cycles
TiO ₂ (C)	No color	Gray or blue	10 ³ cycles
Nb ₂ O ₅ (C)	No color	Brown, gray	10 ⁴ cycles
V ₂ O ₅ (A/C)	Light yellow	Brown, green	10 ³ cycles
Ni(OH) ₂ (A)	Light green	Brown	10 ³ cycles
Co(OH) ₂ (A)	Light brown	Dark brown	10 ³ cycles
CuO _x (A/C)	No color	Brown, purple	10 ² cycles

1.3 Materials

This section is introducing materials used in experimental part of the work. These materials include chromogenics, polymers and solvents in overall. Tungsten, tungsten oxide, tungsten hexachloride as tungsten compounds, PVP as the polymer and DMF as solvent are briefly discussed below.

1.3.4 Tungsten

Tungsten has the highest melting point of all the metallic elements and because of this has its first significant commercial application as the filament in incandescent light bulbs and fluorescent light bulbs. Tungsten is available as metal and compounds in the form of foil, sputtering target, and rod, and compounds as submicron and nano powder. It is the primary metal in heating elements for electric furnaces and in any components where high pressure/temperature environments are expected, such as aerospace and engine systems. Tungsten gets its name from the Swedish words tung and sten meaning heavy stone [49].

Tungsten is a Block D, Group 6, Period 6 element. The number of electrons in each of Tungsten's shells is 2, 8, 18, 32, 12, 2 and its electronic configuration is $[\text{Xe}]4f^{14}5d^46s^2$. Tungsten is considered to be only mildly toxic.

Nanoparticles and nanopowders provide ultra-high surface area which nanotechnology research and recent experiments demonstrate function to create new and unique properties and benefits.



Table 1.4: Tungsten Compounds Variaty.

Name	Material	Solvent
Tungsten powder	W-Metallic	H ₂ O ₂
Tungsten(VI) oxide	WO ₃	NaOH
Tungsten(IV) chloride	WCl ₆	Ethanol
Tungsten(VI) dichloride dioxide	WO ₂ Cl ₂	THF
Tungsten Carbide	WC	Water
Ammonium tungsten oxide	(NH ₄) ₂ WO ₄	warm water
Tungsten(VI) isopropoxide	W Isopropoxide - C ₁₈ H ₄₂ O ₆ W	FLUID
Acetylated Peroxotungstic Acids	AIPTA	FLUID

1.3.5 Tungsten Oxide

Oxides of tungsten are available in forms including powders and dense pellets for such uses as optical coating and thin film applications. Oxides tend to be insoluble [49].

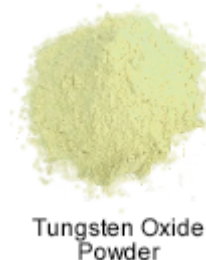


Table 1.5: Properties of WO_3 .

Mol. Wt.	Appearance	Melting Point	Boiling Point	Density	Exact Mass	Charge
231.85	Yellow Powder	1473°C	1700 °C	7.16g/cm ³	231.936g/mol	-6

Tungsten Oxide is a highly insoluble thermally stable. Oxide compounds are not conductive to electricity. Metal oxide compounds are basic anhydrides and can therefore react with acids and with strong reducing agents in redox reactions. Tungsten Oxide is also available in pellets, pieces, sputtering targets, tablets, and nanopowder. Tungsten Oxide is generally immediately available in most volumes.

Tungsten has several oxidation states, and therefore oxides:

- Tungsten (III) oxide (W_2O_3)
- Tungsten (IV) oxide, also known as tungsten dioxide (WO_2)
- Tungsten pentoxide (W_2O_5)
- Tungsten (VI) oxide, also known as tungsten trioxide (WO_3)

Tungsten Trioxide (WO_3)

Tungsten trioxide is used as pigments in ceramics and as color-resistant mordants for textiles and for many purposes in everyday life and in industry [50]:

- Electrochromic & photochromic windows
- Fireproofing fabrics
- Gas sensors
- Pigment in ceramics and paints
- Tungstates for x-ray screen phosphors

1.3.6 Tungsten hexachloride (WCl_6)

Tungsten hexachloride or hexachlorotungsten is a blue-black crystalline solid at room temperature. It is an important starting reagent in the preparation of tungsten compounds. Tungsten in WCl_6 has a valance of +6 and needs 6 electrons to change to zero state [51]. Tungsten hexachloride is readily soluble in alcohol, soluble in water at 15°C, and does not become hydrolyzed in water until the temperature

reaches 60°C. Tungsten hexachloride can be prepared by chlorinating tungsten metal in a sealed tube at 600°C. ($W + 3Cl_2 \rightarrow WCl_6$)

1.3.7 PVP

Polyvinylpyrrolidone (PVP), also commonly called Polyvidone or Povidone, is made from the monomer *N*-vinylpyrrolidone as in Figure 1.10.

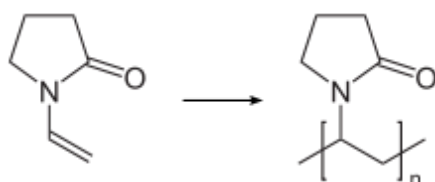


Figure 1.10: PVP molecule structure.

PVP is soluble in water and other polar solvents. When dry it is a light flaky powder, which readily absorbs up to 40% of its weight in atmospheric water. In solution, it has excellent wetting properties and readily forms films. This makes it good as a coating or an additive to coatings. PVP is a branched polymer, meaning its structure is more complicated than linear polymer, though it too lies in a two-dimensional plane.

PVP was initially used as a blood plasma substitute and later in a wide variety of applications in medicine, pharmacy, cosmetics and industrial production. PVP is also used in many technical applications:

- As an adhesive in glue stick and hot-melt adhesives
- As a special additive for batteries, ceramics, fiberglass, inks, inkjet paper and in the chemical-mechanical planarization process
- As a photoresist for cathode ray tubes (CRT) and so on.

1.3.8 DMF

Dimethylformamide is an organic compound with the formula $(CH_3)_2NC(O)H$. Commonly abbreviated as DMF (though this acronym is sometimes used for dimethylfuran), this colourless liquid is miscible with water and the majority of organic liquids. DMF is a common solvent for chemical reactions. Pure dimethylformamide is odorless whereas technical grade or degraded dimethylformamide often has a fishy smell due to impurity of dimethylamine.

Its name is derived from the fact that it is a derivative of formamide, the amide of formic acid.

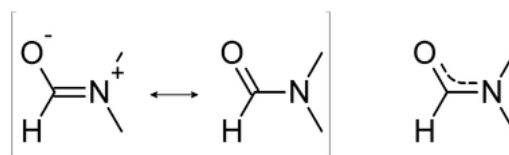


Figure 1.11: The two resonance forms of DMF.

Dimethylformamide is a polar (hydrophilic) aprotic solvent with a high boiling point. It facilitates reactions that follow polar mechanisms, such as $\text{S}_{\text{N}}2$ reactions. Due to the contribution of the two possible resonance structures of an amide, the bond order of the carbonyl $\text{C}=\text{O}$ bond is reduced, while that of the carbon-nitrogen bond is increased. Thus the infrared spectrum of DMF shows a lower $\text{C}=\text{O}$ stretching frequency at 1675 cm^{-1} than an unsubstituted $\text{C}=\text{O}$ bond.

1.4 Measurement Systems

Thicknesses of the coatings were measured by profilometer. X-ray diffractometer has been used for phase analyses. UV-Vis. spectrophotometer has been used to measure the optical transmittance of tungsten thin films. SEM and optical microscope were used to examine the microstructure and the surface morphology of the films deposited on glass substrates. Table 1.6 shows some of the material characterization methods covered in this dissertation and their physical principles.

Table 1.6: Characterization methods and their physical principles.

Method	Physical Principle
Scanning Electron Microscopy (SEM)	Scattering of electron
Fourier Transform Infrared Spectroscopy (FTIR)	Absorption of polychromatic IR light in vibrational bands
Raman Spectroscopy (RS)	Scattering of monochromatic light in vibrational bands
X-Ray Diffraction (XRD)	Diffraction of X-Ray from crystals lattices
X-Ray Photoelectron Spectroscopy (XPS)	Extracted electrons, analyzed according to their kinetic energies
Energy Dispersive Spectroscopy (EDS)	Fluorescent X-Ray during SEM

1.4.1 SEM

The scanning electron microscope (SEM) enables the investigation of specimens with a resolution down to the nanometer scale. A high-resolution SEM image can show detail down to 25 Angstroms, or better. When used in conjunction with the closely related technique of energy-dispersive X-ray microanalysis (EDX, EDS, EDAX), the composition of individual crystals or features can be determined. There are many different ways that scanning electron microscopy and X-ray microanalysis can aid studies of materials. A normal scanning electron microscope operates at a high vacuum.

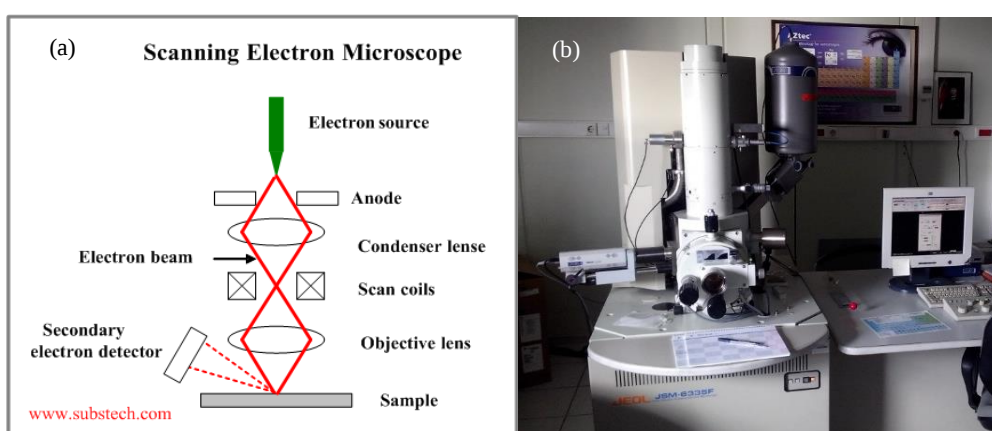


Figure 1.12: (a) SEM system operation diagram (b) SEM system instrument.

The basic principle is that a beam of electrons is generated by a suitable source, typically a tungsten filament or a field emission gun as showed in Figure 1.12. The electron beam is accelerated through a high voltage (e.g.: 20 kV) and pass through a system of apertures and electromagnetic lenses to produce a thin beam of electrons, then the beam scans the surface of the specimen by means of scan coils. Electrons are emitted from the specimen by the action of the scanning beam and collected by a suitably-positioned detector. The microscope operator is watching the image on a screen. Imagine a spot on the screen scanning across the screen from left to right. At the end of the screen, it drops down a line and scans across again, the process being repeated down to the bottom of the screen [52].

1.4.2 UV-Vis Spectrophotometer

The spectrophotometer has well been called the workhorse of the modern laboratory. In particular, ultraviolet and visible spectrophotometry is the method of choice in most laboratories concerned with the identification and measurement of organic and

inorganic compounds in a wide range of products and processes. In every branch of molecular biology, medicine and the life sciences, the spectrophotometer is an essential aid to both research and routine control [53].

1.4.3 XRD (X-Rays Diffraction)

X-Rays are electromagnetic radiations which lie between ultraviolet light and gamma rays in the electromagnetic spectrum. X-Rays are characterized by the relatively short wavelengths of 0.01-100 Å, with Hard X-Ray on one hand and Soft X-Ray on the other. X-rays are conventionally produced by either the conversion of the kinetic energy of charged particles into radiation (continuous spectrum of X-rays) or by the excitation of atoms in a target upon which fast moving electrons impinge [54].

Two different processes are involved in interactions of X-rays with matter: excitation of, or scattering with the medium.

X-Ray Diffraction is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. X-Ray Diffraction is based on the elastic scattering. That is the change of direction of the electromagnetic waves motion without any energy loss. Diffraction results from the coherent sum of all the electromagnetic waves that are diffused from the atoms belonging to the same family of reticular planes.

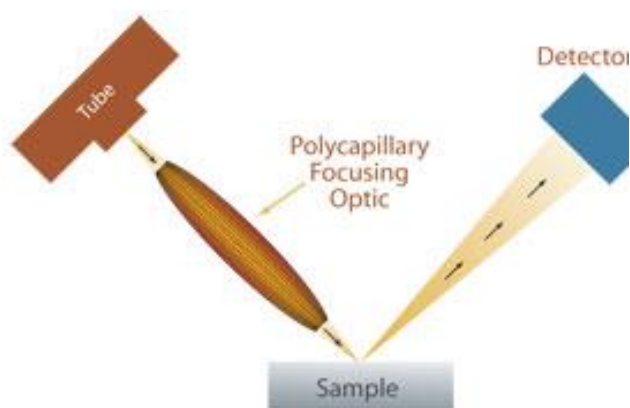
Only when Bragg's Law ($2d\sin(\theta) = n\lambda$) condition is satisfied the detector will give a peak corresponding to the radiation diffracted by the sample along θ direction.

By varying the angle theta, the Bragg's Law conditions are satisfied by different d-spacing's in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the sample. Diffraction patterns constitute evidence for the periodically repeating arrangement of atoms in crystals.

The X-ray Diffraction experiment requires an X-ray source, the sample under investigation and a detector to pick up the diffracted X-rays as in Figure 1.13.



(a)



(b)

Figure 1.13: (a) XRD instrument and (b) its operation schematics.

Today about 50,000 inorganic and 25,000 organic single component, crystalline phases and diffraction patterns have been collected and stored on magnetic or optical media as standards [55]. The main use of powder diffraction is to identify components in a sample by a search/match procedure. Furthermore, the areas under the peak are related to the amount of each phase present in the sample.

About 95% of all solids can be described as crystalline. In some materials, the predictable long-range geometric order characteristic of crystalline solids break down. These are the non-crystalline amorphous or glassy solids exemplified by silica glass, inorganic oxide mixtures, and polymers [1].

1.4.4 EDS

Energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on the investigation of an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are for most due to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum.

To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains

ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.

Four primary components of the EDS setup are [56]:

1. the excitation source (electron beam or x-ray beam)
2. the X-ray detector
3. the pulse processor
4. the analyzer

1.4.5 XPS

X-ray photoelectron spectroscopy (XPS) is a widely used technique to determine the chemical composition of a surface (atomic percentages, chemical states, lateral and depth distributions). XPS is becoming a standard technique in order to understand the properties of a solid surface.

