

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL

**INVESTIGATION OF THE DOPED TiO₂ NANOFIBERS AS ETM LAYER IN
PEROVSKITE SOLAR CELLS**



KÜBRA ERDOĞAR

**A THESIS OF DOCTORATE
PHYSICS DEPARTMENT**

ADVISOR: ASST. PROF. DR. ÖZGÜN YÜCEL

JANUARY 2024

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LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

KATKILANMIŞ TiO_2 NANOFİBERLERİN PEROVSKİT GÜNEŞ
HÜCRELERİNDE ETM TABAKASI OLARAK İNCELENMESİ

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Dedication

*To my
Family*

ABSTRACT

Perovskite solar cells (PSCs) are rapidly becoming impressive solar cells due to the effective physicochemical properties of the absorber layer. This layer should ideally be placed between a stable hole transport material (HTM) layer and a conductive electron transport material (ETM) layer. These outer layers play a critical role in the current densities and cell voltages of solar cells. In this work, we successfully fabricated Mg-doped TiO₂ nanofibers as ETM layers via electrospinning. The diameter of the produced nanofibers was calculated as a maximum of 299 nm in undoped fibers, and after calcination at 500°C, this value decreased to 125 nm. Here, the area covered by the fibers is 77% of the entire area, while the porosity obtained in doped fibers is in the range of 50-68%. A certain range of porosity was achieved in the structure. This work systematically investigates the morphological and optical properties of Mg-doped nanofibers as porous ETM layers. The presence of the Mg element in the cage was confirmed by XRD and XPS. In XRD analysis, it was observed that anatase and rutile phases of TiO₂ were successfully obtained after calcination at 500°C. Additionally, the presence of Mg was demonstrated by elemental analysis in the SEM image. These optical characterizations show that Mg doping widens the energy band gap and shifts the conduction band minimum edge up. The band gap for undoped TiO₂ was calculated as 3.20 eV, and this value increased to 3.28 eV for Mg-doped TiO₂. With this, it is thought that the open circuit voltage (V_{oc}) and short current density (J_{sc}) can be increased. With the photoluminescence measurement, it was seen that the electron-hole recombination rate was reduced for Mg-doped samples and the separation efficiency increased with Mg doping. In the study, the ETM layer was also produced by the sequential percolation synthesis method, which is an alternative method, and the current was obtained by photoelectrochemical measurements. The results showed that using magnesium-doped nanofibers as ETM layer could improve the efficiency of PSCs.

Keywords: Nanofibers, Mg-Doped TiO₂, Perovskite, Electron Transport Material

ÖZET

Perovskit güneş pilleri (PSC'ler), soğurucu katmanın etkili fizikokimyasal özellikleri nedeniyle hızla etkileyici güneş pilleri haline gelmektedir. Bu katman ideal olarak kararlı bir delik taşıma malzemesi (HTM) katmanı ile iletken bir elektron taşıma malzemesi (ETM) katmanı arasına yerleştirilmelidir. Bu dış katmanlar, güneş pillerinin akım yoğunlukları ve hücre gerilimlerinde kritik bir rol oynamaktadır. Bu çalışmada, elektrosponning yoluyla ETM katmanları olarak Mg katkılı TiO_2 nanofiberleri başarıyla ürettik. Üretilen nanofiberlerin çapları katkılanmamış fiberlerde maksimum 299 nm olarak hesaplanmış 500°C 'de kalsinasyon sonrası bu değer 125 nm'ye kadar düşmüştür. Burada fiberlerin kapladığı alan tüm alanın %77'si kadarken katkılanmış fiberlerde elde edilen porozite %50-68 aralığındadır. Yapıda belirli bir aralıkta gözeneklilik elde edilmiştir. Bu çalışma, gözenekli ETM katmanları olarak Mg katkılı nanofiberlerin morfolojik ve optik özelliklerini sistematik olarak araştırmaktadır. Kafes içindeki Mg elementinin varlığı XRD ve XPS ile doğrulanmıştır. XRD analizinde 500°C de kalsinasyon sonrasında TiO_2 'in anataz ve rutil fazlarının başarılı bir şekilde elde edildiği gözlemlenmiştir. Ayrıca SEM görüntüsünde elementel analiz yapılarak Mg varlığı gösterilmiştir. Bu optik karakterizasyonlar, Mg katkısının enerji bandı aralığını genişlettiğini ve iletim bandı minimum kenarını yukarı kaydırıldığını göstermektedir. Katkılanmamış TiO_2 için bant aralığı 3.20eV olarak hesaplanmış olup Mg katkılı TiO_2 için bu değer 3.28eV'a çıkmıştır. Bununla da açık devre voltajını (V_{oc}) ve kısa akım yoğunluğunu (J_{sc}) artırılabilceği düşünülmektedir. Yapılan fotoluminesans ölçümü ile Mg katkılı örnekler için elektron-delik rekombinasyon oranının düşürülmüş olduğu görülmüş ve Mg katkısı ile ayırma verimliliği artmıştır. Çalışmada ayrıca ETM katmanı alternatif bir yöntem olan ardışık sızma sentezi yöntemi ile üretilmiş ve fotoelektrokimyasal ölçümleri yapılarak akım elde edilmiştir. Sonuçlar, magnezyum katkılı nanofiberlerin ETM katmanı olarak kullanılmasının PSC'lerin verimliliğini artırabileceğini göstermiştir.

Anahtar Kelimeler: Nanofiberler, Mg Katkılı TiO_2 , Perovskit, Elektron Taşıma Malzemesi

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LIST OF SYMBOLS AND ABBREVIATIONS

ALD	: Atomic Layer Deposition
CBM	: Conduction Band Maximum
cTiO ₂	: Compact TiO ₂
DP	: Dual Porous
ETL	: Electron Transfer Layer
ETM	: Electron Transfer Material
FF	: Fill Factor
FTO	: Fluorine Doped Tin Oxide
HOMO	: Highest Occupied Molecular Orbital
IO	: Inverse Opal
ITO	: Indium Doped Tin Oxide
J _{sc}	: Short circuit current density
mpTiO ₂	: Mesoporous TiO ₂
NB	: Nano bowl
PCE	: Power Conversion Efficiency
PSCs	: Perovskite solar cells
SG	: Sol Gel
TO	: Thermal Oxidation
VBM	: Valance Band Maximum
Voc	: Open Circuit Voltage

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1. INTRODUCTION

TiO₂ is an inorganic material used as ETL in photovoltaic applications. In addition to its good electron mobility, TiO₂'s VBM value is much lower compared to perovskite, which is important for its ability to effectively block holes. Doping is a way to reduce electron trap levels and improve electron mobility and therefore enhance the electrical conductivity. Electrical and optical properties can be improved by doping. Amalathas et.al. studied Li doping for mesoporous TiO₂. Li doping suppresses the trap states therefore faster electron transfer is achieved (Peter Amalathas et al., 2019). Zhang et al. Studied Mg Doped TiO₂ planar architecture for perovskite solar cells. This contribution raises the free electron density and moves the ETL's Fermi energy level upward and they achieved 19.08 % power conversion efficiency (H. Zhang et al., 2016). In addition, that, doped mesoporous electron transfer layer can boost the efficiency for solar cells. For dye sensitized solar cell, mesoporous Electron transfer layer fabricated with nanofibers and power conversion efficiency 6.47% obtained (Horie et al., 2013). Xiang et al added the samarium element to the TiO₂ compact ETL layer with a planar structure. The results showed that the Fermi energy level of the samarium-doped structure shifted upwards, the conduction of the carriers improved and recombination decreased. While the power conversion efficiency was 10.3% in the undoped samples, it was measured as 14.10% in the samarium-doped samples (Xiang et al., 2017).

1.1. Aim of The Thesis

In this thesis mesoporous TiO₂ nanofibers will be fabricated as electron transfer layer for perovskite solar cells to achieve high efficiency. As it's known from other solar cells doping enhances the cell efficiency. Ion doping is an efficient technique that to reduce the trap states and increase the conductivity of the cell. In this thesis different from literature Mg Doped mesoporous TiO₂ nanofibers will be fabricated, and investigation of doping effect on the cell depends on nanofibers diameters and maximum efficiency will be achieved. Mg doping will change the Fermi energy level up as a result free

electron density will increase. Thus, TiO_2 resistivity will decrease with this issue the cells resistivity decrease. Besides, Mg doping decrease the photoexcited electrons transfer time due to this, power conversion efficiency will enhance.



2. BACKGROUND OF SOLAR ENERGY

Both industrialized and developing nations now have high levels of energy demand and environmental consciousness due to widespread technological use and population growth. Solar energy is an important option for the future that can help to reduce fossil fuel use and the growing environmental concern such as global warming. Over the past few years, due to their inexpensive material components, straightforward solution production method, and steadily rising the efficiency of power conversion for perovskite solar cells (PSCs) have generated a lot of interest (Rong et al., 2018).

2.1. Perovskite Solar Cells

In an effort to reduce device expenses and improve power conversion efficiency, third-generation solar cells, like quantum dot solar cells, organic solar cells, and dye-sensitized solar cells, have been thoroughly investigated. However, most of these solar cells have low PCEs (about 10%–12%). Major reasons are poor efficiency of light absorption, imperfect device fabrication, and unexpected charge recombination (Tong et al., 2015). Perovskite materials based on organometal halide $\text{CH}_3\text{NH}_3\text{PbX}_3$ holding promise for these problems, strong light absorption, bipolar transport capabilities, balanced electron and hole diffusion lengths, reduced charge recombination, and ease of manufacture are among its favorable qualities for solar cells (Q. Dong et al., 2015). In 2009, perovskite material was used as a sensitizer in liquid dye-sensitized solar cells by Miyasaka and associates, who showed a comparatively low PCE of about 3.8% (Kojima et al., 2009). Afterwards in 2012 stable, mesoscopic, solid-state device with a PCE of 9.7% was fabricated (H. S. Kim et al., 2012). In 2013, Julian and colleagues employed the sequential deposition technique to achieve optimal perovskite layer shape, resulting in a PCE of 14.1% for the device (Burschka et al., 2013). Late in the year, the application of hybrid halogen components of perovskite layer resulted in a PCE of 16.2% (Jeon et al., 2014).

Recently, the Korean Research Institute of Chemical Technology (KRICT) recorded a record PCE of 20.1%. (W. S. Yang et al., 2015) which the National Renewable Energy Laboratory (NREL) has already verified in late 2014 (Tong et al., 2015). Figure

1 shows that time-series analysis of perovskite solar cells' power conversion efficiency (PCE) (J. Y. Kim et al., 2020).