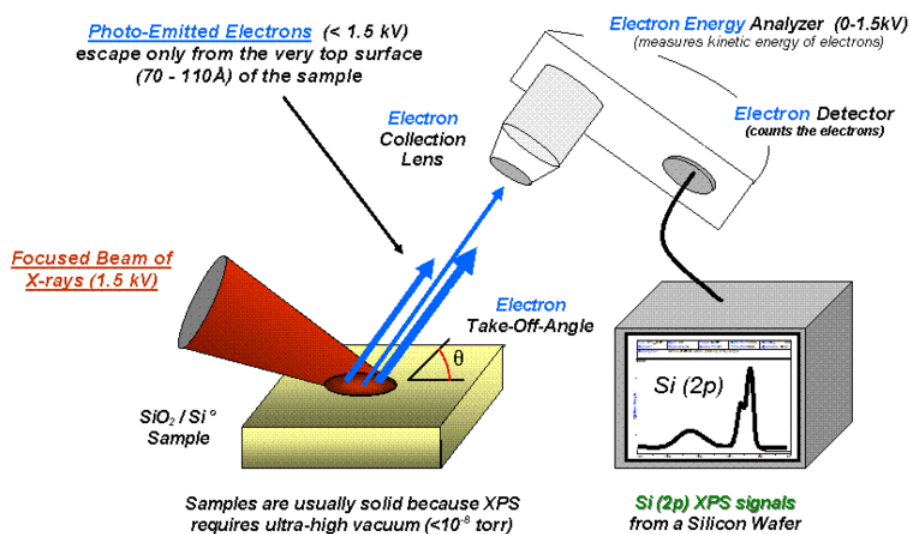


Figure 1.14: Basic components of a monochromatic XPS system.

It is very important to understand the surface phenomena and surface reactions in order to find solutions to problems related with surfaces.

Figure 1.14 shows the functioning principle of an XPS analysis from a silicon wafer sample.

XPS is used to measure:

- Elemental composition of the surface (top 1–10 nm usually)
- Empirical formula of pure materials
- Elements that contaminate a surface
- Chemical or electronic state of each element in the surface
- Uniformity of elemental composition across the top surface (or line profiling or mapping)
- Uniformity of elemental composition as a function of ion beam etching (or depth profiling)

1.4.6 FTIR (Fourier Transform Infrared)

Absorption in the infrared region results in changes in vibrational and rotational status of the molecules. The absorption frequency depends on the vibrational frequency of the molecules, whereas the absorption intensity depends on how effectively the infrared photon energy can be transferred to the molecule, and this depends on the change in the dipole moment that occurs because of molecular vibration. Consequently, a molecule will absorb infrared light only if the absorption causes a change in the dipole moment.

Thus, all compounds except for elemental diatomic gases such as N_2 , H_2 and O_2 , have infrared spectra and most components present in a flue gas can be analyzed by their characteristic infrared absorption.

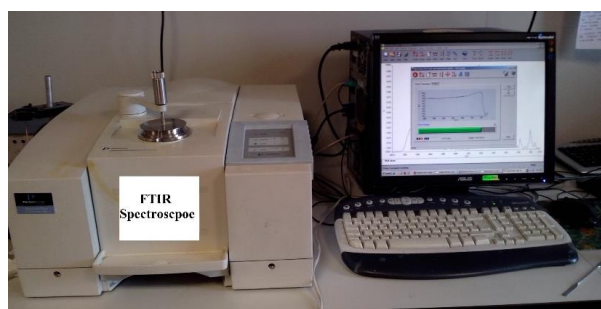


Figure 1.15: FTIR Spectroscopy instrument.

For quantification of several components absorbing in the mid-infrared region (400-5000 cm^{-1}), either conventional dispersive infrared analysis or Fourier Transform Infrared (FTIR) spectroscopy can be used. Compared to dispersive IR analysis, FTIR analysis is faster and has a better signal-to-noise ratio [57]. Figure 1.15 shows our FTIR instrument.

1.4.7 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the sample and then reemitted. Frequency of the reemitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman Effect.

This shift provides information about vibrational, rotational and other low frequency transitions in molecules. Raman spectroscopy can be used to study solid, liquid and gaseous samples [58].

A Raman system typically consists of four major components (see, Figure 1.16):

1. Excitation source (Laser).
2. Sample illumination system and light collection optics.
3. Wavelength selector (Filter or Spectrophotometer).
4. Detector (Photodiode array, CCD or PMT).

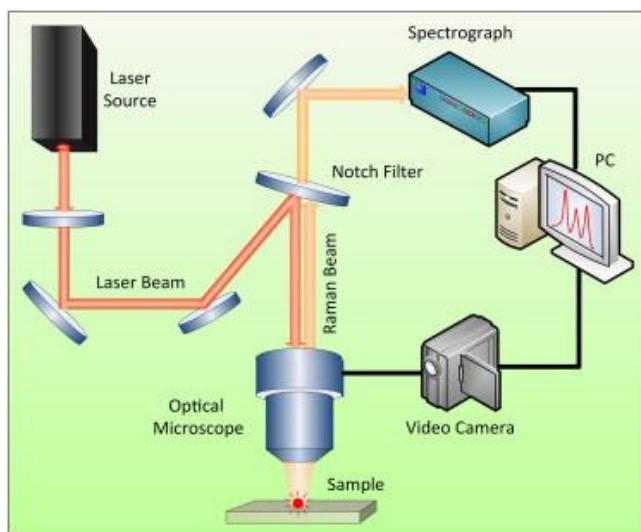


Figure 1.16: Schematics Representation of Raman Spectroscopy [59].

2 EXPERIMENTAL PROCEDURES

Organic/inorganic blend is prepared using different precursors and concentrations for two main reasons; first to study the effect of the amount of polymer on color modulation and second to prepare suitable solutions and blends for various thin film creation techniques.

There are 4 ingredients in each solution. Two of them are solvents; others are inorganic precursor like tungsten powder or tungsten hexachloride and a polymer which is mainly PVP in this work. DMF is the solvent used for PVP, tungsten metallic powder is solved in H_2O_2 and tungsten hexachloride is solved in ethanol.

In general procedure of preparation of the organic/inorganic blend, first we solve the polymer and the inorganic precursor in their solvents separately and stir them for 15 minutes. Then the inorganic solution is added to the polymeric one gradually while stirring, this is followed by two hours of extra stirring in closed container, to let the blend become homogenous. It is recommended that before applying the blends for thin film or fiber production, they should stay in room condition for half an hour with no agitation. Additionally a small hole should be opened to the cover of the container to evaporate residual solvents.

2.4 Substrate Preparation

Corning glasses and indium tin oxide (ITO)-coated glasses are used as substrates. The substrates were cleaned with detergent and flushed with copious amounts of deionized water. Finally, the substrates were sequentially rinsed with acetone, methanol and ethanol and dried in air. Figure 2.1 shows the SEM image of surface of an ITO glass used as a substrate.

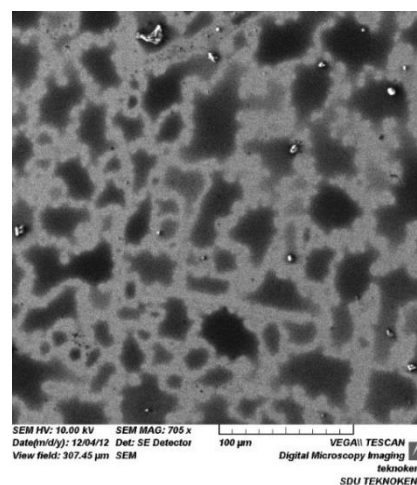


Figure 2.1: Planar SEM view of ITO glass substrate.

In overall, we used various substrate for film deposition according to the requirements of the employed technique. In this work we use glass, ITO coated glass, Al foil, Cu plate and paper as substrates.

2.5 Preparation of Blends

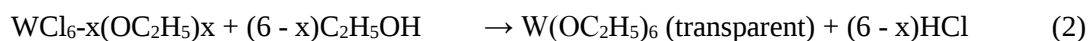
We used various precursors to produce thin layers of tungsten oxides such as metallic tungsten, AIPTA, tungsten hexachloride, and WO₃.

Tungsten hexachloride (WCl₆ ≥ 99.9% trace metals basis) powder is bought from Alfa Aesar and solved in analytical grade Ethanol (CH₃CH₂OH), then mixed with polyvinylpyrrolidone (PVP) by molecular weight of 1.300.000 and N,Ndimethylformamide was used as solvent.

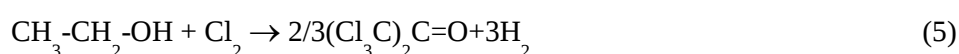
In the first step of the solution preparation, we have to solve the inorganic powder (WCl₆) in its solvent (ethanol). The solution turned yellow immediately after the addition of WCl₆ to the solvent and successively became green and then blue as tungsten oxide was reduced as shown in the Figure 2.2. This procedure is prepared in fully dark environment to prevent the photon energy effect of light on the sample.

The color of the WCl₆ solution dissolved in ethanol turned from yellow to blue, to transparent with time. A chloride-alkoxide tungsten solution with a blue or yellow color was formed with a reaction of WCl₆ and ethanol. A pure, transparent tungsten-ethoxide solution was formed by an accelerated reaction at 70°C.

The reactions are summarized as follows [60]:



During the process, these reactions were occurred:



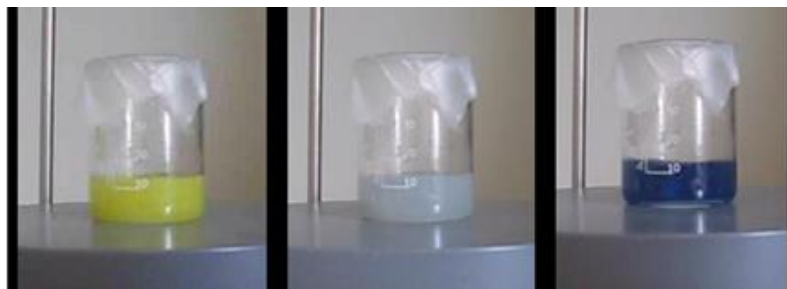


Figure 2.2: Preparation of WO_3 sol by WCl_6 precursor.

To obtain the polymeric form of the mentioned solution, the mixture is prepared in four different concentrations as listed in Table 2.1. The amount of polymer is the main variable for changing the concentration. The quantity of polymer has a direct effect on photochromic behavior of the resulting thin film and determines the technique of film or fiber production.

Table 2.1: Concentrations of WCl_6 and PVP solution with the solvents.

CODE	B1	B2	B3	B4
WCl_6	0.50 g	0.50 g	0.50 g	0.50 g
PVP	0.50 g	1 g	1.5 g	2 g
Ethanol	4.2 ml	4.2 ml	4.2 ml	4.2 ml
DMF	1.8 ml	3.5 ml	3.5 ml	3.5 ml

The same procedure is applied to tungsten metallic powder and AIPTA. For polymeric blend, metallic tungsten was solved in H_2O_2 and then mixed with a PVP/DMF solution. Since AIPTA is solution, it can be mixed with polymer solution directly with no further process

All applied techniques are explained in details in the following.

2.6 Thin Layer Formation Techniques

We obtained two different types of thin layers, films and fibers, using various precursors for our organic/inorganic blends, which are listed below.

Film Formation Techniques:

- Electrodeposition
- Spin coating
- Encapsulating
- Applying as writing ink

Nanofibers and Microfibers:

- Electrospinning of W/PVP blend
- Electrospinning of AIPTA/PVP blend
- Electrospinning of WCl_6 /PVP blend
- Drawing of WCl_6 /PVP blend

When the diameters of polymer fiber materials are shrunk from micrometers (e.g. 10–100 μm) to submicrons or nanometers, several amazing characteristics such as very large surface area to volume ratio, flexibility in surface functionalities, and superior mechanical performance (e.g. stiffness and tensile strength) compared with any other known form of the material appear. These outstanding properties make the polymer nanofibers to be optimal candidates for many important applications [61]. We investigated the functionality of electrospun nanofibers of tungsten oxide using various precursors.

2.3.1 Film formation by Electrodeposition Techniques

Solution for electrodeposition was prepared by dissolving tungsten metal powder in hydrogen peroxide. 0.44 g tungsten metal powder (99.9 %) was added in 8 ml hydrogen peroxide. In order to decompose excess hydrogen peroxide, platinum plate was immersed into the solution after tungsten metal powder is completely dissolved in solution. The next step is addition of stabilizers. Equal amounts of water and ethanol was added to the solution in order to enhance the durability of the solution. After this step a waiting period of solution enhances the deposition performance of the solution. A flowchart of this process is given below in Figure 2.3.

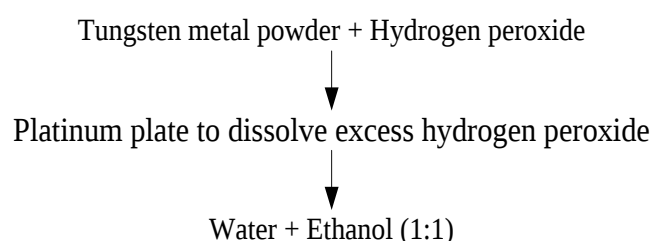


Figure 2.3: Preparation of tungsten oxide with W powder precursor.

In order to prepare tungsten oxide based electrochromic thin film by using sodium tungstate precursor, 0.5 M solution was prepared by dissolving alkaline tungsten salt ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) in deionized water. Obtained solution was passed through cation exchange resin to exchange Na^+ ions with H^+ ions in order to acidify solution. For this process ion exchange, resin column was used. Solution was passed through resin column with the flow rate of 2 ml/min. By the end of this process tungstic acid solution was obtained. Then hydrogen peroxide was added to enhance the stability of the solution by delaying the gelation of the solution. The solution was mixed for an hour. In the next step to remove excess hydrogen peroxide, acetic acid (100 %) was

added to solution and refluxed for 3 hours at 55°C. By the end of this process a stable peroxotungstic acid has been obtained. This solution was used in electrodeposition. Preparation of this process is given in the flowchart as shown in Figure 2.4.

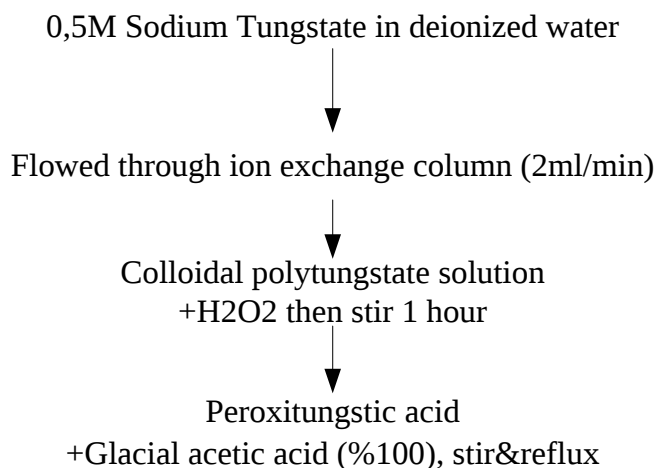


Figure 2.4: Preparation of tungsten oxide by sodium tungstate precursor.

Deposition of tungsten oxide thin films were made by the electrodeposition method on the ITO coated glass substrates. Three electrode configuration was used in this study. Platinum rod, silver rod and ITO were used as counter, reference and working electrodes during the coating process. It has been observed that after the preparation of solutions, one week stabilization time enhanced the coating performance of the films.

2.3.2 Tungsten oxide films formation by spin-coating (Sol-Gel)

Spin-coated tungsten oxide film has been prepared using two different procedures. First one is completely inorganic, and the second is an inorganic/organic blend. This way we will be able to compare the functionality results and record the improvements and advantages of polymeric blend. In the inorganic solution, the only components are tungsten hexachloride and ethanol. In the polymeric one, PVP and DMF are added to the solution.

2.3.2.1 Inorganic solution

For the first experiment, the coating solutions were prepared by mixing 1 g of WCl_6 (Aldrich) with 10 g of ethanol. The spin-coating speed was set at 2000 rpm. The as-deposited standard sol-gel film showed a blue color as expected.

2.3.2.2 Organic/inorganic blend

For the second experiment, we used the $\text{WCl}_6/\text{PVP}/\text{EtOH}/\text{DMF}$ blends number B1, B2 and B3 (see, Table 2.1) to coat a glass substrate by spin coating. A corning glass cut in $2.5 \times 2.5 \text{ cm}^2$ size was pre-cleaned and coated by $150 \mu\text{l}$ of the blend in 2000 rpm rotation speed (for sample 1), $150 \mu\text{l}$ in 3000 rpm (for sample 2) and also $200 \mu\text{l}$ in 2000 rpm (for sample 3). The resulting coatings are shown in Figure 2.5. Coated glass substrate was waited for a night in air and room temperature to get dry. UV-Vis transmittance measurements are available in section 3.2.

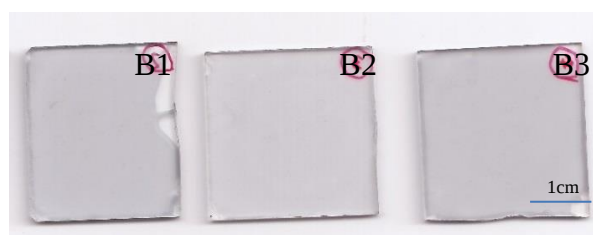


Figure 2.5: Image of spin-coated tungsten oxide films with polymeric blend.

2.3.3 Film formation by dip-coating (Sol-Gel)

Dip-coated tungsten oxide films by polymeric blend, which is prepared with the same procedure as for spin-coating, form a uniform and transparent light-blue thin film. This thin film can be used as an electrode for electrochromic devices that performs acceptably good and it is the best choice for this type of devices.

2.3.4 Film formation by encapsulating

All of the concentrations of tungsten hexachloride/ $\text{PVP}/\text{EtOH}/\text{DMF}$ solutions are able to form a thin film when encapsulated between two pieces of glass. We drop a droplet of few microliters of the solution upon a glass substrate and put another piece of glass on the top. By applying a little pressure by hand or by using a hard material, the droplet starts to disperse smoothly in the middle of two glass pairs as shown in Figure 2.6.



Figure 2.6: Image of sandwich structure of capsulated tungsten oxide films.

These sandwich structures are dark when wet, but after a while they become dry and highly transparent. UV-Vis transmittance measurements are available in section 3.4.

2.3.5 Applying WCl_6 /PVP blend as writing ink

We can apply all four concentrations of WCl_6 /PVP/EtOH/DMF solutions to sort of papers and most textile substrates, which is the application as “writing ink”. We use a painting brush or a piece of cotton to rub the ink. After the blend is applied to the paper, it takes a few hours to dry out. In this period, it becomes almost colorless and invisible as depicted in Figure 2.7.

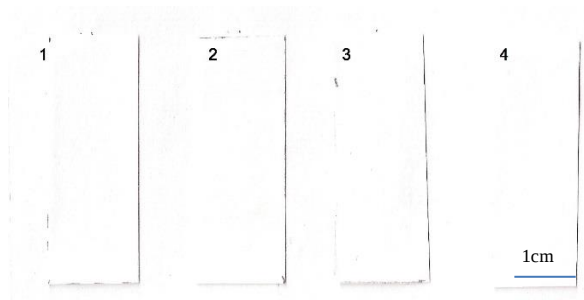


Figure 2.7: Image of papers which used for writing ink.

2.3.6 Electrospinning of W/PVP blend

10 ml of cold 30% H_2O_2 solution was added to 0.67 g metallic tungsten powder. After longtime stirring (6 h), the powder dissolved completely and a faint greenish-yellow solution (tungstenic acid) was obtained. Then 10 ml ethanol and 1.0 g of PVP (Aldrich, $M_w = 1.300.000$) were added into the above solution, followed by magnetic few hours. Then the solution was loaded into a plastic syringe equipped with a 15 cm long needle made of copper. The needle was connected to a high-voltages supply that is capable of generating DC voltages up to 50 kV. In our experiment, a voltage of 15 kV was applied for electrospinning in the air conditions.

A piece of flat aluminum foil was placed 12 cm from the tip of the needle to collect the nanofibers. To prepare tungsten oxide nanofibers, obtained electrospun nanofibers were annealed at 500 °C for 2h in the air atmosphere [62].

2.3.7 Electrospinning of WCl_6 /PVP blend

The prepared WCl_6 /PVP/EtOH/DMF blend B2 (see, Table 2.1) is used for electrospinning process and forms a network of fine nanofibers of tungsten oxide.

In this experiment, 20 kV was applied for electrospinning, and the distance between the spinning nozzle and the collection plate was 15 cm, feeding rate was 6 $\mu\text{l}/\text{min}$, substrate was a glass on aluminum foil. Room temperature was 25°C and no special pressure was applied. As mentioned previously, Figure 1.1 shows our electrospinning setup in this work. After collecting the fibers, they were calcined in 3 steps starting from 100°C to 500°C. The calcination pattern is given in

Figure 2.10 in the following.

2.3.8 Electrospinning of AIPTA/PVP blend

Acetylated peroxotungstic acid (AIPTA) obtained from ion exchange can be used as such for depositing films or can be isolated as a solid precursor material by drying under reduced pressure at 55°C. AIPTA has shown solubility in water as well as alcohol [63]. A concise scheme illustrating the synthesis of ITA and AIPTA is given in

Figure 2.8. We used the obtained AIPTA as a precursor for electrospinning process with the same polymeric of previous experiments.

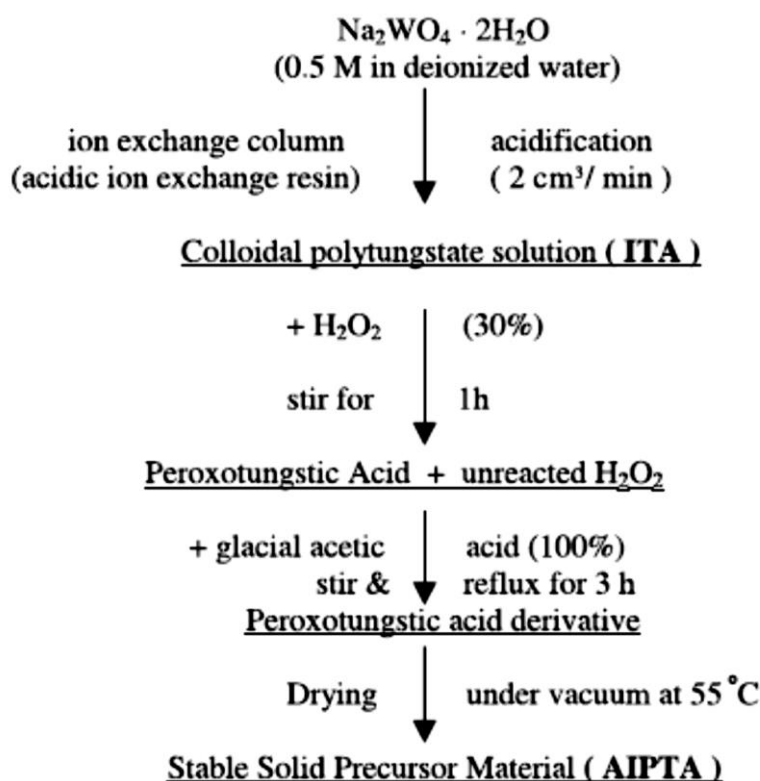


Figure 2.8: Flowchart of preparing AIPTA.

The sol-gel AIPTA precursor was mixed with a 10% PVP solution in ethanol loaded in the syringe with (2:1) ratio after stirring for 2h. Although the obtained solution was viscous and homogenous, the result of electrospinning in voltage range of 15 to 22 kV and distances of 10 to 20 cm and feed rate of 8 $\mu\text{l/h}$ was not a nanofiber layer, but a thin film instead! In fact, it shows that the electrospinning procedure is not accomplished, but as an experiment, a thin layer of a tungsten compounds is produced eventually. In addition, the thin film was calcined at 500 °C for 2 hours. As a result, the polymer and solvents were moved away from the film.

2.3.9 Drawing of WCl_6/PVP blend

Blend 4 from table 1 is drawn in 3 grades of mesofibers, microfibers and macrofibers as illustrated in Figure 2.9.

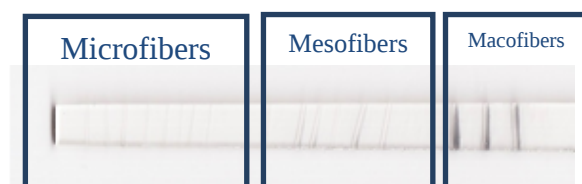


Figure 2.9: Image of drawing microfibers, mesofibers and macrofibers of B4 blend on glass substrate.

The drawing process is done in room conditions. It is regardless of substrate type, such as glass, ITO, Al foil, etc.

In this work, we prefer glass because it helps the fibers to show their transparency well. After drawing the fibers, they are held in a clean box in room temperature until it dries which takes 2 days.

2.7 Calcination Process

Calcination (also referred to as calcining) is a thermal treatment process in presence of air applied to ores and other solid materials to bring about a thermal decomposition, phase transition, or removal of a volatile fraction. The calcination process normally takes place at temperatures below the melting point of the product materials. Calcination is not the same process as roasting. In roasting, more complex gas–solid reactions take place between the furnace atmosphere and the solids.

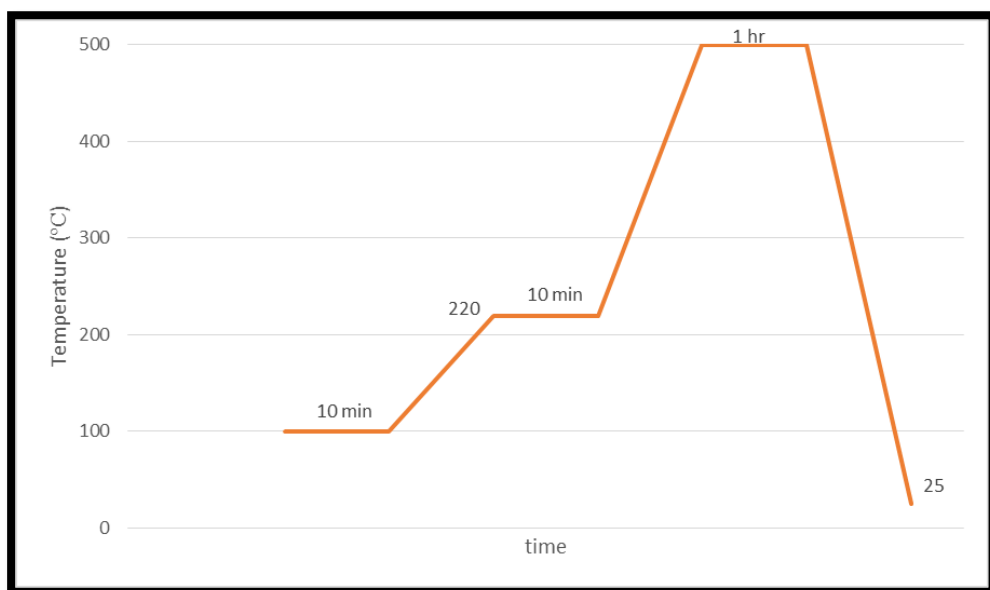


Figure 2.10: Calcination pattern of electrospun nanofibers.

The calcination temprature pattern in our work is depicted in

Figure 2.10 which is held in 3 levels starting from 100°C to 500°C. It is started with a light heat shock at 100°C, then it is kept for 10 minutes at 220 °C to make sure that solvents evaporate for the most. After all it is exposed to 500 °C heat for 1 hour to produce tungsten oxide crystals.

In the next section the results of the experiments are going to be explained in details.

3 RESULTS AND DISCUSSION

In this section, we explore our investigation on functionality test results of films and fibers by means of various spectroscopy techniques such as SEM, XRD, XPS, FTIR, UV-Vis and optical microscopy. Our major aim is to find out the chemical and physical structure of thin films regarding the photochromic phenomenon. As on the most interesting chromogenic systems, photochromism is the main function of our thin layers. We expose the films to a UV light source (a UV lamp operating in room conditions, no vacuum nor special gas applied) to check out the responses. The expected response can be a color change in visible electromagnetic spectrum range or only a change in chemical structure. Therefore, we need to characterize each film or fiber separately, once before applying UV light (as prepared form) and then after UV irradiation in a specific time domain.

3.1 Electrodeposited films

Although the electrodeposited tungsten oxide films do not show photochromic properties, but we have obtained a suitable coating which has been investigated by SEM and EDS analysis.

3.1.1 Structural Analysis of electrodeposited films

A JEOL 6320 FV FE-SEM was used to examine the microstructure and the surface morphology of the films deposited on glass substrates. INCA energy dispersive spectroscopy (Oxford, UK) attached to the SEM was used for elemental analysis.

Microstructural analyses of tungsten oxide films deposited by sol-gel and electrodeposition were investigated by FE-SEM observations and results are presented in Figure 3.1.

As can be seen from the figure, dense, well adherent and homogenous tungsten oxide films were successfully deposited onto the substrates. The SEM and EDS analysis confirmed that the films deposited by both sol-gel and electrodeposition on glass and

ITO substrates were uniform and composed of tungsten oxide (identified by microanalysis).

Many fine grains along with small cracks are formed over the surface of electrodeposited tungsten oxide films with WCl_6 precursor. The tungsten oxide granules display a spherical geometry and form agglomerates, thus generating more bulky aggregates with a wrinkled morphology on the sub micrometric scale, and a mean radius of 770 nm, as illustrated in Figure 3.2. The radius of granules changes from 550 nm to 835 nm. Whilst the tungsten oxide films with WCl_6 precursor granules display a spherical geometry and form agglomerates, the tungsten oxide films with W metal powder precursor granules display a non-spherical geometry and these granules disappear for tungsten oxide films with AIPTA precursor as showed in Figure 3.1, 3.2 and 3.3.

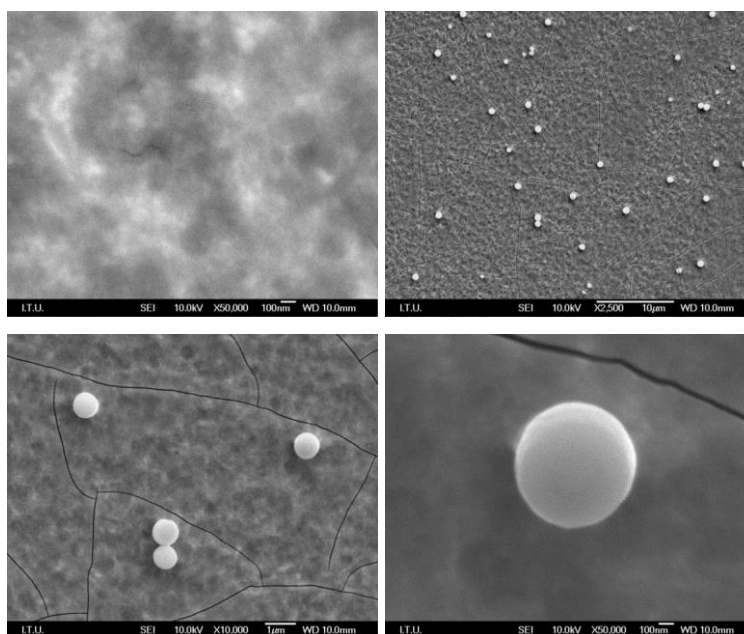


Figure 3.1: SEM images of electrodeposited tungsten oxide with WCl_6 precursor on ITO with different scales.