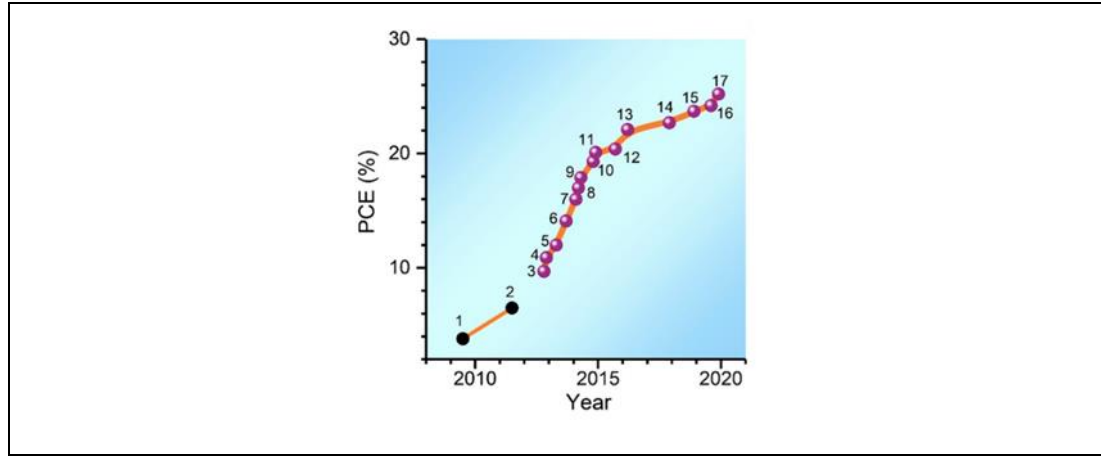


Figure 2.1: Time-series analysis of perovskite solar cells' power conversion efficiency (J. Y. Kim et al., 2020).

2.2. Perovskite Solar Cells Architecture and Working Principle

Figure 2.2a shows the general layout of perovskite solar cells, , perovskite layer is sandwiched between an electron transport material (ETM), and hole transport material (HTM) and along with additional metal electrode and fluorine doped tin oxide (FTO) or indium doped tin oxide (ITO) substrates. Working principle of cell is showed in figure 2.2b, incident light is absorbed by the perovskite layer, producing a hole and an electron, which are extracted and transported by ETMs and HTMs, respectively. Ultimately, electrodes gather these charge carriers to constitute perovskite solar cells. (Tong et al., 2015). Particularly, The highest occupied molecular orbital (HOMO) of HTMs and the conduction band minimum (CBM) of ETMs must be greater than the valence band maximum (VBM) of perovskite materials and lower than the CBM of perovskite materials, respectively, to achieve effective hole and electron transport and extraction.

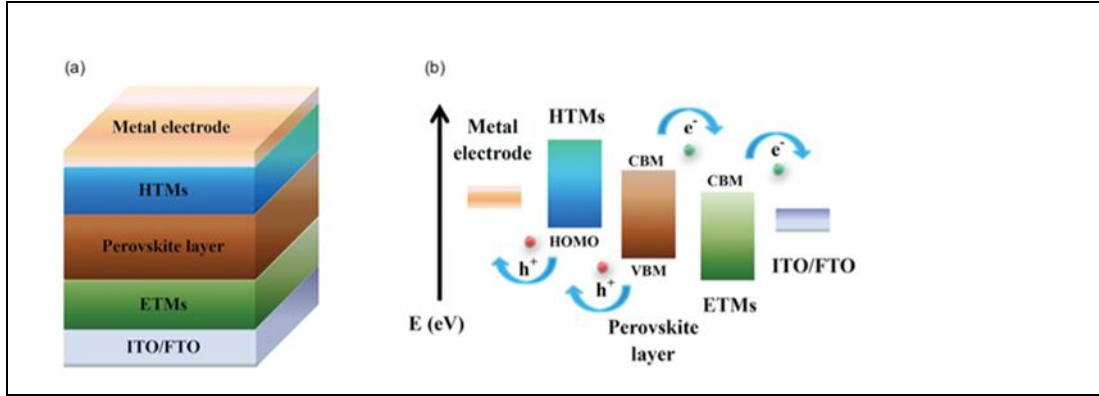


Figure 2.2: **a)** General Layout of Perovskite Solar Cells **b)** Working principle of normal perovskite solar cells (Tong et al., 2015).

2.3. Structure of The Mesoporous Electron Transport Layer

A photovoltaic device with spaces in the ETL layer that let perovskite materials infiltrate is referred to as a mesoporous structured PSC. The materials utilized in the mesoporous ETL structure of PSCs have two primary functions. Firstly, they take in the perovskite absorber's photoexcited electrons and then transfer the charged particles to the FTO substrate, to facilitate the creation of a perovskite absorber (Y. Li et al., 2015). There is an advantage of using a mesoporous ETL structure with using mesoporous layer. Faster charge transfer is possible because it can create greater contact between the perovskite active layer and the electron transport material. Additionally, this arrangement increases charge mobility while lowering bulk defects and impurities in the device. When compared to planar heterojunction-based devices, mesoporous features, such as nanorods, nanoparticles, have been demonstrated to help PSC devices maintain their stability for a longer period. In PSCs, a mesoporous ETL can significantly improve the development and nucleation of the perovskite materials compared to planar heterojunction devices. Stated differently, the mesoporous ETL both produces and confines perovskite precursors within the minuscule volume of nanopores. As a result, incident photon absorption will be enhanced, boosting the device's efficiency and photocurrent generation. Furthermore, the mesoporous ETL's existence helps to avoid pinhole creation in the compact HBL, which would otherwise impede the shunting of internal devices. Within the mesoporous framework the morphology of perovskite also distinct from the nanocrystals generated in planar heterojunction devices, resulting in variations in device performance. TiO₂, ZnO, or SnO₂ are examples of ETL materials whose CBM is less than that of perovskite absorbers. Additionally, it is crucial to make sure that every nanopore inside the

scaffolding architecture are entirely filled with perovskite components for efficient charge collection. Compared to the construction of a planar heterojunction, mesoporous structures have been shown to aid PSC devices in maintaining their efficiency for extended periods of time (Fakharuddin et al., 2015). Even though a planar heterojunction PSC can have a greater initial PCE, the performance quickly declined(Fakharuddin, Di Giacomo, Ahmed, Wali, et al., 2015). In the meanwhile, using a thick ETL layer that is mesoporous lowered the charge transport characteristics and initial PCE while also it creates some surface defects and miniaturize the perovskite crystal domains. The perovskite layer degraded when air was introduced to the cells due to an interaction with the moisture in the air.

2.4. Titanium oxide (TiO₂)

One common inorganic substance that is utilized in PSCs as an ETL is TiO₂ (G. Yang et al., 2016). Its CBM is -4.2 eV relative to vacuum level, and its electron mobility is concerning $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Tiwana et al., 2011). Since TiO₂'s CBM is around 0.3 eV it's less than the value of MAPbI₃ perovskite, injecting photogenerated electrons from a perovskite to ETL is made easier. Additionally, TiO₂ has a considerably lower VBM than perovskite materials, which results in effective hole-blocking ability. There are many well-developed fabrication techniques available today to create a good mesoporous or compact TiO₂ layer with the proper shape (H. Liu et al., 2016). Simply after it is turned into nano crystallites, TiO₂ has good electrical conductivity. Thus, the creation of nano crystallites from TiO₂ demands high temperature procedure (about 500°C) (Green et al., 2014). The rutile and anatase phases of TiO₂ are the ones with the greatest research value (Hanaor & Sorrell, 2011b). Generally, a tetragonal unit cell is present in both TiO₂ phases. The octahedra in their crystal formations are made of TiO₆. The broad band gaps of the rutile and anatase TiO₂ phases are around 3.03 eV and 3.20 eV, respectively. (Scanlon et al., 2013) In contrast to anatase TiO₂, which, as Figure 2.3 illustrates, shares four edges, (Hanaor & Sorrell, 2011a) the degree of crystal alignment is higher in rutile TiO₂ with each crystal unit sharing just two edges.

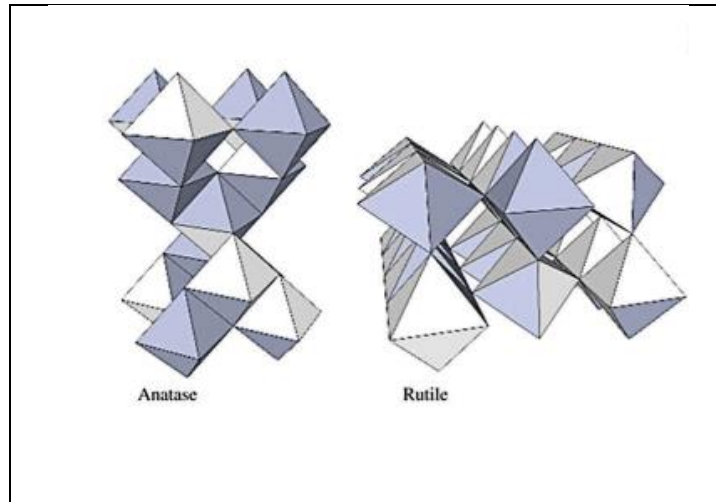


Figure 2.1: Anatase and Rutile Phases of TiO_2 (Hanaor & Sorrell, 2011a).

Due to its exceptional V_{oc} of 1.11 V, Yella et al. (Yella et al., 2014) were able to achieve a 13.7% PCE for the device with a rutile base in the planar PSC configuration, which is seen to be approximately four times greater than that of the counterpart based on anatase. The mesoporous PSC based on rutile, created by Lee and colleagues (Lee et al., 2014) showed improved performance of device, achieving PCE of 14.5% while attaining a little reduced V_{oc} . It is explained by the stimulating electron extraction that transfers from the perovskite to rutile TiO_2 , best atoms and lattice structure are found on the rutile (001) surface, which is compatible with a MAPbI_3 perovskite (Geng et al., 2016). A stronger surface interaction and simpler charge transfer are also indicated in the rutile TiO_2 perovskite system, the bond lengths are less than those discovered in a TiO_2 anatase perovskite system (Geng et al., 2016).

2.5. TiO_2 Compact Layer

Both planar and mesoporous PSCs need a compact TiO_2 layer to provide highly effective extraction and transfer of electrons to TCO from the perovskite absorber. The fabrication processes, which regulates the compact layer's roughness and thickness, have an impact on the morphology of TiO_2 . The surfaces of the FTO are rough that are roughly 30 nm RMS (root mean square) (C. Li et al., 2015), making it challenging to deposit an optimum thin layer with a uniform thickness and no pinholes. Therefore, it's crucial to choose the right fabrication techniques to build a compact layer that is thick enough to prevent the microporous of any pinholes on the film. However, the photovoltaic characteristics of the PSCs will 'be influenced by the ETL's thickness

and roughness. According to the majority of reports that have carried out comprehensive research for ETL on compact TiO₂ in different thicknesses, perovskite cells generally exhibit a rise in device performance as the thickness of the compact ETL increases until a specific ideal thickness. It is succeeded by a decline in performance (Ke et al., 2014; Lu et al., 2015a). Table 2.1 provides an overview of how the compact TiO₂ layer's thickness affects PSC device performance. The ideal ETL thickness varies according on the fabrication techniques used.