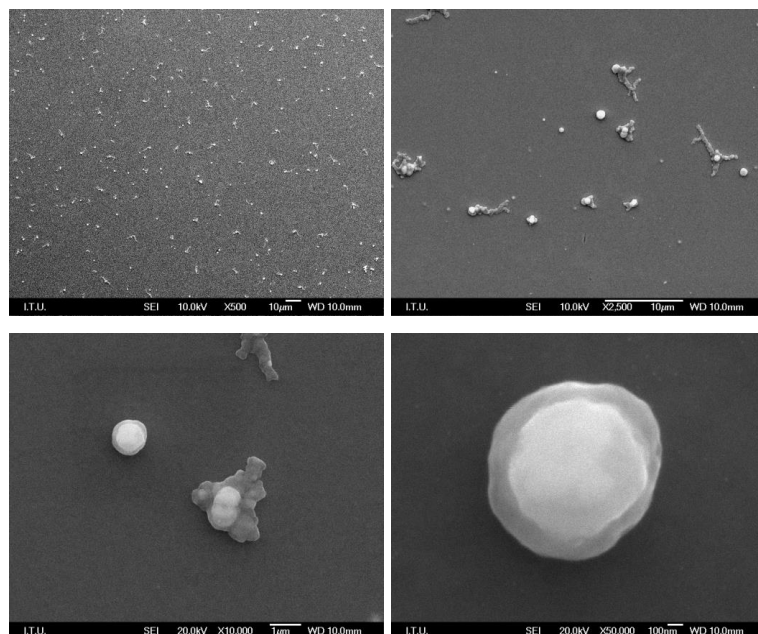


Figure 3.2: SEM images of electrodeposited tungsten oxide with W powder precursor on ITO with different scales.

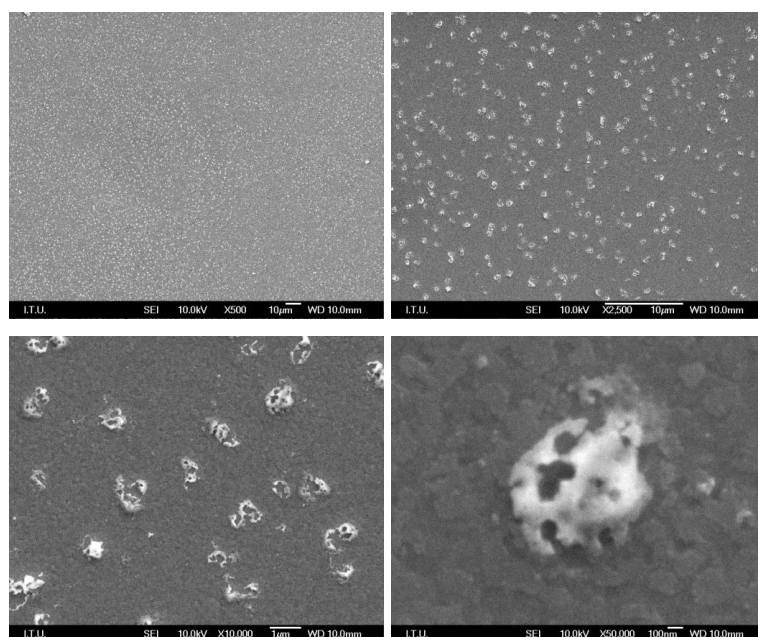


Figure 3.3: SEM images of electrodeposited tungsten oxide with AIPTA precursor on ITO with different scales.

Chemical analysis of the films was examined by EDS represented in Table 3.1. EDS results were taken from the flat, spot areas and including both flat and spot overall area from the SEM images. EDS results showed that tungsten and oxygen concentration was approximately the same in the different regions of the films. Other elements listed in the tables are constituents of the substrate.

Table 3.1: EDS results of the electrodeposited films in weight percentage. Samples 1, 2 and 3 represent tungsten oxide films prepared with WCl_6 , W metal and AIPTA precursors respectively.

Spectrum	O	Na	Mg	Al	Si	Ca	In	Sn	W	Total
1-Spot	26.82	1.94	0.61	0.20	11.24	2.92	14.71	2.07	39.48	100.00
1-Flat	25.16	3.94	1.64	0.21	32.27	6.57	23.26	3.68	3.28	100.00
1-Genel	26.19	3.93	1.38	0.74	31.85	6.88	23.93	4.57	0.52	100.00
2-Genel	19.31	0.84	0.49	0.04	12.29	2.87	15.12	1.88	47.15	100.00
2-Spot	21.44	0.45	0.24	0.08	4.80	1.11	9.16	1.86	60.85	100.00
2-Flat	20.75	1.11	0.39	0.08	12.74	3.19	16.78		44.97	100.00
3-Genel	23.89	2.62	1.13	0.38	24.94	5.75	21.91	1.39	17.98	100.00
3-Spot	22.84	1.15	0.63	0.24	10.45	1.56	15.38	2.14	45.61	100.00
3-Flat	23.78	2.63	0.77	0.45	25.08	5.79	23.37	4.48	13.66	100.00
Base	25.81	4.25	1.66	0.77	33.58	7.82	24.16	1.94		100.00

3.2 Dip-coated tungsten oxide films

Dip-coated tungsten films with WCl_6 precursor are performed by a dip-coater system with 100 mm/min speed. Samples are prepared in one-layered, two-layered and three-layered formats in order to obtain thicker films.

3.2.1 Structure analysis of sol-gel deposited films

While sol-gel made tungsten oxide has a porous structure as expected, the surface of tungsten oxide films is uniform and flat in macroscale as shown in Figure 3.4. The cross sectional SEM image shows that tungsten oxide has sticky and spongy structure.

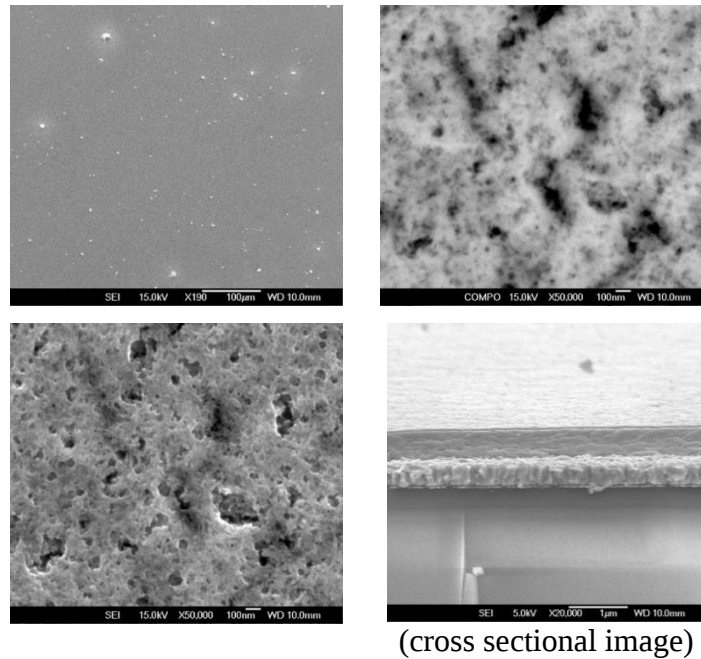


Figure 3.4: SEM images of sol-gel made tungsten oxide films on glass substrates with different scales and the cross sectional image.

Table 3.2: EDS result of sol-gel made tungsten oxide films.

Element (%)	C	O	W
Tungsten Oxide	29.72	14.54	55.73

SEM and EDS analysis confirmed that tungsten oxide films deposited by sol-gel technique were uniform and composed of tungsten oxide represented in Table 3.2.

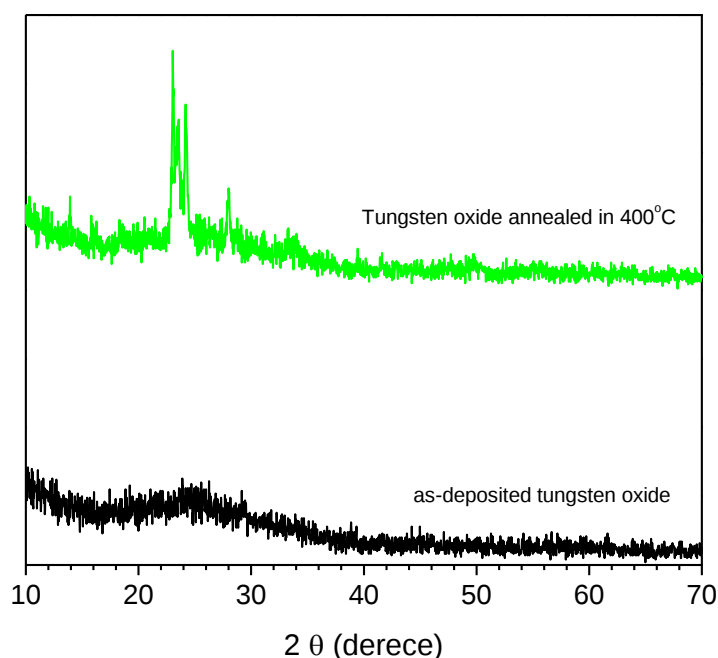


Figure 3.5: XRD result of tungsten oxide films deposited by sol-gel technique.

Heat treated films were coated on substrate and heated in air between at 400°C. XRD spectra of the as-deposited and heat treated tungsten oxide at 400°C are shown in Figure 3.5. As-deposited tungsten oxide remains almost amorphous up to 400°C and start to fully crystallize at 400°C. By a spectral deconvolution analysis of the spectra in the XRD pattern, three peaks can be identified at 2θ values of 23.10°, 23.60° and 24.23°. These peaks are consistent with a triclinic crystalline structure and correspond to 002, 020 and 200 diffractions, respectively.

3.3 Spin-coated tungsten oxide films with organic blends

As mentioned previously in section 2.3.2, inorganic solutions and organic/inorganic blends are applicable to form thin films of tungsten oxide by spin-coating technique. The photochromic tests upon both films revealed that inorganic films of tungsten oxide do not show a considerable color change when exposed to UV light.

For single tungsten oxide, it generally exhibits poor photochromic reversibility. Additionally thermally bleached tungsten oxide sample cannot be photocolored again

and low fatigability. They cannot be cycled many times while maintaining performance. One solution to these problems is to combine the tungsten oxide with suitable organic molecules. Herein, PVP organic molecules were used with tungsten oxide. Unlike the inorganic solution, the spin-coated B1, B2 and B3 blends (see, Table 2.1) for developing reversible photochromic phenomenon by illumination under UV light for less than 3 minutes. Figure 3.6 shows the effect of UV exposure on the spin-coated thin films after 8 minutes. Away from direct UV light source in the darkness or in visible light, the bleaching process takes about 3 hours.

The ability to combine inorganic and organic components at the nanometer or molecular level represents an extraordinary implications for developing multifunctional materials. Since the photochromism of the inorganic and organic components is closely related to the charge transfer between these molecules, it is of great importance to construct a bridge in the hybrid, through which the charges can reversibly transfer between the two constituents upon photoexcitation.

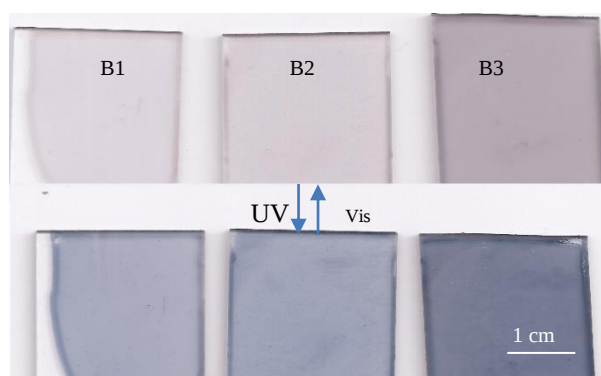


Figure 3.6: Images of spin-coated blends before and after UV irradiation.

Before and after the exposure we measured the UV transmittance of the sample in the range of 200nm to 1200nm, illustrated in Figure 3.7. UV-Visible spectrophotometry analysis result of spin-coated sample shows that the transmittance values are reducing by UV irradiation.

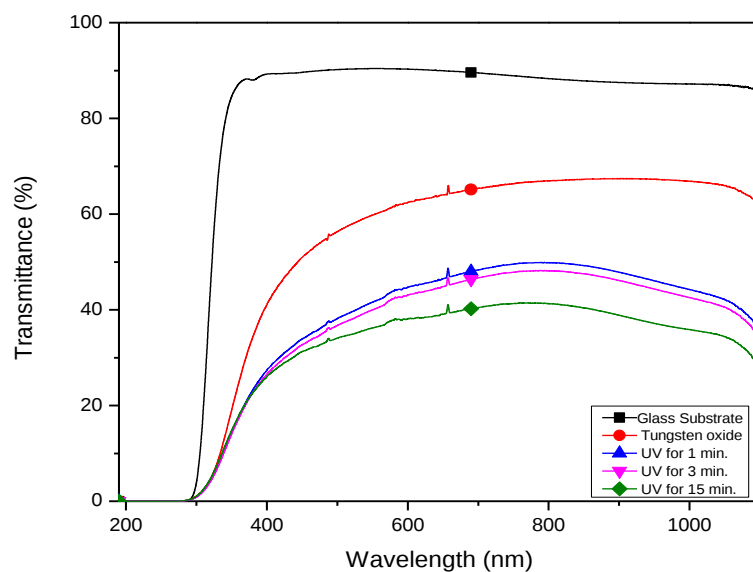


Figure 3.7: UV-Vis. spectrophotometry results of spin-coated thin film.

Compositional characterization of the spin-coated thin film with organic blend were carried out by X-Ray Photoelectron Spectroscopy (XPS) tests by thermo scientific k-alpha model instrument, using Al source, probe depth 10 nm (90° take-off angle). It was aimed to determine the constituents of the coatings, as well as binding structures. Figure 3.8 shows the spectra of the coated films obtained from XPS where a general surface survey was performed.

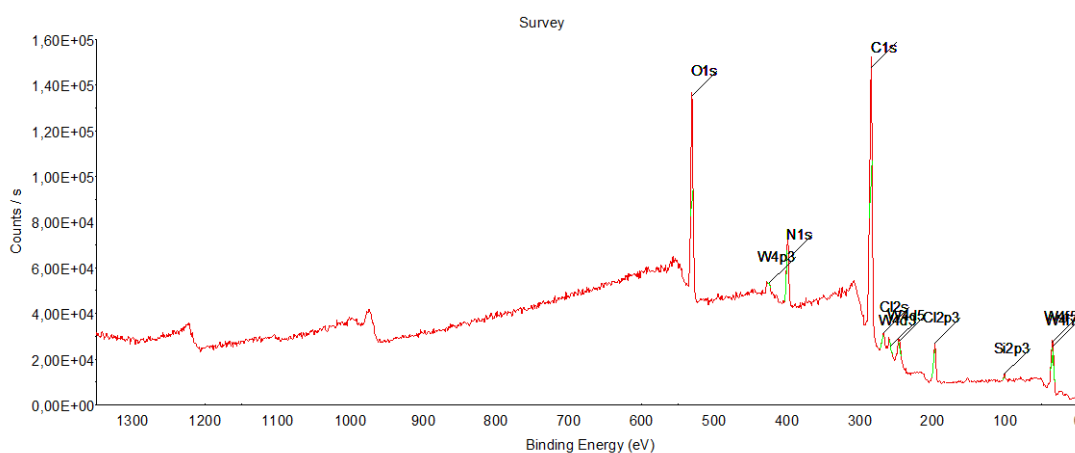


Figure 3.8: XPS survey scan spectra of as-prepared tungsten oxide film formed by spin-coating technique.