Table 2.1: The impact of the compact TiO₂ layer thickness on PSCs' device performance.

Structure of the Device	Fabrication method	PCE (%)	FF	c-ETL thickness (nm)	J _{sc} (mA cm ⁻²)	V _{oc} (V)	Ref.
FTO_cTiO ₂ _MAPbI ₃ _spiro OMeTAD_Ag	SG	1.5	0.19	95	9.9	0.83	(Lu et al., 2015a)
FTO_cTiO ₂ _MAPbI ₃ -xCl _x _P3HT_Ag	ALD	12.5	0.56	5	23.6	0.95	(Lu et al., 2015a)
FTO_cTiO ₂ _MAPbI ₃ xCl _x _P3HT_Ag	ALD	13.6	0.57	10	24.3	0.98	(Lu et al., 2015a)
FTO_cTiO ₂ _MAPbI ₃ -xCl _x _P3HT_Ag	ALD	11.4	0.55	15	21.8	0.95	(Lu et al., 2015a)
FTO_cTiO ₂ _MA PbI ₃ -xCl _x _P3HT_Ag	ALD	10.6	0.47	20	23.2	0.98	(Ke et al., 2014)
FTO_cTiO ₂ _mp-TiO ₂ + MAPbI ₃ _spiro OMeTAD_Au	TO	12.3	0.56	5	20.7	1.07	(Ke et al., 2014)
FTO_cTiO ₂ _mp-TiO ₂ + MAPbI ₃ _spiro OMeTAD_Au	TO	14.6	0.60	10	22.2	1.09	(Ke et al., 2014)
FTO_cTiO ₂ _mpTiO ₂ + MAPbI ₃ _spiro OMeTAD/Au	TO	15.1	0.63	15	22.0	1.09	(Ke et al., 2014)
FTO_cTiO ₂ _mpTiO ₂ + MAPbI ₃ _spiro OMeTAD_Au	TO	14.8	0.64	20	21.3	1.09	(Ke et al., 2014)
FTO_cTiO ₂ _mpTiO ₂ + MAPbI ₃ _spiro OMeTAD_Au	TO	14.2	0.62	25	21.1	1.09	(Ke et al., 2014)

For instance, excellent performance PSCs were achieved by using vapor-phase techniques for deposition, like atomic layer deposition (ALD), which produced a compact TiO_2 layer of 10 nm (Lu et al., 2015a). On the other hand, compact TiO_2 has to be at least 65 nm thick for solution-based deposition processes like spin coating to produce high performance devices. Pinhole creation is more likely with a thinner ETL, which in turn generates a point of direct contact between the FTO substrate and the perovskite layer. As a result of the inadequate hole blocking capability or significant current leaks at the interfaces perovskite and ETL, the J_{sc} and FF values eventually degrade. While this is happening, the increase in ETL thickness causes an increase in electron hole recombination and series resistance, which reduces the devices FF and J_{sc} . Fig. 2.4 depicts how the ETL thickness affects electron extraction and transport. According to reports, a thick layer of ETL lowers light transmittance because it scatters light more intensely and absorbs photons with energies higher than the band gap of the ETL (Ke et al., 2014; Lu et al., 2015b).

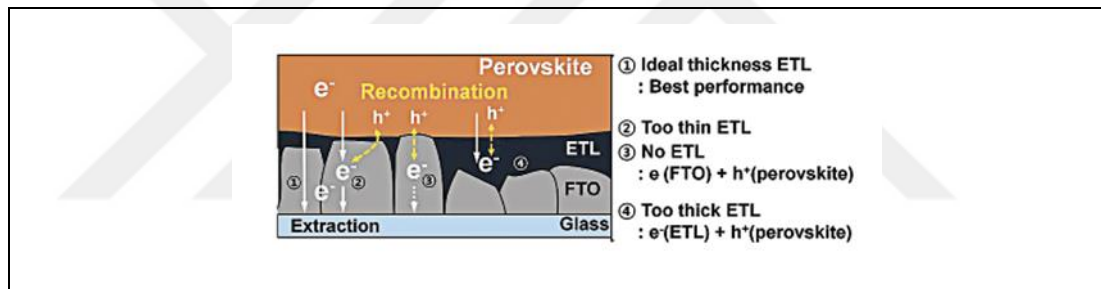


Figure 2.2: The mechanics of electron transit and transfer at various ETL thicknesses (Ke et al., 2014; Lu et al., 2015b).

Consequently, small quantity of photons reaches the perovskite layer and afterwards lessens the active layer's absorption of photons. This also explains why there won't be much current produced, as the ETL's photon absorption only makes a little contribution to the photocurrent. Because it is simple to use and has a long history of use, spin coating is now the method most frequently used to create compact layers of TiO_2 . With a sol-gel method Wu et al. synthesized TiO_2 nanoparticles to create PSC devices, yielding a PCE of 8.4%. (Mohamad Noh et al., 2018). However, there are some drawbacks about this deposition technique. For instance, the ETL produced by this method typically has a poor-quality film and thickness is hard to regulate. Additionally, the spin coating process is not suitable for producing PSC on a large scale for commercialization (C. Chen et al., 2015). Because of the uneven surface of

the FTO substrate, spin coating can result in a very smooth top layer, but the ETL thickness is not uniform across the entire deposited area. In general, any deposition processes that allow for the creation of without pinholes and extremely thin ETL significantly increase the J_{sc} of PSC devices, increasing the device efficiency. Among these are liquid-based techniques (Su et al., 2015). vapor-based procedures like ALD (Wu et al., 2014), and other adapted procedures like thermal oxidation (Ke et al., 2014). The compact ETL's thickness and homogeneity, which affect its series resistance and J_{sc} value, are the key causes (Su et al., 2015). According to Lu and colleagues, (Lu et al., 2015b) in planar PSC, PSCs made using the ALD process and based on a TiO_2 compact layer displayed a PCE that was approximately 56% greater than a spin coated TiO_2 compact layer. PCE enhancement was also noticed by Wu et al. with comparing their ALD built TiO_2 device to its spin coating or spray pyrolysis based competitors (Wu et al., 2014). The compact TiO_2 surface produced by the ALD process has a rougher surface like the FTO substrate surface. But it was capable of producing a pinhole free layer that was only 10 nm thick, benefit of having low resistance to transport of charges (Lu et al., 2015b).

A thermal oxidation procedure can be used to simultaneously deposit TiO_2 as an HBL and mesoporous layer (Choi et al., 2016). Since each of the materials used has advantages and disadvantages of its own, it is discovered that the addition of ZnO and TiO_2 double-layered compact ETLs improves the PSCs of planar heterojunctions PCE by 30.3% (Xu et al., 2015). This might be because ZnO showed greater recombination rates with quicker injection of charge at the interfaces than TiO_2 , which had lower interfacial recombination but somewhat inferior charge extraction properties. To minimize charge accumulation and optimize the transit of photogenerated electrons to inhibit surface recombination inside the devices, these materials were combined. (Figure 2.5a)

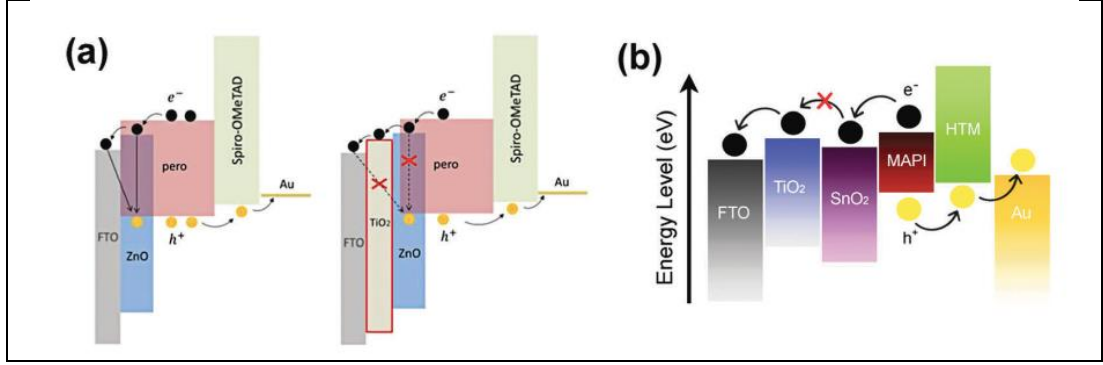


Figure 2.3: A schematic representation of the double layered compact ETL's band alignment and charge transport in the cells. **(a)** The PSC with the double layered ETL of TiO_2/ZnO . **(b)** The PSC equipped with a double layered ETL of $\text{TiO}_2/\text{SnO}_2$ (Mohamad Noh et al., 2018).

For the excellent performance of the PSC, it is essential to choose and organize the inorganic components based on their energy levels, while building the double compact ETL layers, such as by adjusting the CBM and VBM levels to be compatible. To effectively block electron transport from the perovskite layer, TiO_2 was inserted between the SnO_2 and FTO layers. This enhanced carrier recombination because of charge attraction and reduced PCE to 2.2% (Mohamad Noh et al., 2018). The optimal thickness of the compact ETL and the relationship between performance of device and fabrication process are summarized in Table 2.2

Table 2.2: The impact of the manufacturing processes on the PSCs' device performance.

Structure of the Device	Fabrication Method	PCE (%)	FF	c-ETL thickness (nm)	J_{sc} (mA cm^{-2})	V_{oc} (v)	Ref.
FTO_cTiO ₂ _MAPbI _{3-x} Cl _x _P3HT_Ag	ALD	13.6	0.57	10	24.3	0.98	(Lu et al., 2015a)
FTO_cTiO ₂ _MAPbI _{3-x} Cl _x _P3HT_Ag	SC	8.7	0.51	n/a	18.4	0.92	(Lu et al., 2015a)
FTO_cTiO ₂ _MAPbI ₃ _spiro_OMeTAD_Au	PA	15.2	0.70	40	20.5	1.06	(Choi et al., 2016)
FTO_cTiO ₂ _MAPbI ₃ _spiro_OMeTAD_Au	SC	12.5	0.67	40	18.1	1.03	(Choi et al., 2016)
FTO_cTiO ₂ _MAPbI ₃ _spiro_OMeTAD_Au	RFMS	12.1	0.54	60	20.6	1.09	(C. Chen et al., 2015)

Table 2.3 Continue: The impact of the manufacturing processes on the PSCs' device performance.