There are visible peaks that belong to Si, N, Cl and C elements, there are also significant W and O peaks, indicating tungsten and oxygen elements.

Several windows (C1s, N1s, Cl2s, Cl2p, Si2p, O1s, W4p, W4d, W4f) were rescanned to get detailed information about elemental peaks (see Figure 3.9). The source of N peak was not determined. This might be due to the peaks from substrate and contamination.

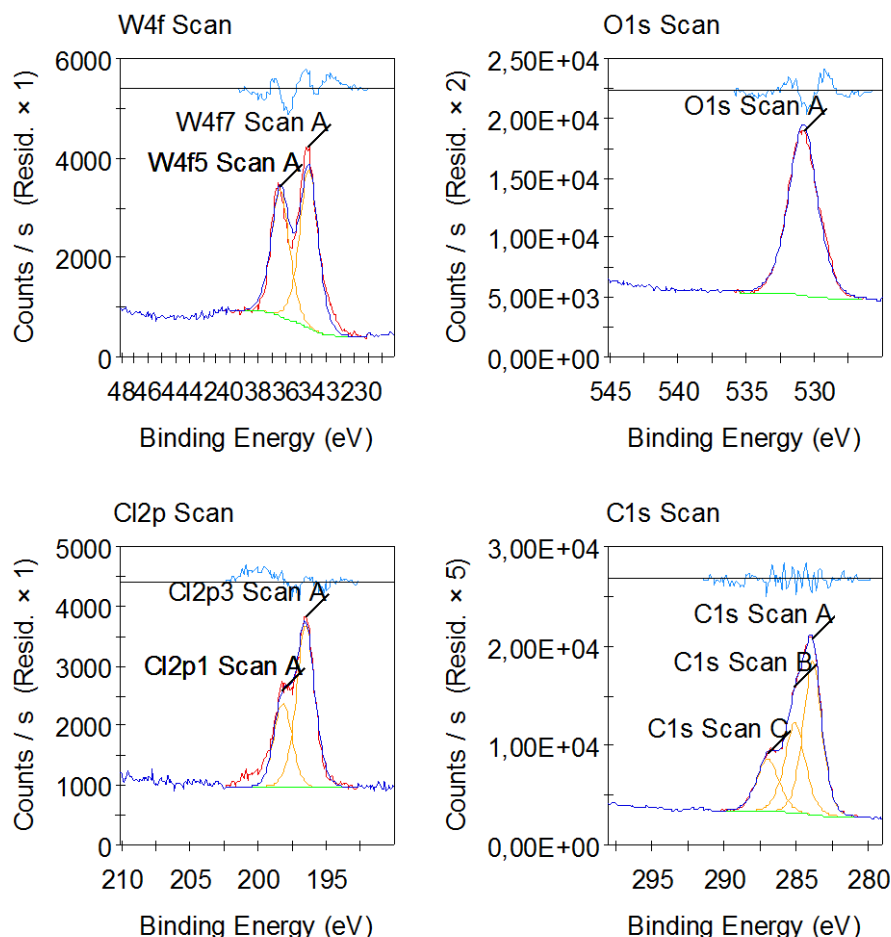


Figure 3.9: Detailed XPS spectra of as-prepared spin-coated tungsten oxide film.

It was initially seen that carbon peak is the dominant peak in as-prepared spin-coated tungsten oxide film. After calcinations (shown in Figure 3.10), there is a total decrease in the relative intensity with a pronounced increase in the carbon peak intensity. This is thought to be due to the partial removal of PVP from the coating, giving rise to tungsten signals to be transmitted strongly from the underlying film layers, along with nitrogen signals coming from species.

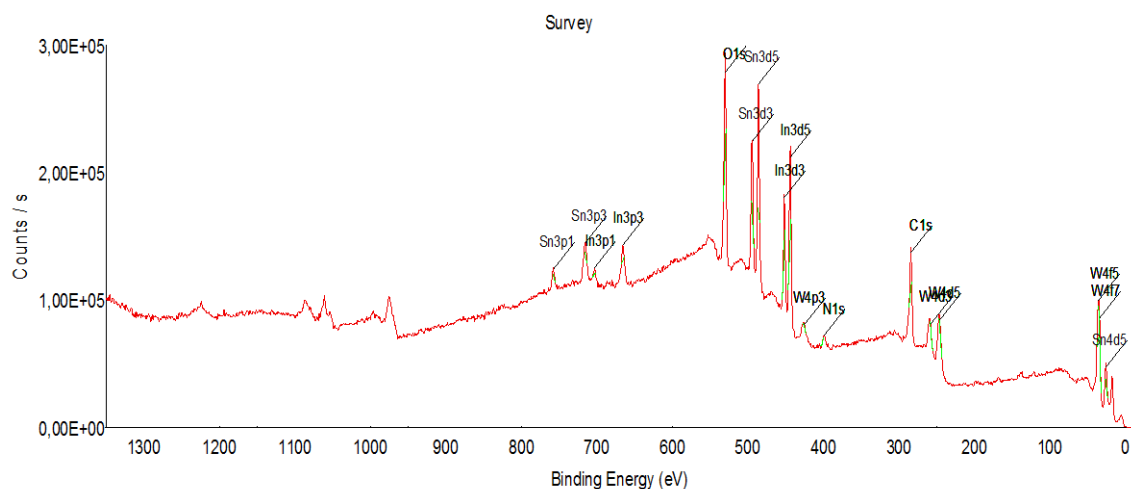


Figure 3.10: XPS survey scan spectra of calcined tungsten oxide film at 500°C formed by spin-coating technique.

Nevertheless, the peaks require further fitting analysis for exact determination of phase compositions and stoichiometry.

3.4 Casting of tungsten oxide blend with WCl_6/PVP

To determine the microstructure of the dried blend and comparing with the calcined blend, we cast the tungsten hexachloride polymeric blend on a Corning glass substrate. XRD analysis has been performed to examine the microstructure of the blend before and after calcination. The calcination pattern is represented in Figure 2.10.

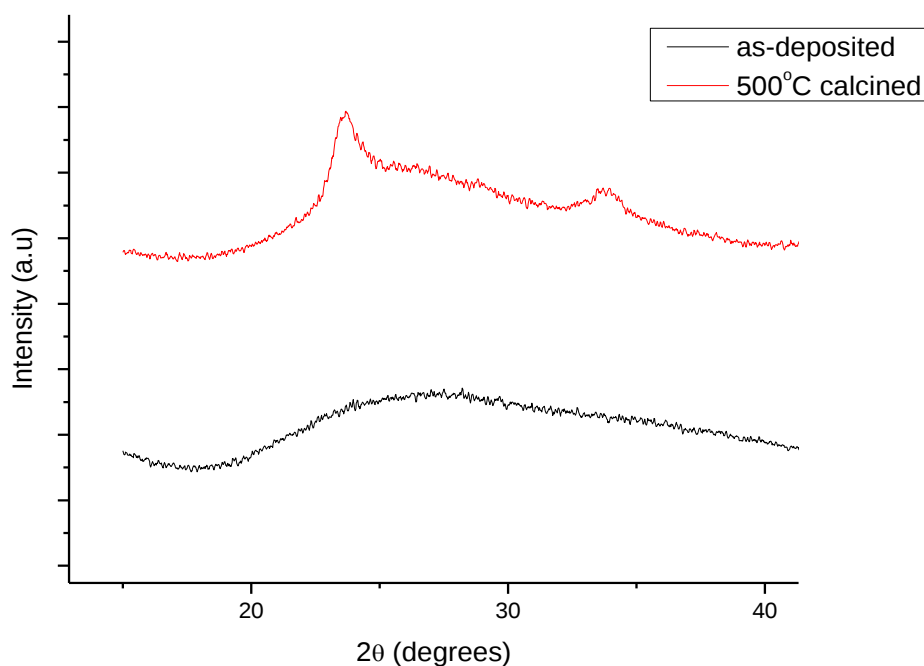


Figure 3.11: XRD patterns of B1 blend (heat treated at 70°C) and calcined tungsten oxide.

Figure 3.11 shows the X-ray diffraction patterns of tungsten oxide before and after calcination at 500°C for 4 hours. XRD pattern of tungsten oxide film prepared via B1 blend (heat treated at 70°C) shows that there is no crystallization in the tungsten oxide and it is completely amorphous, the only wide peak in 25 degree is because of PVP polymer crystal structure [64] [65]. Verification of peaks the XRD pattern for the sample was assigned based on cell constants of WO₃ with monoclinic (pseudo-orthorhombic) symmetry ($a = 7.306$, $b = 7.540$, and $c = 7.692$ Å, and $\beta = 90.88^\circ$) [66].

Compositional characterization of the thin film formed by casting on glass substrate with organic blend were carried out by XPS. It was aimed to determine the constituents of the coatings, as well as binding structures. Figure 3.12 and Figure 3.13 show the spectra of the coated films obtained from XPS where a general surface survey was performed respectively. The same result was obtained from XPS survey of spin coated samples. There are visible peaks that belong to Si, N, Cl and C elements, there are also significant W and O peaks, indicating tungsten and oxygen elements.

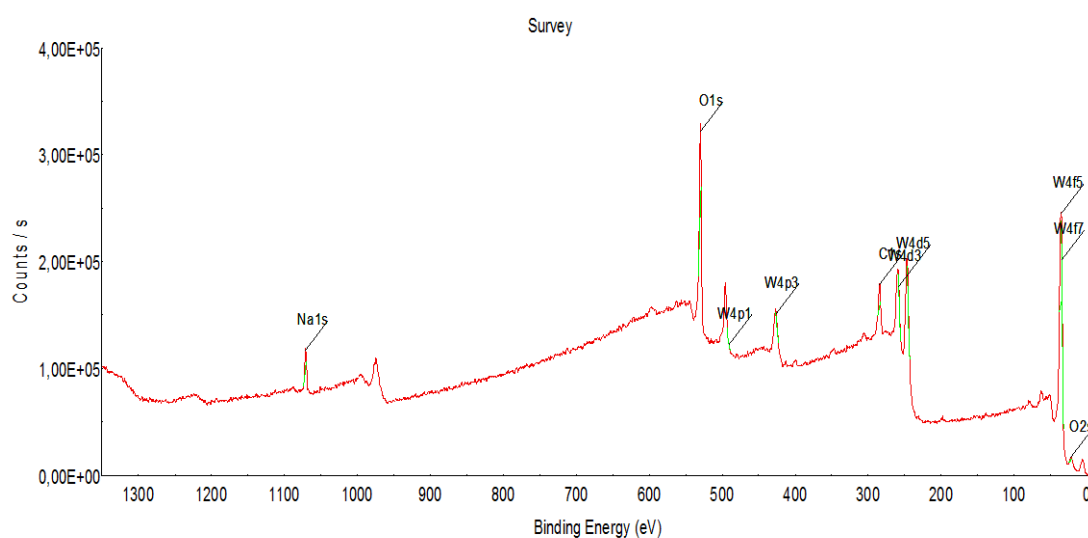


Figure 3.12: XPS survey scan spectra of tungsten oxide blend film formed by casting on glass.

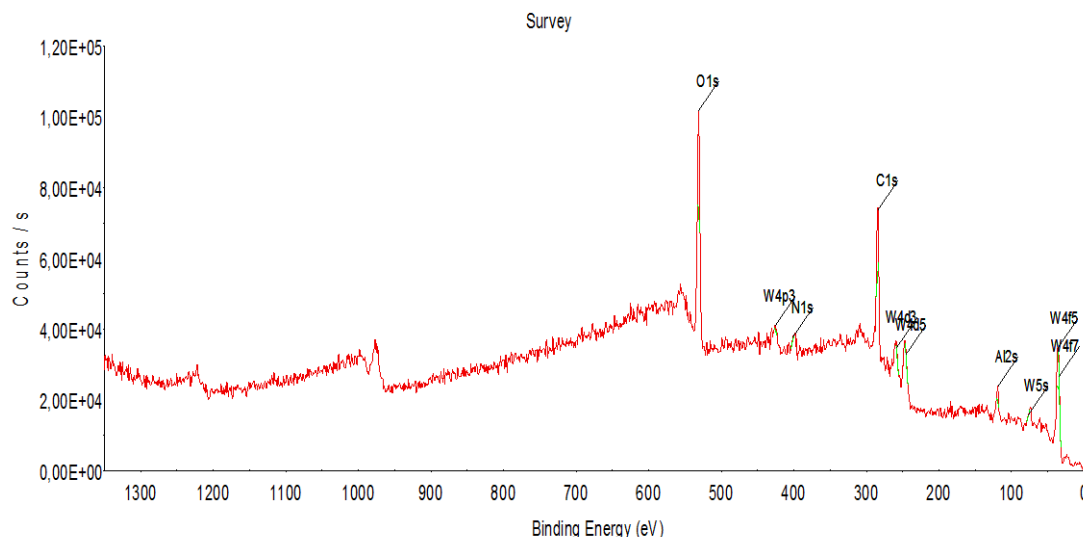


Figure 3.13: XPS survey scan spectra of calcined tungsten oxide film at 500°C formed by casting.

3.5 Electrospun of tungsten oxide with AIPTA/PVP blend

The sol-gel AIPTA precursor mixed with a 10% PVP solution in ethanol loaded in the syringe with (2:1) ratio after stirring for 2h. The electrospinning was carried out at room temperature. Many different precursor solutions were selected for this part. The solutions varied in the concentrations of the different constituents. Extensive research has been done on the stability of PVP-based nanofiber systems. Also, PVP is an excellent capping reagent of various metal nanoparticles. Hence, PVP was chosen as the primary binding polymer. PVP solution was prepared by dissolving PVP powder in DMF and stirring at room temperature. A solution of AIPTA in EtOH (ethanol) was prepared for use in precursor preparation to obtain tungsten oxide fibers by electrospinning and calcination. However, SEM images of tungsten oxide fibers with AIPTA precursor represent that fibers could not be collected well on the substrates.