FTO/cTiO ₂ _mpTiO ₂ + MAPbI ₃ _spiro OMeTAD_Au	ALD	12.6	0.72	50	18.7	0.93	(Wu et al., 2014)
FTO/cTiO ₂ _mpTiO ₂ + MAPbI ₃ _spiro OMeTAD_Au	SP	8.8	0.58	50	17.4	0.87	(Wu et al., 2014)
FTO_cTiO ₂ _mpTiO ₂ + MAPbI ₃ _spiro OMeTAD_Au	SC	6.5	0.54	50	15.3	0.79	(Wu et al., 2014)
FTO_cTiO ₂ _mpTiO ₂ + MAPbI ₃ _spiro OMeTAD_Au	DC	12.8	0.73	55	20.1	0.88	(Hong et al., 2015)
FTO_cTiO ₂ _mpTiO ₂ + MAPbI ₃ _spiro OMeTAD _Au	SC	11.0	0.70	99	18.9	0.83	(Hong et al., 2015)
FTO_cTiO ₂ _mpTiO ₂ + MAPbI ₃ _spiro OMeTAD_Au	ED	13.6	0.68	29	20.0	1.00	(Su et al., 2015)
FTO_cTiO ₂ _mpTiO ₂ + MAPbI ₃ _spiro OMeTAD_Au	SC	10.4	0.60	60	17.1	1.02	(Su et al., 2015)
FTO_cTiO ₂ _mpTiO ₂ + MAPbI ₃ _spiro OMeTAD_Au	TO	15.1	0.63	15	22.0	1.09	(Ke et al., 2014)
FTO_cTiO ₂ _mpTiO ₂ + MAPbI ₃ _spiro OMeTAD_Au	SC	13.5	0.58	60	21.2	1.09	(Ke et al., 2014)
FTO_NS-cTiO ₂ _mpTiO ₂ +MAPbI ₃ _spiro OMeTAD_Au	ED	10.7	0.64	14	17.2	0.97	(C. Li et al., 2015)
FTO/TiO ₂ _ZnO_ MAPbI ₃ _spiro OMeTAD_Au	SC/SG	17.2	0.71	10/50	20.8	1.08	(Xu et al., 2015)
FTO_TiO ₂ _SnO ₂ _ MAPbI ₃ _spiro OMeTAD_Au	SP/SC	2.2	0.32	80/22	11.2	0.62	(H. Wang et al., 2015)

2.6. Mesoporous TiO₂

Mesoporous TiO₂ (mp-TiO₂). based ETLs are among the most common and effective device architecture structures in PSCs. Researchers have already developed a number of distinct mesoporous structure types for usage in PSCs. According to their dimension, mesoporous TiO₂ can generally be separated into four nanostructure groups: zero dimensional mesoporous TiO₂, is nanoparticles; one dimensional mesoporous TiO₂, nanotubes, nanowires, nanorods, nano cones ,nano helices, and; two dimensional mesoporous TiO₂ such as nanosheets; three dimensional mesoporous TiO₂, such as nanofibers, and nanowires. The various mesoporous TiO₂ nanostructures employed in PSCs are shown in Figure 2.6.

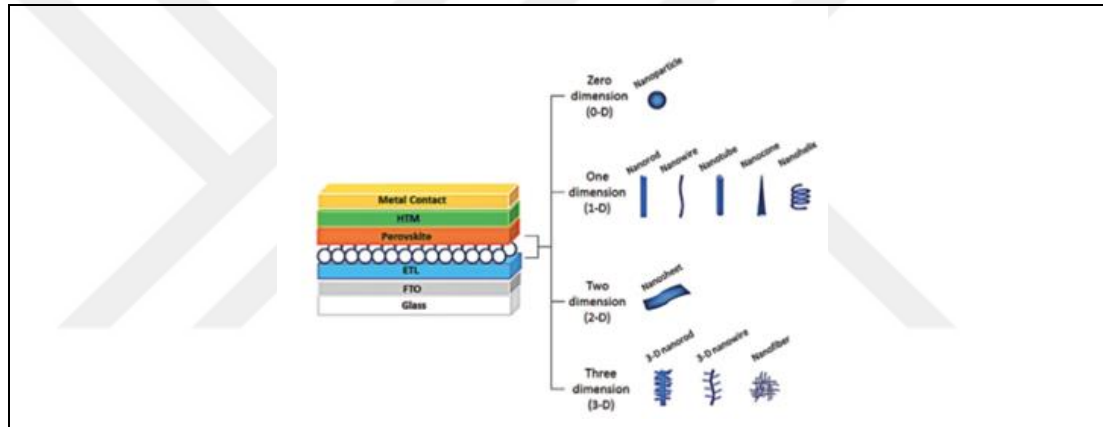


Figure 2.4 Diagrammatic representations of the various TiO₂ nanostructures used in PSCs as the mesoporous ETLs (Mohamad Noh et al., 2018).

Performance of device is affected by the tunable morphological characteristics of the mesoporous layer, such as rod diameters, particle sizes, and layer thicknesses, which are covered in more detail below.

2.6.1. Zero-Dimensional (0D) TiO₂ Nanostructure

Nowadays, mesoporous perovskite solar cells frequently use nanostructures made of TiO₂ nanoparticles as scaffolds (mp-PSCs). However, due to their labyrinthine networks, nanoparticle based TiO₂ has trouble allowing perovskite to fill the framework's nanopores. Due to the presence of grain boundaries that increased charge recombination, this mesoporous structure also displayed substantially slower electron transporting properties in comparison to other TiO₂ nanostructures. Therefore,

optimizing the thickness and mesoporous layer structure, as well as the shape and size of the TiO_2 nanoparticles, are essential elements in creating highly effective PSCs. Due to the impacts of effective contact area, porosity, pore size, and electron injection at the interface between perovskite and TiO_2 and electron transport via the nanoparticles of TiO_2 are dependent on the shape, and particle size of the mp TiO_2 . Several research groups have looked into how particle size affects PSC efficiency. they used varying diameters of TiO_2 nanoparticles to create mesoporous PSCs (Sung et al., 2015). Basically, larger mp TiO_2 nanoparticles produce larger pore diameters, which create wider and simpler pathways for perovskites to penetrate into the bottom of the mpETL. Higher JSC and FF values result from this as it also improves and completes the areas of interaction between the electron transport layer and perovskite nanocrystals. By improving the perovskite TiO_2 contact areas, more photoexcited electrons will be injected into mp- TiO_2 , which will increase the rate of injection. Due to the diminished grain boundaries, reducing the series resistance or electron carrying resistance within the film can also be achieved by adding larger TiO_2 nanoparticles. Prior to the perovskite layer being deposited, however, the porosity between the TiO_2 nanoparticles and the specific surface area discovered to diminish as the TiO_2 nanoparticles grew. Low capacity to capture light and thus a negative impact on the JSC of the solar cell are caused by lower porosity, which limits the amount of space inside the mesoporous TiO_2 scaffold that perovskite materials can occupy. Additionally, increasing the mesoporous TiO_2 nanoparticles' size will shorten photoexcited electrons' lifespan, which is linked to a higher recombination rate and lowers FF and V_{OC} . It's interesting to note that the size change of the electron transfer layer nanoparticles has no impact on the charge transfer resistance, which results from selective contact or interface. According to Sarkar et al., PCE was 9% higher in TiO_2 nanoparticles with a 15 nm diameter on mesoporous PSCs than in those with 10 nm based TiO_2 nanoparticles, demonstrating that the mesoporous layers nanoparticle size had a significant influence in influencing the efficiency of the PSCs (Sarkar et al., 2014). To produce consistent mesopores, a spherical shape for the mesoporous TiO_2 nanoparticles is preferred. By changing the solvent solution in a typical hydrothermal process, Sung and colleagues successfully created single-crystals made of spherical mesoporous TiO_2 nanoparticles. Manufactured devices produced a PCE of 17.2% using mp TiO_2 nanoparticles with a size of 50 nm (Sung et al., 2015). The vast improvement in PCE is ascribed to the improvement in connection and contact between the spherical

TiO₂ nanoparticles, which produce mesopores with homogenous mesopore sizes and shapes for enhanced perovskite material infiltration. In brief, it is discovered that the FF and PCE device performance of the PSC increased with the expansion of the individual TiO₂ nanoparticles to a 50 nm diameter, which was followed by a decline in performance. The effectiveness of the device could be increased even further by creating spherical aggregates from the individual main nanoparticles, though To find the appropriate size, more research is required. The perovskite material's ability to fill pores, capture light, and collect electrons at the perovskite/mp-TiO₂ interfaces are all significantly influenced by the thickness of the TiO₂ nanoparticle layer. The production of TiO₂ based mesopore PSCs resulted in generally identical reflectance spectra for all the devices, even though varied combinations of the mesoporous electron transfer layer and perovskite overlayer were used(Jeon et al., 2013). However, as the perovskite and mesoporous layer thickness varied, various device performances were observed. Only interlayers with compact structures or overlayers made of perovskites that were too thick and had mp-ETL layers that were too thin generated significant charge recombination. This is because in such a device, photogenerated electron-hole pairs have a limited capacity to go through and separate from one another at the perovskite/HBL interfaces. To improve electron injection from the perovskite to TiO₂, the fabricated device will have a thicker TiO₂ nanoparticle layer and a greater region of the perovskite mesoporous ETL interface for mesoporous PSCs. Greater loading of the perovskite components is made possible by the thicker mesoporous layer, increasing light absorption, and strengthening the J_{sc}. The low-frequency capacitance decreases with increasing mesoporous thickness, which also makes the hysteresis behavior less noticeable (H. S. Kim et al., 2015; Snaith et al., 2014). The maximum PCE of 11.1% was initially seen in PSCs with a 160 nm thickness of mp-TiO₂ nanoparticles, however following 100 days of being in contact with outside air, this value dropped to less than 7% (Yin et al., 2015). Mesoporous electron transfer layers' filling with perovskite is a challenging technical task, because of the tiny domain size of the mesopores, which is a limitation for devices based on TiO₂ nanoparticles. To change the mesoporous structure, Zheng et al. created PSCs using a TiO₂-based dual porous ETL. In the creation of this structure, spin-coated polystyrene spheres with a diameter of 220 nm were placed on top of compact TiO₂/FTO substrates. The polystyrene spheres are then evaporated from the deposited solution, which is then dried and heated to create mesopores and microporous sphere-like voids

throughout the film. Optimum device attained a PCE of 9.8% by optimizing the tiny HBL. The same group created TiO₂ nano bowl-based devices through additional modification of the production process, with a maximum PCE of 12.0% (Zheng et al., 2016) Chen et al. (X. Chen et al., 2015) also employed the polystyrene-assisted approach to create an inverse-opal-like TiO₂ nanostructure, which had a similar dual-porous structure but slightly variable pore widths because different diameters of polystyrene were used. After manufactured PSCs achieved a 13.1% device efficiency. All these nanostructure frameworks were able to support the filling of perovskite materials, that rised the interface contact for effective extraction of charges and charge transfer.

2.6.2. One- Dimensional (1D) TiO₂ Nanostructure

It was already indicated, the labyrinthine shape of the nanoparticles, presence of grain boundaries interfered with the electron transport channels within the mpTiO₂ nanoparticles could cause issues with perovskite loading in the mesoporous layer that used them. To solve this problem, numerous one-dimensional TiO₂ nanostructures have been used as ETLs in PSCs, including nanorods, nanowires, nanotubes, and nano cones.

TiO₂ nanorods were commonly generated for use in PSCs either on a thin coating of TiO₂ or on FTO using a hydrothermal technique, resulting in a vertical configuration for the nanorods. (Fakharuddin, Giacomo, Ahmed, et al., 2015);(Fakharuddin, Di Giacomo, Palma, Matteocci, et al., 2015);(H. S. Kim et al., 2013) According to several studies, the electron mobility of perpendicular nanorods was two orders of magnitude higher than that of the nanoparticle-based ETL (H. S. Kim et al., 2013). The improvement of the J_{sc} in PSC d2evices was facilitated by the use of vertical nanorods. Perovskite sensitized TiO₂ nanorod solar cells' PCE's more than 9% has been reached early in the development of PSCs. (H. S. Kim et al., 2013) According to research by Fakharuddin et al., TiO₂ nanorod-based PSCs demonstrated superior PCE and stability compared to their planar or nanoparticle-based counterparts (Fakharuddin, Di Giacomo, Ahmed, Wali, et al., 2015). The significant increase in the J_{sc} in nanorod-based devices was credited with contributing to the improvement of the PCE. Despite the well-known instability of perovskite materials, nanorod-based devices showed anomalous behavior in terms of stability when the devices' J_{sc} and PCE increased

during many hours of exposure to light. This is explained by the greater chemical stability at the interfaces between perovskite and TiO_2 caused by the rutile TiO_2 nanorods' greater thermodynamic stability over the anatase TiO_2 compact layer and mesoscopic nanoparticles; alternatively, it may be due to the nanorod framework's single crystallinity and increased porous volume, which caused thermodynamic equilibrium. Kim et al. noted that When the perovskite layer was created using one-step spin coating in the early stages of the development of TiO_2 nanorod-based PSCs, the photovoltaic characteristics were better with shorter electron transport (where 0.56 μm nanorods gave a PCE of 9.4%) (H. S. Kim et al., 2013). This was due to the fact that shorter TiO_2 nanorods generated uniform configurations with good vertical alignment, but longer nanorods had less order and alignment. Longer nanorods therefore had lower pore filling factors, which resulted in lower J_{SC} , V_{OC} , and PCE values. The porosity of the scaffold can be tailored by changing the density, diameter, and orientation of the TiO_2 nanorods. This will change the quantity of perovskite production, the amount of contacting surface area, and the capacity to penetrate. Customizing these settings is essential for assessing the PSCs' performance. In the past, extending the hydrothermal reaction's growth time resulted in a longer nanorod while simultaneously increasing the diameter of the TiO_2 nanorod. However, it was found that the nanorods' surface area was not inversely related to their length (H. S. Kim et al., 2013). Recently, Cai et al. (Cai et al., 2015) explained that by altering certain hydrothermal reaction parameters, such as the nanorods' growth time and the concentration of glycerol, titanium (IV) tetraisopropoxide, and disodium ethylenediamine-tetraacetate dehydrate (Na_2EDTA). The nanorods' density, length, and diameter may all be adjusted separately.

TiO_2 nanowire and nanorod-based PSCs share a number of similarities, although the nanowire's structure varies from the nanorod's with regard to the ratio in relation to diameter and length. Typically, a nanorod has a diameter that is comparatively thicker than its length and a shorter length between the tens and hundreds of nanometers. Similar to TiO_2 nanorod-based devices, TiO_2 nanowire-based PSCs showed behavior where the values of PCE and J_{SC} improved with increasing length of TiO_2 nanowires up to an ideal value before performance began to decline (Jiang et al., 2014). The mesoporous thickness increased as a result of the extending of the nanowires, allowing for more perovskite production and higher photon absorption. Once more, nanowire

thickness achieved its ideal, further extension of the nanowire produced higher series resistance due to the expansion of the charge carrier transit distance, which decreased the J_{SC} . The perovskite's photogenerated holes' diffusion length was constrained, which degraded the V_{OC} and increased the charge recombination rate. The TiO_2 nanowires' diameter and density are two additional factors can affect the performance of device in proportion to the scaffold thickness. TiO_2 nanowire's low density made the spaces between them wider, which allowed more perovskite materials to infiltrate and form a meso- porous layer with reduced dead volumes (Jiang et al., 2014). The PSC performance was limited as a result of a TiO_2 nanowire with an enormous diameter that decreased the nanowire's contact area and perovskite surfaces (Qiu et al., 2013).

TiO_2 nanotube based ETL showed significantly greater absorption of light throughout the entire spectrum as a result of better light trapping capabilities (J. Zhang & Pauporté, 2015). However, TiO_2 nanotubes are more difficult to manufacture than TiO_2 nanorods or nanoparticles, and as a result, PSCs based on nanotubes are rarely investigated. Because of this, nothing is known about how the PSC's performance is affected by the morphological characteristics of the nanotubes, such as their, diameter, thickness, length, and density. Currently, it is understood that increasing nanotube length led to more perovskite filling, nonetheless, with length, the charge recombination rate rose, as well negatively impacting the device's and J_{SC} and V_{OC} (Gao et al., 2014).

Using templates made of ZnO nanowires, Zhang and colleagues treated PSCs with ammonium hexafluorotitanate, or $(NH_4)_2TiF_6$, after fabricating 1.1 mm long TiO_2 nanotube arrays on them (J. Zhang & Pauporté, 2015). The devices acquired a device efficiency of 9.3% and demonstrated a decrease in the hysteresis index. The shortest nanotubes produced throughout the investigation, measuring 2.3 mm in length, were used in Gao et al (Gao et al., 2014) best-performing . 's devices, which had a PCE of 6.5%. On the other hand, they created PSCs using freestanding TiO_2 nanotubes through two-step electrochemical anodization. Additionally, the TiO_2 nanotube arrays changed how perovskite and HTL were deposited. According to Wang and colleagues, electrochemical anodization can be applied to deposit TiO_2 nanotubes as well an ETL on flexible substrates (X. Wang et al., 2015). A PSC using TiO_2 nanotube arrays that were roughly 60 nm thick, and 300 nm long had a PCE of 8.3%. When Salazar et al. used TiO_2 nanotubes, 0.4 mm in length, as an ETL , they were able to attain a PSC

device efficiency of 5.0%, which is worth highlighting at this point (Salazar et al., 2015). Perovskite layer was coated using a one step solution, which causes insufficient perovskite material infiltration, is likely the cause of the significantly lower PCE acquired for shorter TiO₂ nanotubes. A similar phenomenon took place in the TiO₂ nanorod founded PSCs.

Other ETL nanostructures have also been created in an effort to increase the stability and performance of PSC devices. With an oblique-angle electron beam evaporation process, Lee and colleagues have effectively generated PSCs using mesoporous TiO₂ nano helices with a variety of pitch and radii. Their greatest devices showed a PCE of 12.1% (Lee et al., 2015). Because of their higher grain size and fast dissipation of capacitive charges, TiO₂ nano helices had better electron transport capabilities. Their device also showed no hysteresis behavior. When TiO₂ nanocones were created as an ETL Peng et al. and Zhong et al. observed PCE enhancements of 36% and 18% in comparison to their TiO₂-nanorod-based devices(Cai et al., 2015),(Peng et al., 2016). The TiO₂ nano cones were discovered to have a larger surface-to-volume ratio, allowing for more perovskite loading and a consequent increase in light harvesting efficiency. It was discovered that the TiO₂ nanocones transfer electrons at a rate that is 2-3 times faster than that of TiO₂ nanorods (Zhong et al., 2015a).

2.6.3. Two-Dimensional (2D) TiO₂ Nanostructure

TiO₂ nanosheets are the usual name for two-dimensional (2D) TiO₂ as an ETL. There isn't a lot of research being done on TiO₂ nanosheet-based ETL right now. The PCE of TiO₂ nanosheet-based PSCs was 10.6%, 43% higher than their TiO₂ nanoparticle-based equivalent, as demonstrated by Rong et al (Rong et al., 2014).

2.6.4. Three-Dimensional (3D) TiO₂ Nanostructure

PSCs three dimensional TiO₂ has recently gained interest as a way to develop an ETL with significantly improved morphological electrical, optical, and properties. In comparison to flat films or low-dimensional-based TiO₂ nanostructures, 3D ones have a number of advantages. These nanostructures have (i) greater surface area for quicker transmission of charges, (ii) more nucleation sites to create perovskites (iii) enhanced capacity for electron transport, and (iv) increased light scattering effect-related optical pathways in the perovskite layer (Yu et al., 2015), (Dharani et al., 2014). These

characteristics of the 3D TiO₂ nanostructures result in a decrease in recombination of charges within the device, an improvement in the capacity to harvest light, and an increase in the J_{SC} and PSC efficiency.

Numerous three-dimensional TiO₂ nanostructures have so far been used in PSC devices. PSCs based on 3D hierarchical TiO₂ nanorods were created by Jaramillo-Quintero et al (Jaramillo-Quintero et al., 2016) using two-step low-temperature hydrothermal techniques. Comparing 1D TiO₂-based PSC with planar heterojunction, the device's PCE increased by around 40% and 5%, respectively. While this was going on, Dharani et al devices, which used TiO₂ electrospun fibers as the ETL, had a device efficiency of up to 9.8% (Dharani et al., 2014). This device's PCE improvement is exceedingly challenging, nevertheless, as the fabrication of a homogenous layer less than 413 nm was constrained by the manufacturing technique and the TiO₂ nanofibers' diameter. This is because the perovskite materials were unable to completely penetrate thick and large diameter TiO₂ nanofibers, which decreased light absorption. In addition, using an in situ hydro-thermal approach and surface reaction limited pulsed chemical vapor deposition methodology, three dimensional TiO₂ nanowires were successfully manufactured (Yu et al., 2015).

2.6.5. Combined TiO₂ Nanostructures

Researchers and scientists have developed a new approach to merge various TiO₂ nanostructures into a single ETL. The PSC device's performance is enhanced by this method because it enhances the entire area of surface, the sites available for perovskite synthesis, and the light scattering and characteristics of absorption (Islam et al., 2015), (Mahmood et al., 2015). The device performances of the PSCs are listed in Table 2.3 based on TiO₂ nanostructures utilized as ETLs.

Table 2.4: An overview of the device's performance in PSCs using different mesoporous TiO₂ structures as an ETL.