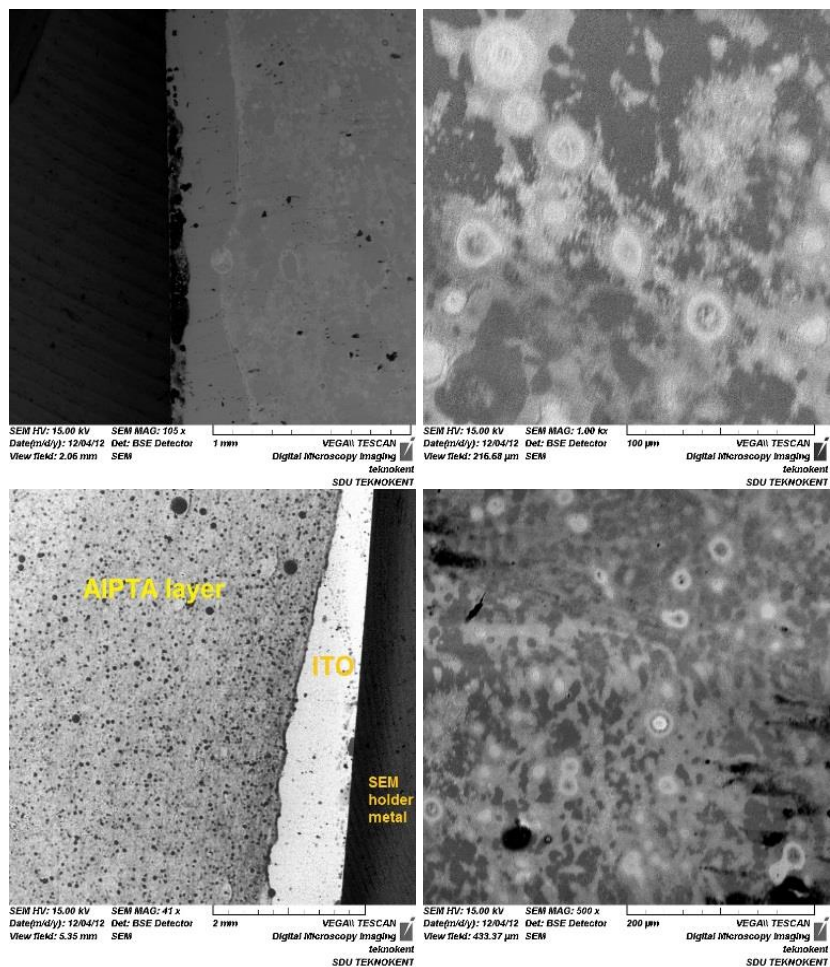


Figure 3.14: SEM images of electrospinning of tungsten oxide with AIPTA solution.

Although expected nanofibers of electrospun tungsten oxide has not been obtained in this test, a continuous thin film of AIPTA solution has been formed as seen in the SEM images (Figure 3.14), which is interesting for further experiments. Moreover, UV tests are failed for both as-prepared and calcined sample films.

3.6 Electrospun of tungsten oxide with W/PVP blend

In this part, we have established a method of incorporating W metal powder precursor in tungsten oxide nanofibers by electrospinning and calcination. PVP solution was prepared by dissolving PVP powder in DMF and stirring at room temperature. A solution of W metal powder in H_2O_2 was prepared for use in precursor preparation to obtain tungsten oxide fibers by electrospinning and calcination. The solutions varied in the concentrations of the different constituents ((1:2) and (1:3) W:PVP). The solution of W metallic in H_2O_2 in the existence of polymer is completely homogenous and viscous. However, there were some

problems like voltage distortion and inappropriate distance of needle to collector during electrospinning process, we could not collect homogenous nanofibers due to environmental conditions such as room temperature and humidity. There are also beads and wet droplets in the fiber mat as seen in Figure 3.15.

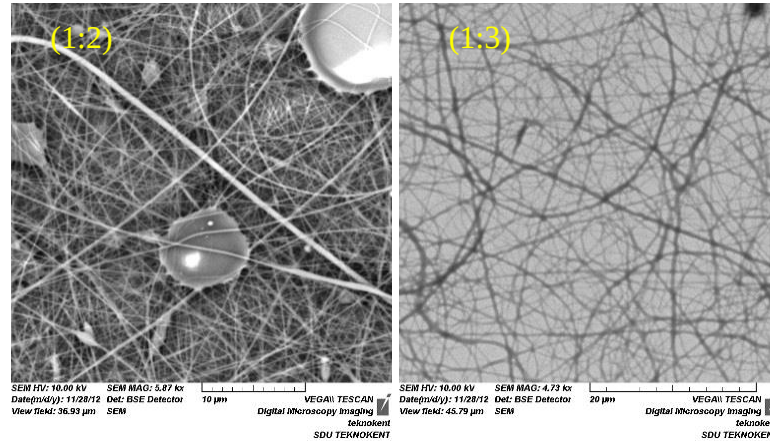


Figure 3.15: SEM of electrospun tungsten oxide fiber with W metal powder ((1:2) and (1:3) W:PVP).

Figure 3.15 shows that the calcined electrospun nanofibers of tungsten oxide with metallic blend in two concentrations of 1:2 and 1:3 (W:PVP). Collected nanofibers were calcined at 500°C for 2 hours. SEM represent that the collected nanofibers images worse than not calcined ones since these fibers are rare and weak and include beads. Although we had thinner fibers compared to the as-prepared sample, but there are more disconnections in the surface.

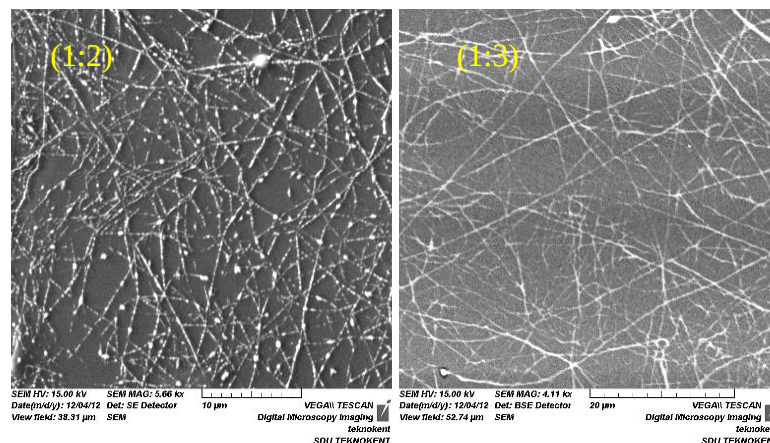


Figure 3.16: SEM of calcined electrospun nanofibers of tungsten oxide with metallic blend in two concentrations of 1:2 and 1:3 (W:PVP).

By resolving the viscosity, concentration and room temperature problems, we obtained homogenous nanofibers of tungsten oxide by metallic tungsten precursor as

depicted in SEM pictures presented in Figure 3.17. Thickness of the nanofibers are in the range of 112nm to 184nm.

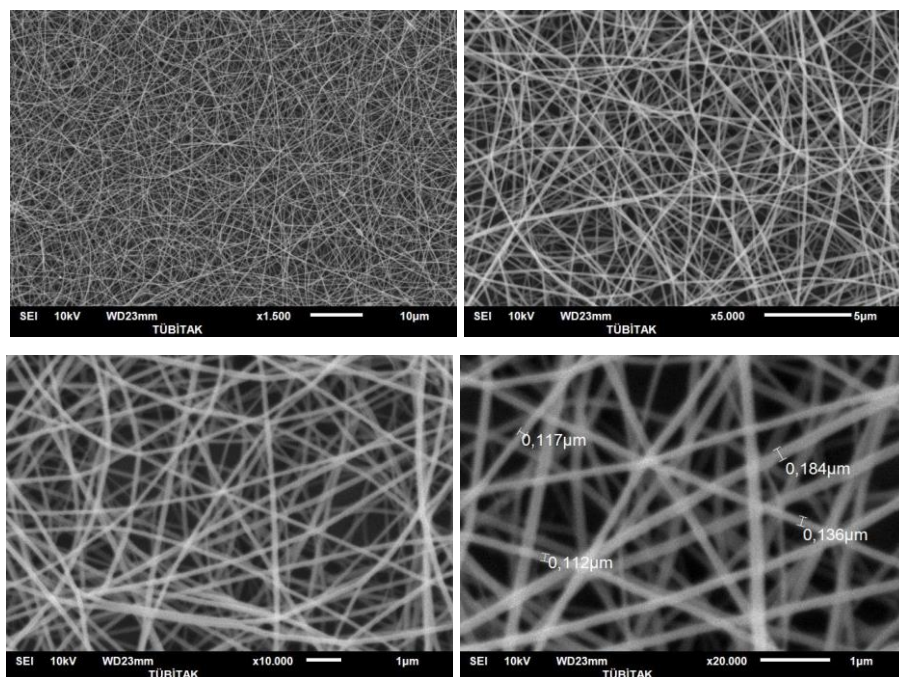


Figure 3.17: SEM images of electrospun tungsten oxide nanofibers of W/PVP (1:2) in different scales.

FTIR analysis of as-prepared electrospun tungsten oxide nanofibers by metallic tungsten precursor is given in Figure 3.24. Inorganic compounds have vibrational bands mainly below 1200 cm^{-1} . The 816 cm^{-1} band is assigned to the out of stretching vibrations of W-O-W mode, when hydrogen is located at a coplanar square of oxygen atoms. A relatively weak band at 1073 cm^{-1} , which is assigned to the plane deformational (bending) W-OH mode, was found. The peak at 1424 cm^{-1} is assigned to $\nu(\text{OH})$ and $\delta(\text{OH})$ in OH, W-O group. In the frequency range of 400 to 1100 cm^{-1} , the peak in 977 cm^{-1} (W=O terminal modes of surface grains) and W-O-W bridging mode 902 cm^{-1} exist exhibiting the stretching vibrations of W-O bounds [67]. In addition, the sharp peak in 1290 cm^{-1} is assigned to C-N stretches of aromatic amines group.

Organic compounds mostly have vibrational bands mainly after 1500 cm^{-1} . The sharp peak around 1652 cm^{-1} is assigned to C=O stretch of α , β -unsaturated aldehydes, ketones functional group. The medium peak at 2950 cm^{-1} reveals the C-H stretch from alkanes group and finally the sharp and broad shoulder around 3340 cm^{-1} is assigned to O-H stretch, from H-bonded alcohols, phenols functional group.

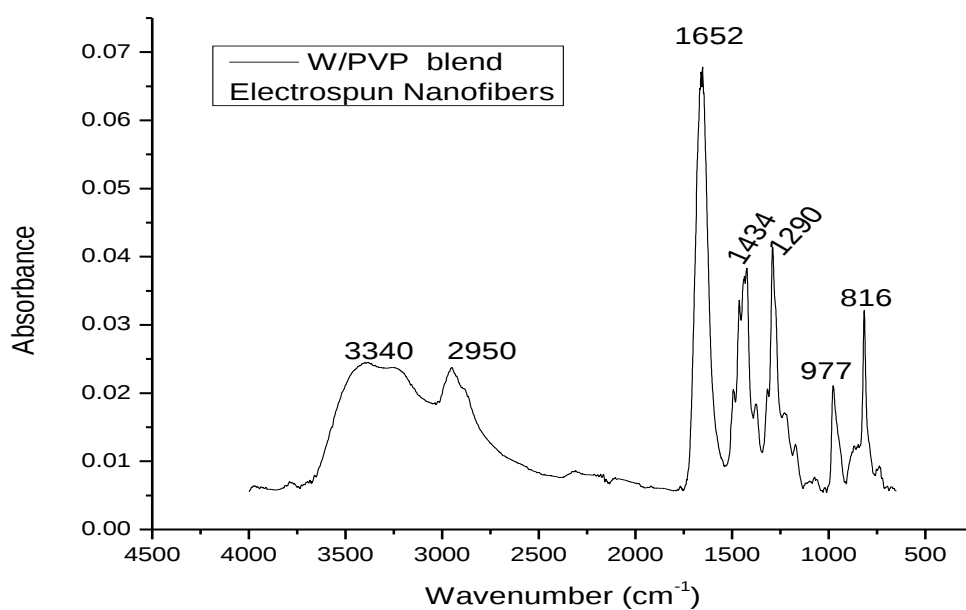


Figure 3.18: FTIR of electrospun tungsten oxide nanofibers of W/PVP using W/PVP blend.

SEM images of calcined nanofibers of tungsten oxide are showed in Figure 3.19. Thickness of the fibers are obviously 35% reduced that is between 42nm and 152nm.

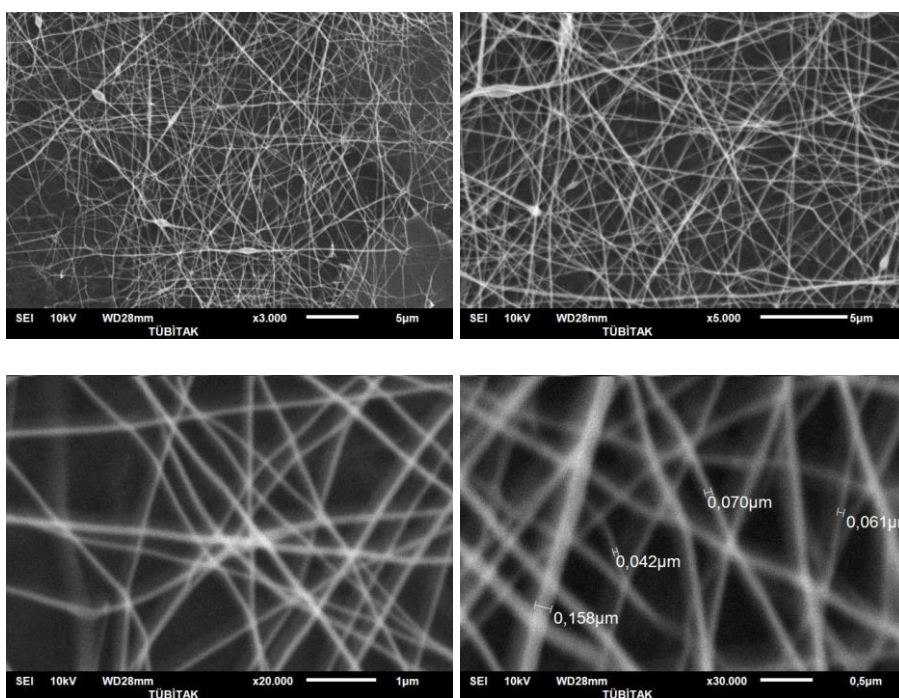


Figure 3.19: SEM images of calcined nanofibers of tungsten oxide by W metallic.

3.7 Electrospun of tungsten oxide with WCl_6 /PVP Blend

Primary experiments of electrospinning of tungsten hexachloride in PVP polymer solution was not as successful as expected. There might be two main reasons: environmental conditions such as humidity and temperature and the non-optimized experimental conditions for nanofibers formation (see, Figure 3.20).

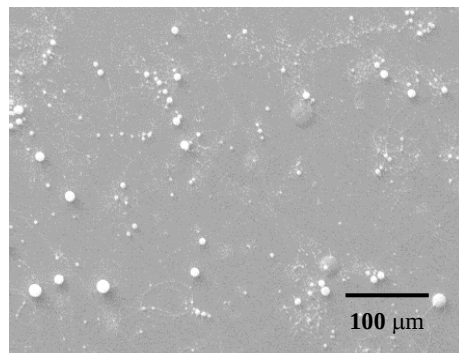


Figure 3.20: SEM image of unsuccessful test of electrospinning of WCl_6 /PVP blend.

In the second tests, by improving the viscosity of solution and selecting PVP 1.300.000 as the suitable polymer, we collected fibers, but not acceptably homogenous.