Structure of the Device	Structure of mp ETL	PCE (%)	FF	J _{sc} (mA cm ⁻²)	V _{oc} (V)	Ref.
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ +spiro OMeTAD_Au	Nanoparticle	9.7	0.62	17.6	0.89	(H. S. Kim et al., 2012)
FTO_cTiO ₂ _mpTiO ₂ _MAPbI ₃ _PTAA_Au	Nanoparticle	12.0	0.73	16.5	1.00	(Jeon et al., 2013)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Au	Nanoparticle	12.5	0.72	18.5	0.94	(H. S. Kim et al., 2015)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Au	Nanoparticle	11.1	0.60	17.8	1.04	(Yin et al., 2015)
FTO_cTiO ₂ _DP-mpTiO ₂ +MAPbI ₃ _C	Nanoparticle	9.8	0.51	21.9	0.88	(Luo et al., 2017)
FTO_cTiO ₂ _NB-mpTiO ₂ +MAPbI ₃ _C	Nanoparticle	12.0	0.53	22.7	1.00	(Zheng et al., 2016)
FTO_cTiO ₂ _IO-mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Ag	Nanoparticle	13.1	0.61	21.9	0.97	(X. Chen et al., 2015)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Au	Nanorod	9.4	0.63	15.6	0.96	(H. S. Kim et al., 2013)
FTO_mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Au	Nanorod	12.2	0.67	22.9	0.78	(Fakharuddin, Di Giacomo, Ahmed, Wali, et al., 2015)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI _{3-x} Cl _x _ spiro OMeTAD_Au	Nanorod	10.5	0.56	22.2	3.37	(Fakharuddin, Giacomo, Palma, et al., 2015)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Au	Nanorod	10.0	0.55	20.9	0.87	(Son et al., 2014)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Au	Nanorod	11.1	0.62	18.6	0.97	(Cai et al., 2015)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI _{3-x} Cl _x _ spiro OMeTAD_Au	Nanorod	11.9	0.68	22.0	0.80	(J. F. Li et al., 2015)
FTO_c-TiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Ag	Nanorod	18.2	0.76	22.9	1.04	(X. Li et al., 2016)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₂ Br ⁺ spiro OMeTAD_Au	Nanowire	4.9	0.59	10.1	0.82	(Qiu et al., 2013)

Table 2.5 Continue: An overview of the device's performance in PSCs using different mesoporous TiO₂ structures as an ETL.

FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Au	Nanowire	11.7	0.68	22.3	0.77	(Jiang et al., 2014)(J. Zhang & Pauporté, 2015)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Au	Nanotube	6.5	0.58	17.9	0.63	(Gao et al., 2014)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Ag	Nanotube	9.3	0.53	20.3	0.87	(J. Zhang & Pauporté, 2015)
Ti foil _ mpTiO ₂ + MAPbI ₃ _spiro OMeTAD + CNT	Nanotube	8.3	0.68	14.4	0.99	(X. Wang et al., 2015)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ _Au	Nanotube	5.0	0.37	19.6	0.67	(Salazar et al., 2015)
FTO_cTiO ₂ _mpTiO ₂ +HC(NH ₂) ₂ PbI ₃ _ spiro OMeTAD_Au	Nanohelice	12.1	0.66	20.1	0.92	(Lee et al., 2015)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Au	Nanocone	11.9	0.62	19.5	0.98	(Zhong et al., 2015b)
FTO_mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Au	Nanocone	11.4	0.67	18.2	0.94	(Peng et al., 2016)
FTO_cTiO ₂ _mpTiO ₂ _mpZrO ₂ +MAPbI ₃ _ C	Nanosheet	10.6	0.61	20.1	0.87	(L. Zhang et al., 2015)
FTO_c-TiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Au	3-D Nanorod	10.5	0.64	17.3	0.95	(Jaramillo-Quintero et al., 2016)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Ag	3-D Nanowire	9.0	0.64	14.8	0.95	(Yu et al., 2015)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Au	3-D Nanowire	9.2	0.73	12.5	1.01	(Tao et al., 2015)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Au	Nanofiber	9.8	0.63	15.9	0.98	(Dharani et al., 2014)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Au	Nanoflower	15.7	0.72	22.0	0.99	(X. Chen et al., 2016)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Ag	Nanoparticle +nanorod	15.2	0.68	21.2	1.06	(Islam et al., 2015)
FTO_cTiO ₂ _mpTiO ₂ +MAPbI ₃ _ spiro OMeTAD_Ag	Nanofiber + nanorod	15.9	0.75	20.5	1.00	(Mahmood et al., 2015)

2.7. Materials Other Than TiO₂ as ETLs

There are several disadvantages to using TiO₂ as an ETL in a PSC. As an example, TiO₂-based PSCs deteriorate quickly under UV light (Leijtens et al., 2013). Leijtens et al. recommended stabilizing the surface of the TiO₂ or employing a ultraviolet filter to prevent UV radiation from penetrating the TiO₂ layer. Furthermore, the electron mobility of pure TiO₂ is still quite low (Tiwana et al., 2011). In addition, TiO₂ normally demands a sintering procedure at a high temperature, roughly 500 °C, (Green et al., 2014) which extends the time it takes for energy to become useful and limits the ability to produce solar cells on flexible substrates. To replace TiO₂ as an ETL in PSCs, researchers and scientists are searching additional inorganic materials, such as metal oxides like, tungsten trioxide (WO₃), SnO₂, ZnO indium (III) oxide (In₂O₃), etc., combined with metal sulfides, such as zinc sulfide (ZnS), indium sulphide (In₂S₃) and cadmium sulfide (CdS), SiO₂, Al₂O₃, and ZrO₂ which's lack the ability to transport electrons, are some of the materials that are merely utilized as scaffolding because their CBM is higher. compared to the perovskite.

2.7.1 Zinc oxide (ZnO)

Similar to TiO₂ the band gap of ZnO is 3.2 eV. Its CBM is less than perovskite light absorber, despite being substantially higher than TiO₂ (Tiwana et al., 2011), (Jeongmo Kim et al., 2016). However, it is discovered that ZnO has an electron mobility that is almost 200 cm² V⁻¹ s⁻¹, which is greater than TiO₂ by two orders of magnitude (Tiwana et al., 2011). A ZnO-based ETL in a PSC is therefore anticipated to possess a high level of electron extraction and transport efficiency. Additionally, high ZnO crystallinity might be obtained without the need for sintering, which would greatly lower production (D. Liu & Kelly, 2014). ZnO can be used as an ETL in both standard and inverted PSC structures, in addition to on both flexible and stiff substrates, thanks to its low temperature processability. (Jeongmo Kim et al., 2016), (D. Liu & Kelly, 2014). It is important to note that PSCs founded on flexible substrates typically perform less well than rigid PSCs, mostly because of the substrate's intrinsic sheet resistance and low light transmittance, rather than the ETL. (Zhou et al., 2015), (Paquin et al., 2015) To raise the shunt resistance (R_{sh}), ZnO is utilize,. And also reduce charge recombination at the TCO surface since it is identical to compact TiO₂ (D. Liu & Kelly, 2014). The ZnO layer's thickness must be optimized since a thin film of compact Zinc

Oxide may boost recombination at the ZnO between perovskite contacts, a thicker layer may increase series resistance and recombination in the device (Zhou et al., 2015).

Liu et al. used a spin coating technique to create a ZnO compact layer without using further sintering or calcination procedures (D. Liu & Kelly, 2014). With a PCE of 15.7%, their best device was created using an ETL constructed of a ZnO layer that was 25 nm thick, which is thinner than a TiO₂ compact layer. that was solution processed (ca. 60 nm). However, this device has very low stability. This is due to the presence of chemisorbed oxygen species like hydroxide on the surface of the unannealed ZnO layer, which could result in the deterioration of the perovskite nanocrystals (Cheng et al., 2015). This problem can be fixed by adding layer of buffer between the ZnO and the perovskite layer or by annealing the ZnO layer first.

A ZnO compact layer has been created using a variety of ways. A ZnO compact layer PSC made using the ALD technique showed a PCE of 13.1%. (X. Dong et al., 2014) In contrast to the solution processed method, the ALD procedure creates a more dense layer, which successfully prevents charge recombination. However, the magnetron sputtering method makes it possible to fabricate a compact ZnO layer built upon thick array of nanorods. (Liang et al., 2014) 22.4 mA cm⁻², a high JSC value, indicates that electron transport was encouraged by the fact that ZnO nanorods with a c-axis orientation were perpendicular to ITO.

ZnO nanorods, which offer bigger gaps for perovskite penetration and a greater light scattering effect, are often the foundation of the mesoporous ZnO layer. This arrangement might enhance the perovskite absorber's capacity to absorb light, which would raise the JSC value. However, because to greater charge recombination brought on by the larger interfacial area, Planar heterojunction devices demonstrated somewhat higher V_{oc} levels than ZnO nanorod-based PSCs (Dharani et al., 2014). On rigid and flexible substrates, Kumar and colleagues found that had efficiencies of 8.9% and 2.6%, respectively (Dharani et al., 2014). To enhance the photovoltaic capabilities of the PSCs, other ZnO nanostructure types have also been developed. Therefore, the PSCs using 800 nm-diameter ZnO nanorods as the ETLs had a verified PCE of 10.4%. Table 2.4 summarizes the PSCs' device performances when using ZnO as the ETLs.

Table2.4: The device performances of mesoporous and planar PSCs with ZnO as the ETL.

Structure of the Device	Structure of ZnO ETL	PCE (%)	FF	J_{sc} (mAcm ⁻²)	V_{oc} (V)	Ref.
ITO_cZnO_MAPbI ₃ _spiroOMeTAD_Ag	Compact	15.7	0.75	20.4	1.03	(D. Liu & Kelly, 2014)
PET_ITO_cZnO_MAPbI ₃ _spiroOMeTAD_Ag	Compact	10.2	0.74	13.4	1.03	(D. Liu & Kelly, 2014)
ITO_cZnO_MAPbI ₃ _PTAA_Au	Compact	17.7	0.78	20.1	1.13	(Heo et al., 2016)
PEN_ITO_cZnO_MAPbI ₃ _PTAA_Au	Compact	15.6	0.76	18.7	1.10	(Heo et al., 2016)
FTO_cZnO_mpAl ₂ O ₃ +MAPbI ₃ _spiroOMeTAD_Ag	Compact	13.1	0.66	20.4	0.98	(X. Dong et al., 2014)
ITO_cZnO_MAPbI ₃ _spiroOMeTAD_MoO ₃ _Ag	Compact	13.4	0.57	22.4	1.04	(Liang et al., 2014)
ITO_cZnO_MAPbI ₃ _spiroOMeTAD_Ag	Compact	10.91	0.52	22.6	0.91	(J. Zhang et al., 2015)
FTO_cZnO_MAPbI ₃ _spiroOMeTAD_Ag	Compact	14.2	0.71	19.5	1.03	(Dehghan & Behjat, 2019)
ITO_cZnO_MAPbI ₃ _spiroOMeTAD_Ag	Compact	13.9	0.65	19.9	1.07	(Song, Bian, et al., 2015)
ITO_cZnO_MAPbI ₃ _PTB7Th_MoO ₃ _Ag	Compact	8.4	0.68	14.3	0.86	(Junghwan Kim et al., 2014)
ITO_cZnO_PCBM_MAPbI ₃ _spiroOMeTAD_MoO ₃ _Ag	Compact	12.2	0.67	18.2	1.00	(Junghwan Kim et al., 2014)
ITO_cZnO_PCBM/MAPbI ₃ _spiroOMeTAD_Au	Compact	6.4	0.46	16.0	0.88	(Cheng et al., 2015)
ITO_cZnO/PEI_MAPbI ₃ _spiroOMeTAD_Au	Compact	10.2	0.69	16.8	0.88	(Cheng et al., 2015)
FTO_cZnO_mpZnO+MAPbI ₃ _spiroOMeTAD_Au	Nanorod	8.9	0.51	17.0	1.02	(Paquin et al., 2015)
PET_ITO_cZnO_mpZnO+MAPbI ₃ _spiroOMeTAD_Au	Nanorod	2.6	0.43	7.5	0.80	(Paquin et al., 2015)
FTO_cZnO_mpZnO+MAPbI ₃ _spiroOMeTAD_Au	Nanorod	1.1	0.56	20.1	0.99	(Son et al., 2014)
ITO_mpZnO+MAPbI ₃ _spiroOMeTAD_Ag	Nanowall	13.6	0.72	18.9	1.00	(B. Wang et al., 2019)
FTO_cZnO_mpZnO+MAPbI ₃ _spiroOMeTAD_Ag	Nanosheet+nanorod	10.4	0.62	18.0	0.93	(Mahmood et al., 2014)

2.7.2. Stannic oxide (SnO₂)

Due to a number of reasons, ZnO is not the best material to use in PSC devices in place of TiO₂ as the ETL. For example, ZnO is naturally hygroscopic, which could lead to perovskite disintegration in ambient air (Heo et al., 2016). Moreover, ZnO has weak chemical stability, since it interacts readily with acids or weak bases. Additionally, PSCs using low temperature produced ZnO as an ETL were critical for the environment. because any hydroxyl residues that remained on the ETL surface may hasten the breakdown structure of the perovskite (Cheng et al., 2015),(Song, Zheng, et al., 2015).

Due to the special characteristics of SnO₂, scientists and researchers have begun to shift their areas of focus in research to the use of SnO₂ as ETL in PSCs. According to a number of studies, compared to its TiO₂ or ZnO equivalents, SnO₂'s band gap is 3.8 eV and 250 cm² V⁻¹ s⁻¹ mobility of electron (Tiwana et al., 2011). Faster electron mobility might improve the ETL's capacity for transporting electrons, yet a wider band gap might prevent the ETL from absorbing photons with high energy, which might result in minimal current loss.(Ke et al., 2015)SnO₂ nanoparticles also benefit from having excellent anti-reflective qualities and thermal stability (Mohamad Noh et al., 2020).

2.8. Electron Transfer Layer Doping

TiO₂ ETM layer suffers from trap states cause low conductivity and carrier accumulation. Its crucial to enhance the ETM layers carrier transport ability to increase the efficiency of the cell (H. Zhang et al., 2016). Ion doping is a useful technique for managing carrier movement and trap states; niobium and lithium dopants, for instance, have been effectively used in these abilities (B. X. Chen et al., 2016)(Ch et al., 2015). Ion doping is an efficient way to change the energy band structure, boost the conductivity and lower the ETM layer's trap density. Sm doped to planar TiO₂ with different concentrations and deposited with spin coating. From 0,3% Sm doped TiO₂ cell power conversion efficiency achieved 13,10% (Xiang et al., 2017).

Planar perovskite solar cells using compact TiO₂ ETL has been enhanced with Mg as an efficient ion dopant. Zhang et al. Mg ion doped to the planar TiO₂ architecture of ETL. It is discovered that magnesium doping can reduce the resistivity of the TiO₂ and

raise the ETL's Fermi energy level. They achieved 19.08 % power conversion efficiency and current density was measured 21,48 mA cm⁻²(H. Zhang et al., 2016). Rafieh et al investigated (Imanah et al., 2018) how doped mesoporous TiO₂ layers containing Al and Mg can enhance the efficiency of power conversion (PCE) in comparison to none doped TiO₂. The band gap of TiO₂ is increased by Mg doping while decreased by Al doping. The Mg doped TiO₂ has a wide band gap, which lowers the rate of electron and hole recombination while raising the J_{SC} and V_{OC}. Photovoltaic parameters summarized in the table 2.5 (Imanah et al., 2018).

Table 2.6: Photovoltaic characteristics from J-V measurements of PSC devices using a pure and doped mesoporous TiO₂ layer.

Anode	V _{OC} (V)	J _{SC} (mAcm ⁻²)	FF	PCE (%)	R _S (Ωcm ²)	R _{Sh} (Ωcm ²)
Pure TiO ₂	1.00	18.62	0.618	11.49	10	254
0.1 mol % Mg TiO ₂	1.06	19.22	0.601	12.27	6.1	201
0.5 mol % Mg TiO ₂	1.06	19.00	0.607	12.24	6.6	227
1.0 mol % Mg TiO ₂	1.02	17.34	0.604	10.64	5.3	267
0.1 mol % Al TiO ₂	1.06	19.79	0.610	12.77	7.4	326
0.5 mol % Al TiO ₂	1.07	20.86	0.630	14.05	6.4	330
1.0 mol % Al TiO ₂	1.07	20.57	0.628	13.88	6.8	353

3. ETM LAYER PREPARATION

3.1. Compact Layer Preparation With Spin Coating

For planar and mesoporous PSCs, a compact TiO_2 layer is necessary to provide effective electron extraction and transportation from the perovskite layer. (Mohamad Noh et al., 2018). The performance of the perovskite cells increases as the compact electron transport layer thickens, reaching an optimal thickness, followed by a performance drop (Lu et al., 2015). Like spin coating techniques for solution based deposition require at least 65 nm of compact TiO_2 thickness to achieve exceptional performance devices (Mohamad Noh et al., 2018). Pinhole development is more likely with a thinner ETL, and as a result, the perovskite layer and ITO substrate come into direct touch. This deteriorates the FF values and J_{SC} because of significant current leakage at the ETL/perovskite contacts or inadequate hole blocking abilities (Mohamad Noh et al., 2018).

The compact TiO_2 layer was deposited onto the ITO-coated glass by spin coating. Sol-gel precursor solution prepared with two different solutions. For the first solution, 1.5 g TTIP and 4.5 ml ethanol were mixed and stirred 15 min on the magnetic stirrer. Then for the second solution, 1 ml acetyl acetone and 3 ml ethanol mixed and stirred 15 min at magnetic stirrer. Then the second solution was added to the first solution drop by drop and stirred for half an hour, and the solution aged 24 hours. The solution is diluted 1:1 with absolute ethanol. The film was successfully deposited by two-step spin coating using a filter; first, at 1500 rpm for 20 s and then 2000 rpm for 20 s. Polo Spin coater and Semiconsoft MProbe Vis Thin Film measurement system are shown in Figure 3.1.

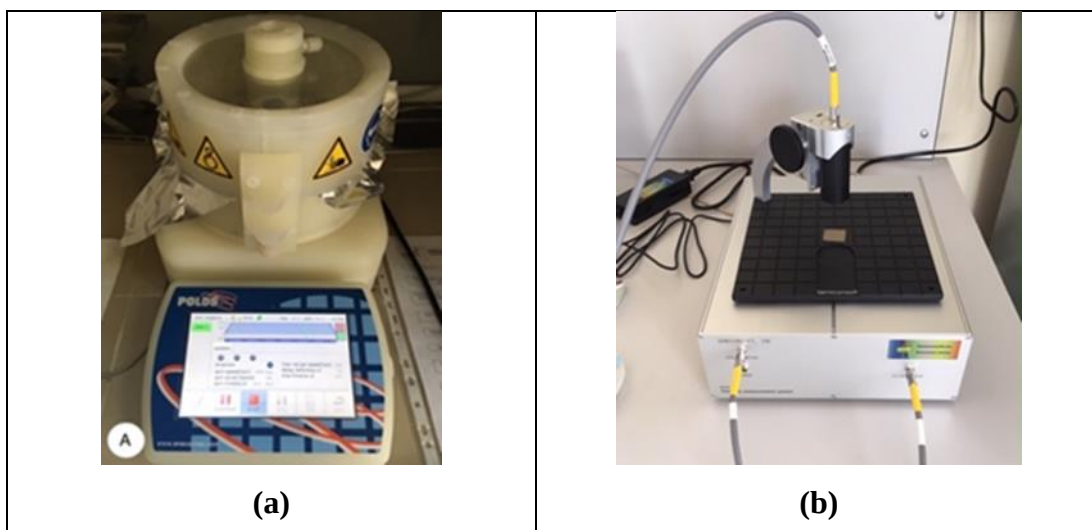


Figure 3.1: a) POLO Spin Coater b) Semiconsoft Thin Film Measurement System.

The compact layer thickness was measured as 90 nm with Semiconsoft MProbe Vis Thin Film measurement system. Then the film was calcined at 600°C for 3 hours. (The heating rate of RT to 250°C was 3°C·min⁻¹ and of 250°C to 600°C was 5°C·min⁻¹). After calcination thickness of the film was reduced to 70 nm. SEM images of the compact film after calcination at 600°C are shown in Figure 3.2.

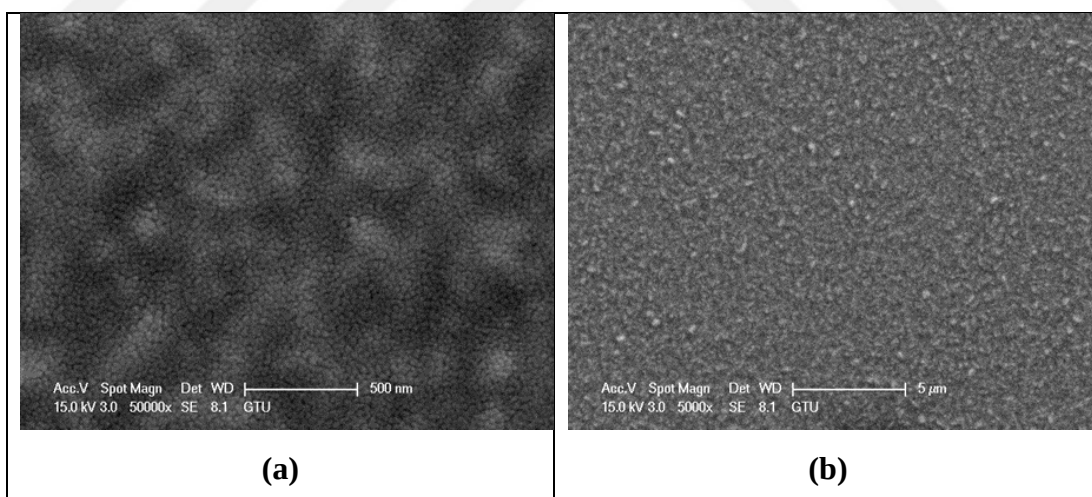


Figure 3.2 SEM images of compact layer after 600°C calcination (a) at 50K (b) at 5K magnifications.