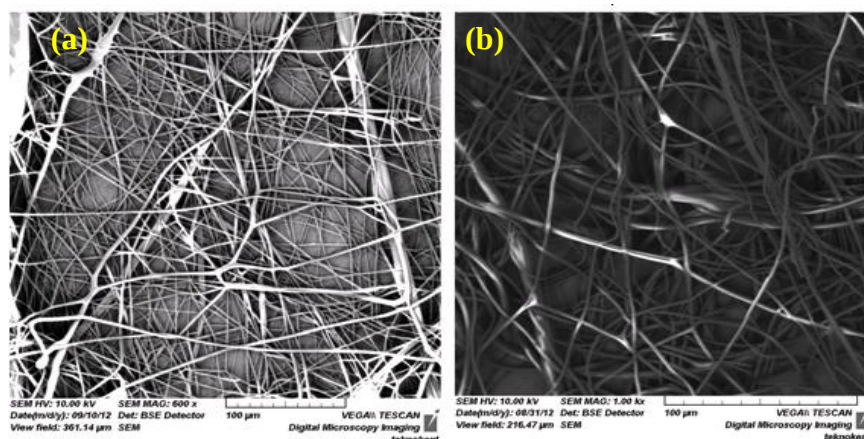


Figure 3.21: SEM image of inhomogeneous electrospun nanofibers of tungsten oxide using WCl_6 /PVP blend (a) before and (b) after calcination.

After optimizing the experimental conditions of electrospinning: 24 kV DC voltage, 15 cm distance and 6 μl/min feed rate at RT, homogenous mat of tungsten oxide nanofibers collected on glass substrate (see, Figure 3.22 (a)), later, as a result of a shock in calcination process on the fibers on the glass surface created cracks and discontinuities as shown in Figure 3.22 (b).

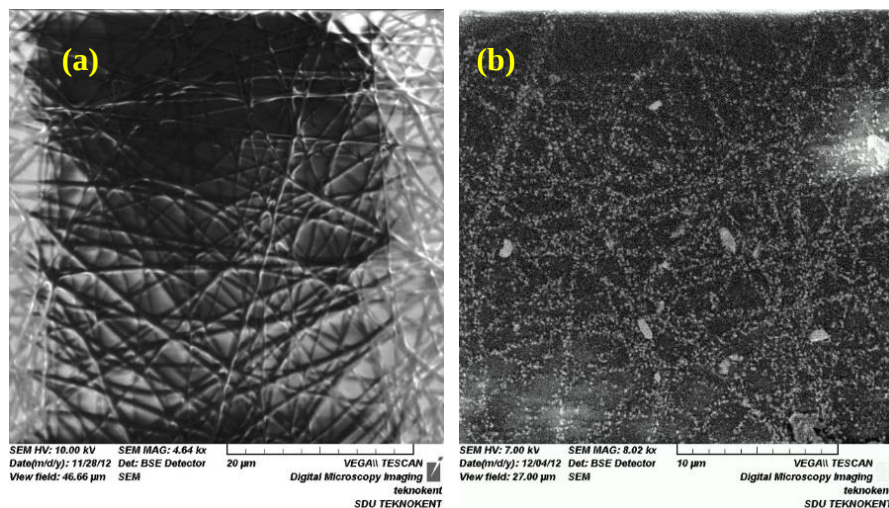


Figure 3.22: SEM image of electrospinning of tungsten oxide nanofibers using WCl_6 /PVP blend (a) before and (b) after calcination.

Finally, the electrospinning process was held at RT using 20 kV DC voltage while the distance was 15 cm, feeding rate was 6 μ l/min, and substrate was a glass on aluminum foil. SEM images of resultant electrospun nanofibers are presented in Figure 3.23. The diameters of the composite nanofibers are distributed in the range of 190 nm and 350 nm with an average diameter of 270 nm, as shown in the inset.

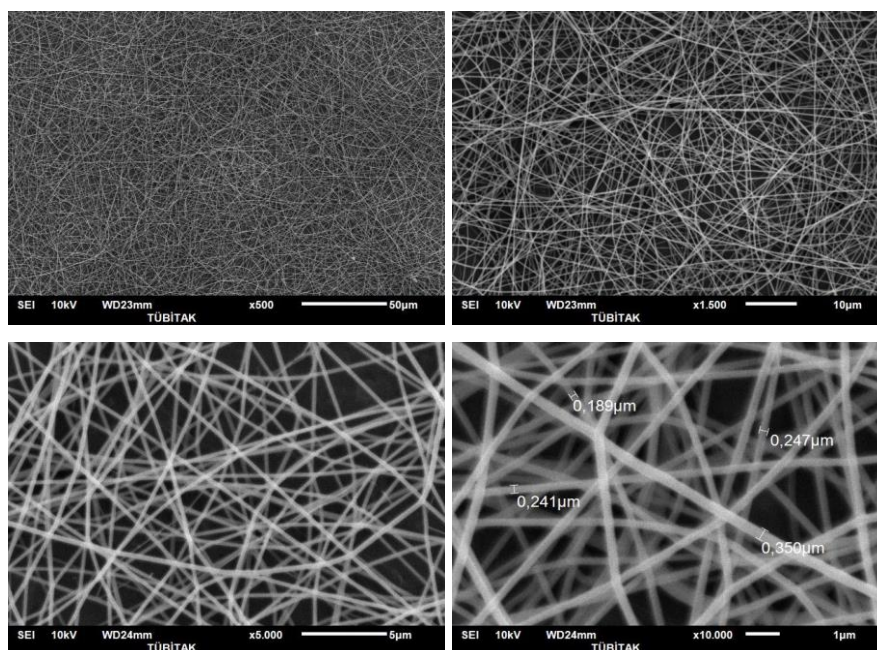


Figure 3.23: SEM images of electrospun nanofibers of tungsten oxide nanofibers by WCl_6 /PVP blend in different scales.

FTIR analysis of as-prepared electrospun nanofibers of tungsten oxide using WCl_6 /PVP blend is given in Figure 3.24. The 679 cm^{-1} band is assigned to the out of

plane deformation W-O-W mode, when hydrogen is located at a coplanar square of oxygen atoms where the 816 cm^{-1} peak is assigned to the out of stretching vibrations of W-O-W mode. A relatively weak band at 1062 cm^{-1} , which is assigned to the plane deformational (bending) W-OH mode, was found. Because of the creation of weakly bonded W-OH groups is formed in the as-deposited film. In the frequency range from 400 to 1100 cm^{-1} , the shoulder around 979 cm^{-1} (W=O terminal modes of surface grains) and W-O-W bridging mode 902 cm^{-1} [67].

Organic compounds mostly have vibrational bands mainly after 1500 cm^{-1} . The sharp peak around 1690 cm^{-1} is assigned to C=O stretch of α , β -unsaturated aldehydes, ketones functional group. The medium peak at 2960 cm^{-1} reveals the C-H stretch from alkanes group and finally the sharp and broad shoulder around 3330 cm^{-1} is assigned to O-H stretch, from H-bonded alcohols, phenols functional group. In addition, the medium peak in 1423 is related to C-H bend of alkanes group.

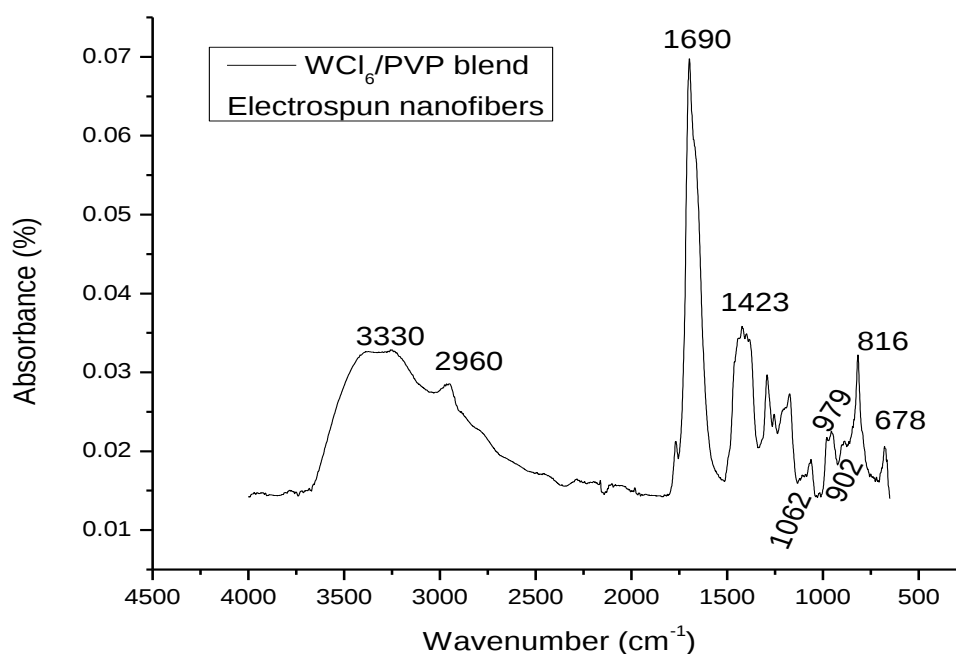


Figure 3.24: FTIR of electrospun tungsten oxide nanofibers by WCl_6/PVP blend.

To eliminate polymeric compounds from the film structure, and obtain an inorganic surface we calcined the nanofiber mat. After calcination at 500°C for 1 hour, we obtained homogenous thin fibers in the range of 57 nm and 110 nm with an average diameter of 85 nm as shown in Figure 3.25. After calcination process, the average diameter of the nanofibers is reduced by nearly 70 percent, proving that organic

compounds have been removed from the film structure and tungsten oxide is the dominant remaining material in the surface.

The as-prepared and calcined films do not show any photochromic effect in visible frequency range.

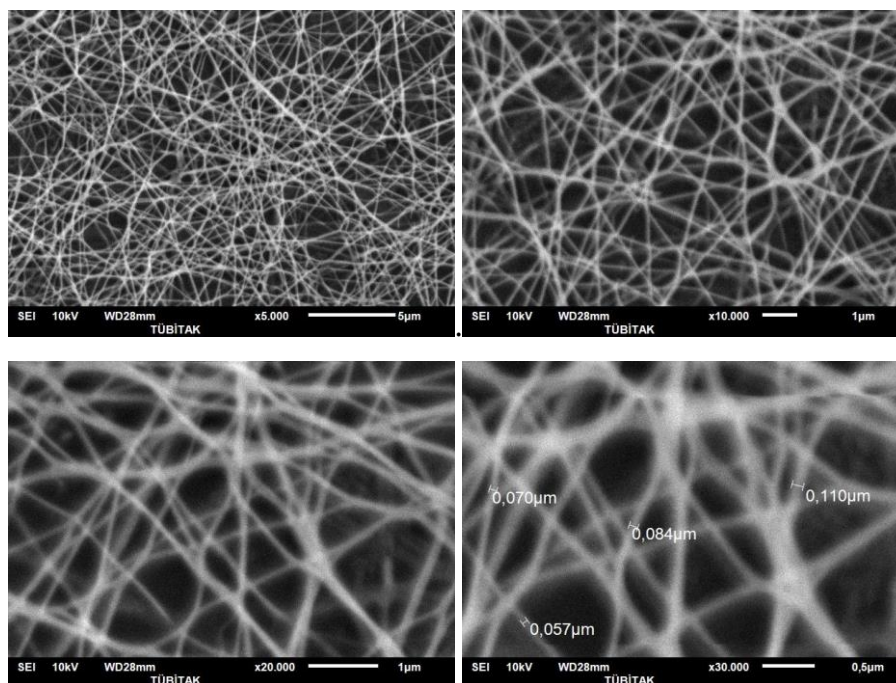


Figure 3.25: SEM images of calcined nanofibers of tungsten oxide by WCl_6 /PVP blend.

During the experiment, an unintended change in the electrospinning setup gave a new result in the produced fibers. By reducing the distance to 10 cm and using a needle which has a wider tip with 1 mm diameter, we obtained micro fibers in the range of 300 μm . The adherence to surface is acceptably good. This microfibers on glass substrate act as a UV detector and represent color alteration under UV lamp and return to their original state after a while as displayed in Figure 3.26. The reversible coloration process takes about 3 minutes while the bleaching process takes about 3 hours. It demonstrates that the photochromic fiber has a good memory effect. The coloration cycling of the material is repeatedly reversible and its durability has been tested several times functioning acceptably well. Color changes in micro and macro sized fibers which are big enough to be observed by naked eye, are photographed simply by an optical microscope. The sample was exposed to UV light for 3 minutes.

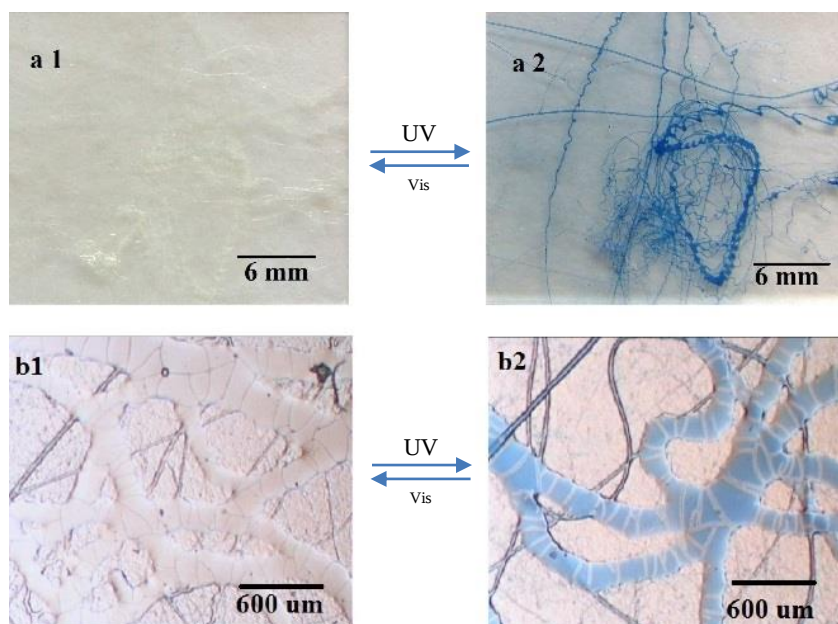


Figure 3.26: Electrospun microfibers of tungsten oxide via WCl_6/PVP blend (a1, b1) before and (a2, b2) after UV illumination.

Colored and bleached fibers under UV light irradiation in the range of 10 to 1000 micrometers are observable by means of optical microscopes as shown in Figure 3.27 and Figure 3.28. For micro and macro fibers, we applied optic microscope to observe the surface. Our microfiber samples are scanned before and after UV irradiation, in which the color change is obviously observed.

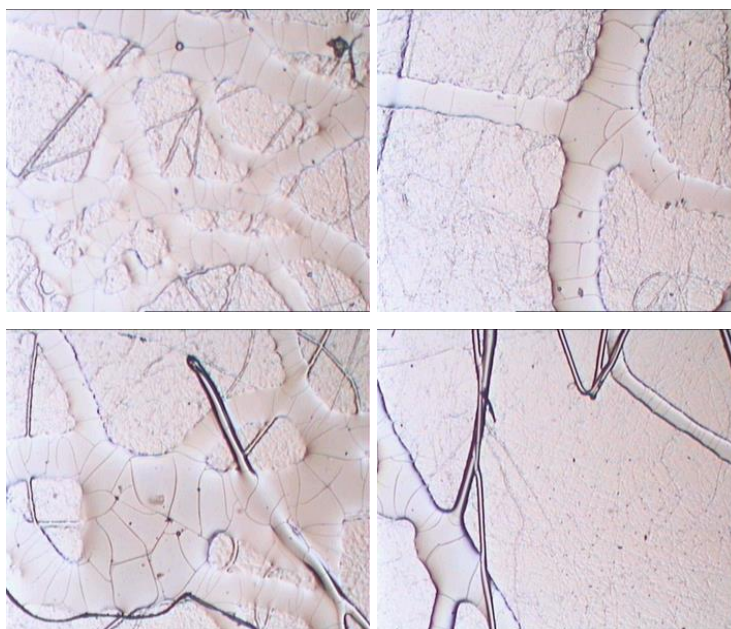


Figure 3.27: 4X zoom optical microscopy of transparent as-prepared tungsten oxide microfibers.

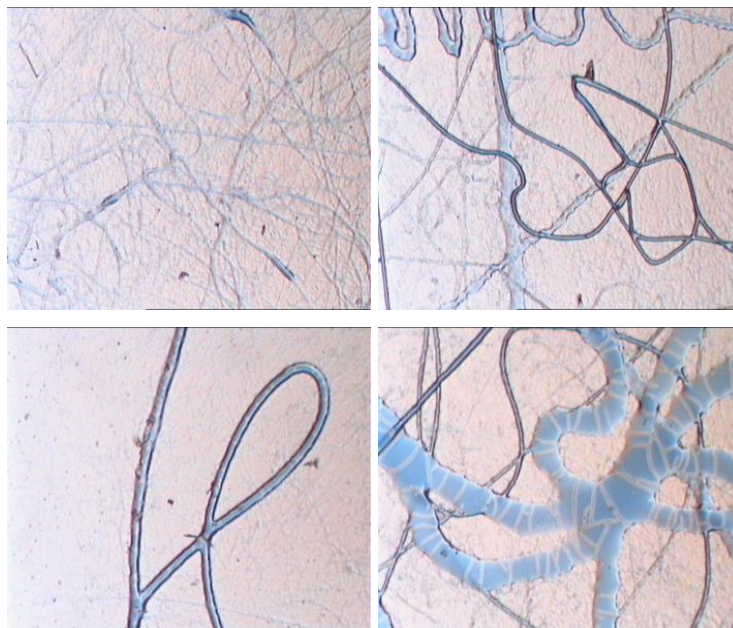


Figure 3.28: 4X zoom optical microscopy of UV irradiated tungsten oxide microfibers.

We use a UV lamp for obtaining transmittance spectra of our sample. Within 100 seconds, the transparent polymeric layer of WCl_6 /PVP changes color to blue as shown in Figure 3.28. Further exposure to UV light makes it darker. The time needed for returning to transparent form is about 4 hours. The durability of the sample is tested by repeating the test 2 times a day, for 40 days and the operation has not changed nor dissolved.

3.8 Capsulated tungsten oxide films with organic blends

Figure 3.29 shows the effect of short-time UV irradiation on encapsulated films of tungsten oxide by means of darkening. A disadvantage of this technique is that the modified thin film is always enclosed with two layers of glass and it is not possible to obtain a single layered film. Therefore, the coloring procedure is not reversible for long time. Therefore, it will not be acceptable as a photochromic device but it is suitable for testing the homogeneity of the prepared solution and its color changing under UV irradiation.

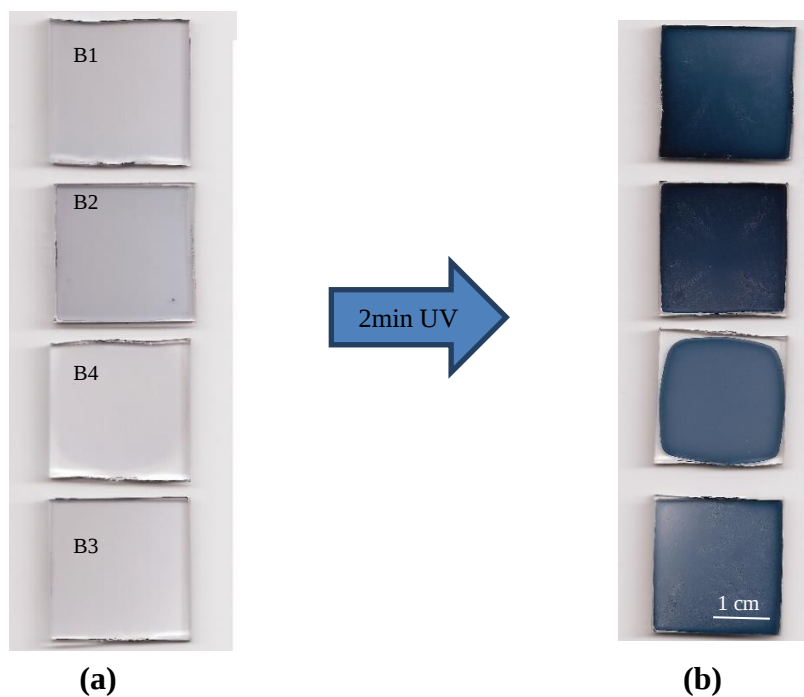


Figure 3.29: Images of thin film of B1, B2, B3 and B4 blends in a sandwich structure (a) before and (b) after UV irradiation.

UV spectrophotometry analysis of the as-prepared and UV irradiated samples are shown in Figure 3.30 which reveals nearly 50 percent decrease in transmittance after 10 min exposure to UV light.

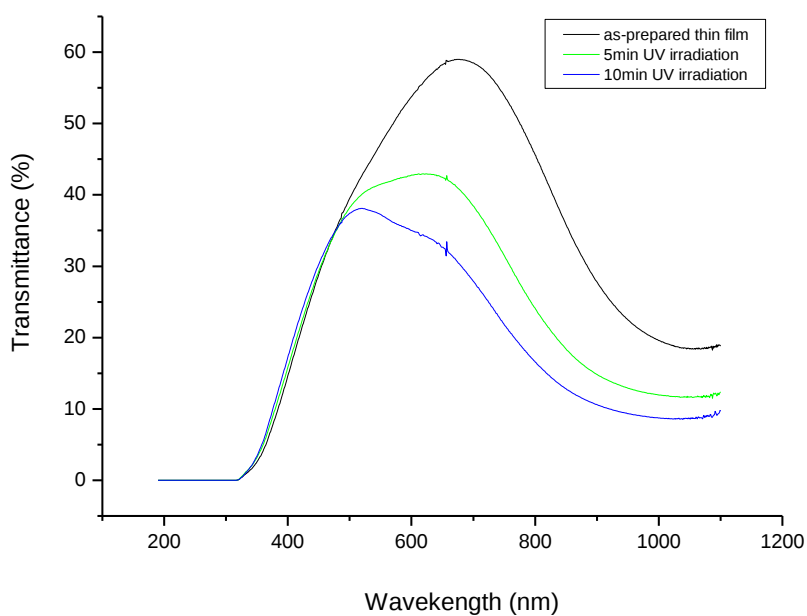


Figure 3.30: UV-Vis. spectrophotometry results of encapsulated sandwich structure of tungsten oxide film using B2 blend.

3.9 Drawn tungsten oxide fibers by WCl_6/PVP Blend

Figure 3.31 shows microfibers produced by drawing technique using the concentration B2 and effect of UV irradiation on the micro fibers in 20 minutes. Away from direct UV light source the bleaching process takes about 4 hours. Micro and macro-fibers' diameter of the produced fibers are in the range of 60 to 2500 μm .

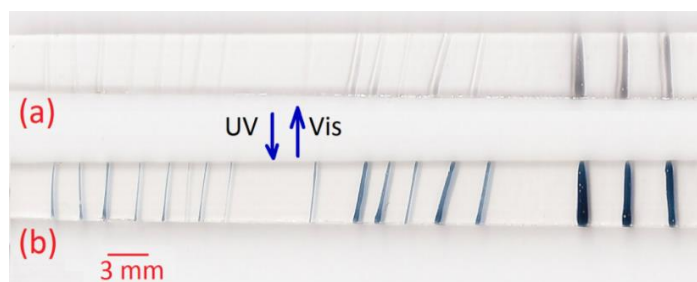


Figure 3.31: Image of drawn tungsten oxide microfibers by B2 before and after UV irradiation.

3.10 Writing ink application

To test the behavior of our samples on cellulose, we applied both samples to a piece of printing paper. This way we have used the organic/inorganic material as an ink. The result coloring by UV irradiation is the same as spin-coated samples.

The overall test, any concentrations of $\text{WCl}_6/\text{PVP}/\text{EtOH}/\text{DMF}$ solution is applicable as an invisible ink, which become visible under UV light. The coloring and bleaching speed as well as the contrast is different for the prepared concentrations. Even by excluding the polymer, photochromic property is observable on paper substrates. However, by removing the polymer, the obtained film is less durable, and has smaller optical density.

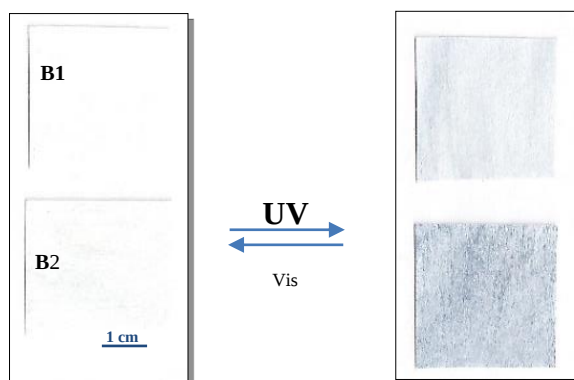


Figure 3.32: Sample B1 (up row) and B2 (down row) applied to paper (left) as prepared and (right) after 20 min of UV exposure.

UV illumination has a significant effect on photochromism of tungsten oxide blend applied to paper substrate as shown in Figure 3.33. This takes only 2 minutes to appear and about 20 minutes to saturate.

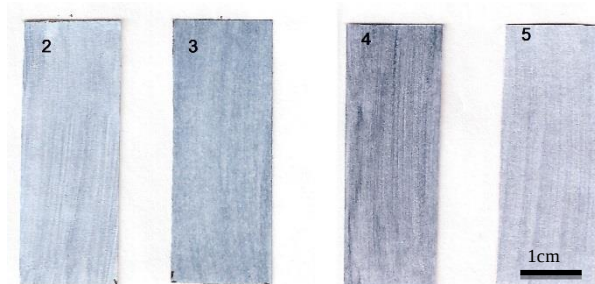


Figure 3.33: Image of effect of UV illumination on 4 concentrations of the blend.

As shown in Figure 3.34, using the blend for ink to write on glass is also possible. Its color changes reversibly from light gray to dark blue in few minutes under UV light.

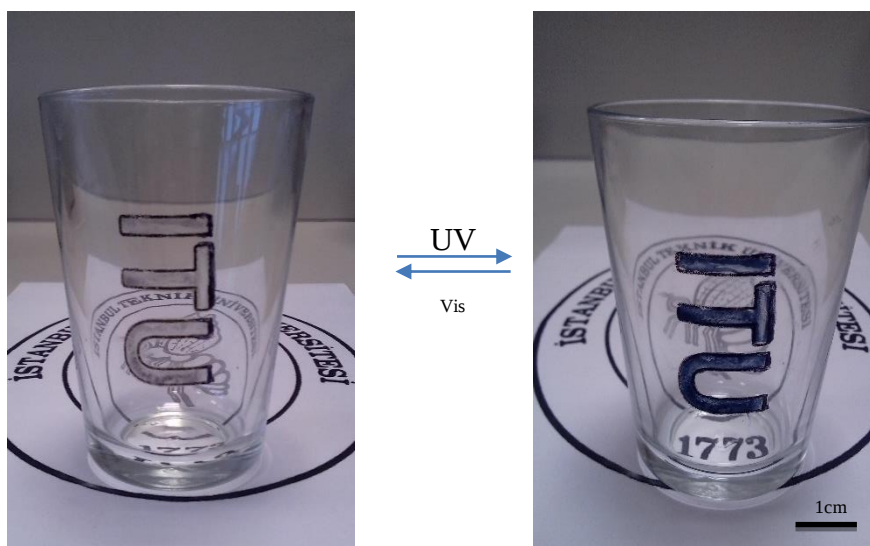


Figure 3.34: Image of UV illumination effect on writing ink on glass substrate.

4 CONCLUSIONS

In this work, we describe a procedure for producing tungsten oxide films from variety of precursors such as tungsten hexachloride (WCl_6), metallic tungsten powder and AIPTA. Furthermore, we have prepared thin films and micro and nano fibers of the organic/inorganic blend of tungsten hexachloride, metallic tungsten and PVP, via electrospinning, spin coating, droplet drawing, casting and writing ink, given that the technique to prepare tungsten oxide is the prime determinant of size of the fibers and formation of the film. The only produced films and fibers by WCl_6 /PVP blends represent photochromic effect under UV light irradiation. Hence, we prepare four different concentrations of WCl_6 and PVP solution with the solvents for examining the PC effect. Each of the solutions is suitable for one or more techniques according to its concentration and viscosity. All of the four blends are applicable for casting between two pieces of glass and for being used as ink to write on paper by a brush. B2 is suitable for electrospinning because it meets the density and electrostatic requirements of that technique. B1, B2 and B3 are suitable for spin coating on a glass or metallic substrate. B4 is feasible to be used for drawing technique. Table 4.1 summarizes applicable techniques according to the solutions. The produced films and fibers are prepared for exhibiting reversible photochromic properties.

Table 4.1: Summary of applicable techniques according to concentrations.

Code/Method	B1	B2	B3	B4
Electrospinning	No	Yes	No	No
Spin Coating	Yes	Yes	Yes	No
Drop Casting	Yes	Yes	Yes	Yes
Drawing	No	No	No	Yes
Ink	Yes	Yes	Yes	Yes

As on the most interesting chromogenic systems, photochromism (PC) is the main function of our thin layers and microfibers. We expose the films to a UV light source to check out the responses. The expected response can be a color change in visible

electromagnetic spectrum range or only a change in chemical structure. Therefore, we need to characterize each film or fiber separately, once before applying UV light (as-prepared form) and then after UV irradiation with UV-Vis. spectrophotometry and optical microscopy. The color alteration of the obtained photochromic thin films under UV light are rapid, have large optical modulation, long memory and long functioning cycle time.

Our results indicate that tungsten oxide in the form of films and microfibers has PC properties (it is also worth noting that we have been unable to detect these PC effects with nanofibers so far, which is currently under investigation in our laboratory).

Prepared tungsten oxide films, as photochromic materials, offers numerous advantages:

- The color change is relatively rapid
- They have large optical modulation
- They possess long memory and long life-time.

To investigate the crystallinity, structural and chemical composition of the tungsten oxide structures were probed with Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, X-Ray Diffraction (XRD) and X-Ray Photoelectron (XPS) methods. FTIR and XPS are two methods used to extract information on the surface of the tungsten oxide.

In overall, we believe that this reported procedure is a novel avenue to prepare photochromic materials, with superior properties.

One of our future aims is to find out the chemical and physical structure of thin films regarding the photochromic phenomenon. There are many parameters that govern a coating process; the effect of each parameter significantly alters the coatings yielded at the end. It was observed superior photochromic effect of tungsten oxide films and fibers under UV illumination in this study, where more characterizations with altered parameters would widen the scope of the study. In further analysis, technical consultancy of an XPS expert would prove useful to determine the exact compositions of the coatings and oxidation products before and after UV illumination.

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