3.2. Preparation of mp ETM PVP_TiO₂ Polymeric Nanofibers

Several techniques have been developed to fabricate one-dimensional TiO₂ nanostructures. Electrospinning offers advantages of simplicity, process controllability, the low production cost for producing industrial quantities (Kumar et al., 2007). A high voltage power supply, a spinneret with a metallic needle, and grounded collecting plates—as seen in Figure 3 are the three main parts of an electrospinning system.

In the electrospinning method, Using a high voltage power source, a polymer solution is put into a syringe fitted with a stainless steel needle and charged. The polymer solution is expelled from the tip to a collector when the electric field falls to a critical point where the repulsive electric force is greater than the surface tension of the solution. The collector received the polymer that was expelled from the needle tip. The solvent, which has a diameter that ranges from hundreds of nanometers to several micrometers, evaporates quickly, causing the electrospun substance to solidify. The injection rate, applied voltage, distance between the collector and needle, and concentration of the polymer solution could all be adjusted to customize the fiber's diameter and shape.

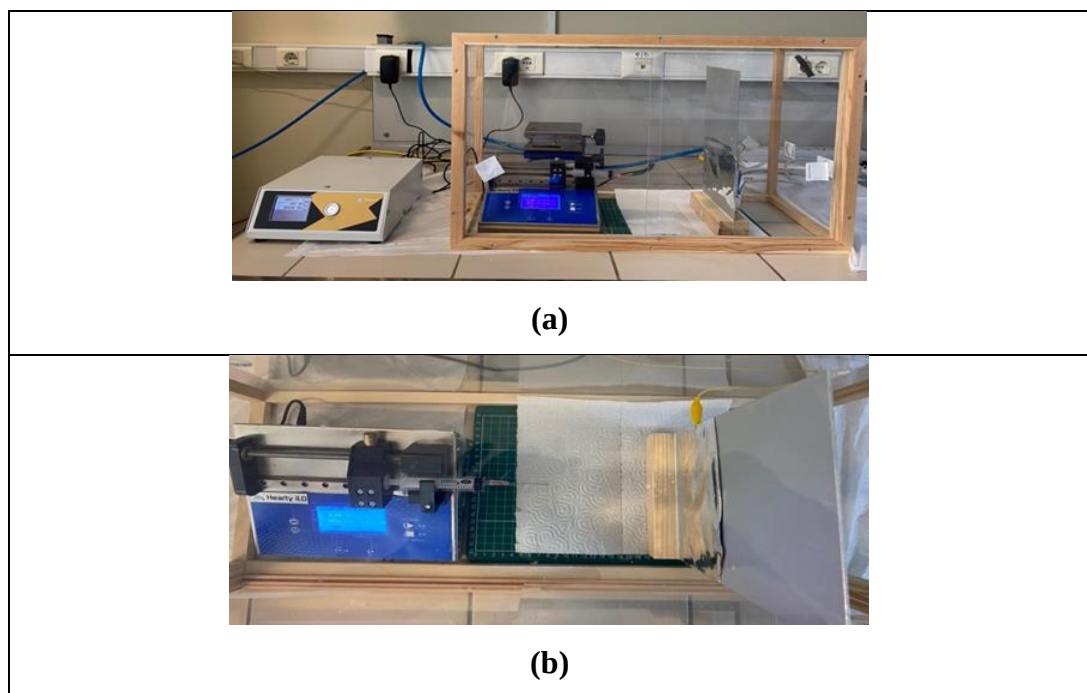


Figure 3.3: (a) Front view (b) Top view of the electrospinning system.

TiO₂ nanofibers were fabricated by electrospinning of TiO₂ solution and poly (vinylpyrrolidone) (PVP; Mw =1 300 000, Sigma- Aldrich) polymer. First, the TiO₂ solution was prepared by hydrolyzing 0.25g titanium tetraisopropoxide [Ti(OiPr)₄ ; 97%, Sigma Aldrich] with a mixture of 1.4 mL of absolute ethanol and 0.6 mL of acetic acid. The solution was stored in a dark medium for 48 hours without stirring. Next, PVP (~ 4 wt %) was separately dissolved in 2.75 mL of ethanol and then added to the TiO₂ sol solution. The mixed precursor solution was stirred for half an hour at room temperature to attain a sufficient viscosity required for electrospinning. The solution was then loaded into a syringe connected to a stainless-steel needle of 25 Gauge. A direct current electric field was applied between the needle and collector plate using a high voltage supply that generates dc voltage up to 30 kV. The feed rate of the precursor solution was controlled using a syringe pump. 1.5 cm x 1.5 cm glass substrates placed over the aluminum foil were used for nanofiber collection. For the first experiment, the feed rate was fixed at 0.5 mL/h, needle gauge fixed to 25 G, and deposition time also fixed to 5 min. The humidity was %35. The needle–collector plate distance(d), applied voltage (V) changed as seen in Table 3.1 For different conditions, different nanofiber diameters (D) were obtained.

Table 3.1: Effect of (V) and (d) to the fiber diameter (D).

Sample ID	V (kV)	d(cm)	D(nm)
(a)	10	10	85
(b)	20	10	70
(c)	10	15	108
(d)	20	15	74

The fiber diameter is dependent on the spinning conditions; the fiber diameters decrease with

- (i) increasing the applied voltage.
- (ii) decreasing with the needle–collector distance.

Figure 3.4 shows the SEM images and histograms of as-spun TiO₂-PVP composite nanofibers.

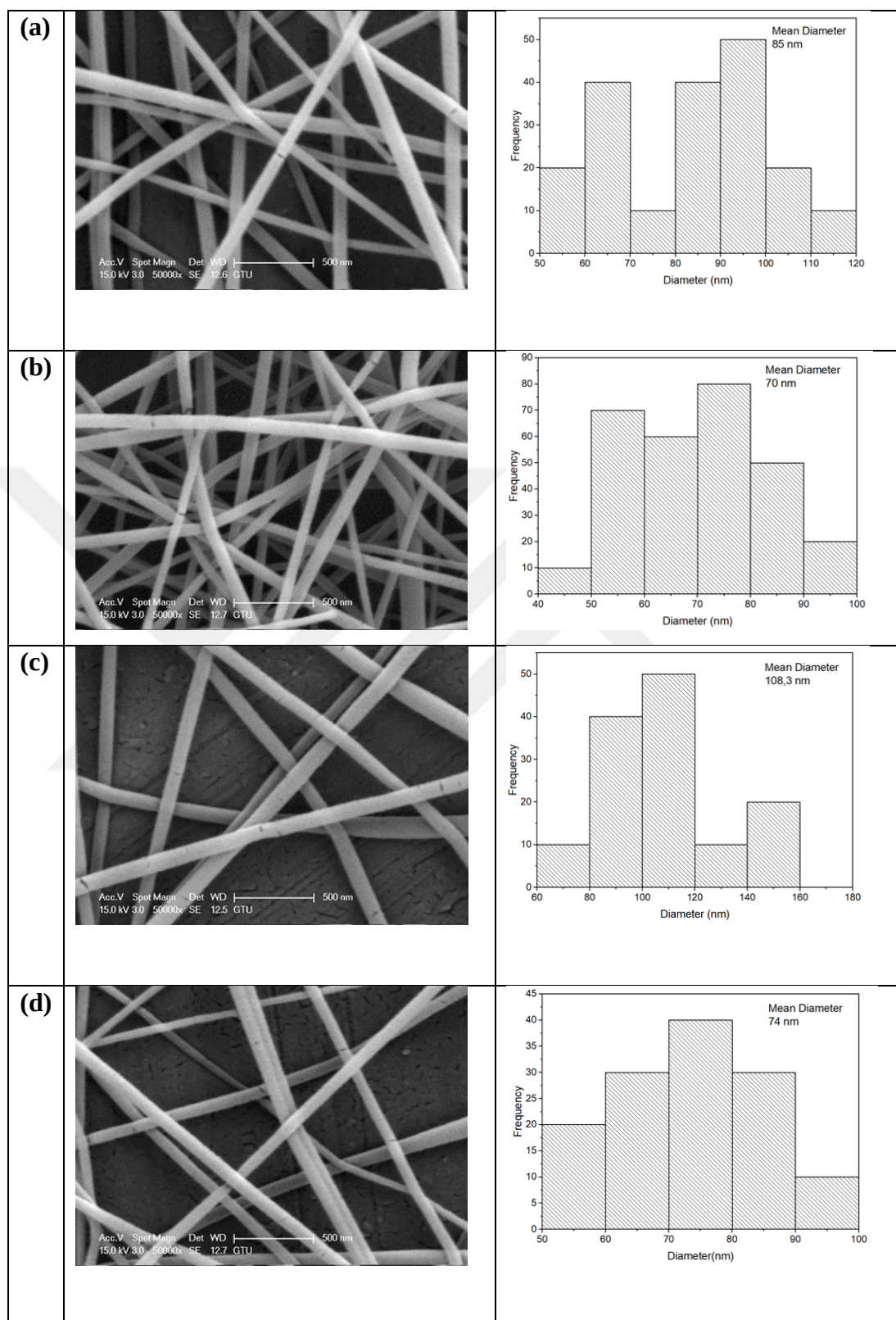


Figure 3.4: SEM micrographs and the histograms of the as-spun TiO₂-PVP composite nanofibers **(a)** 85nm, 10kV, 10cm **(b)** 70nm, 20Kv, 10cm **(c)** 108 nm, 10kV, 15cm **(d)** 74nm, 20Kv, 15cm.

The effect of concentration on fiber diameter was investigated. When the concentration of the polymer solution increases, fiber diameter also increases. Applied voltage fixed to 20kV, collector-needle distance fixed to 15 cm needle gauge fixed to 25G, and deposition time fixed to 30 min. When the polymer (PVP) concentration increased from 4 wt % to 6.5%, fiber diameter increased from 74nm to 157nm. Figure 3.5 (a) shows the SEM image and the histogram of TiO₂-PVP composite nanofiber for 6.5% PVP concentration. (b) shows the SEM image and histogram of TiO₂-PVP composite nanofiber for 8.6% PVP concentration (c) shows the SEM image and histogram of TiO₂-PVP composite nanofiber for 9.7% PVP concentration (d) shows the SEM image and histogram of TiO₂-PVP composite nanofiber for 15.8% concentration.

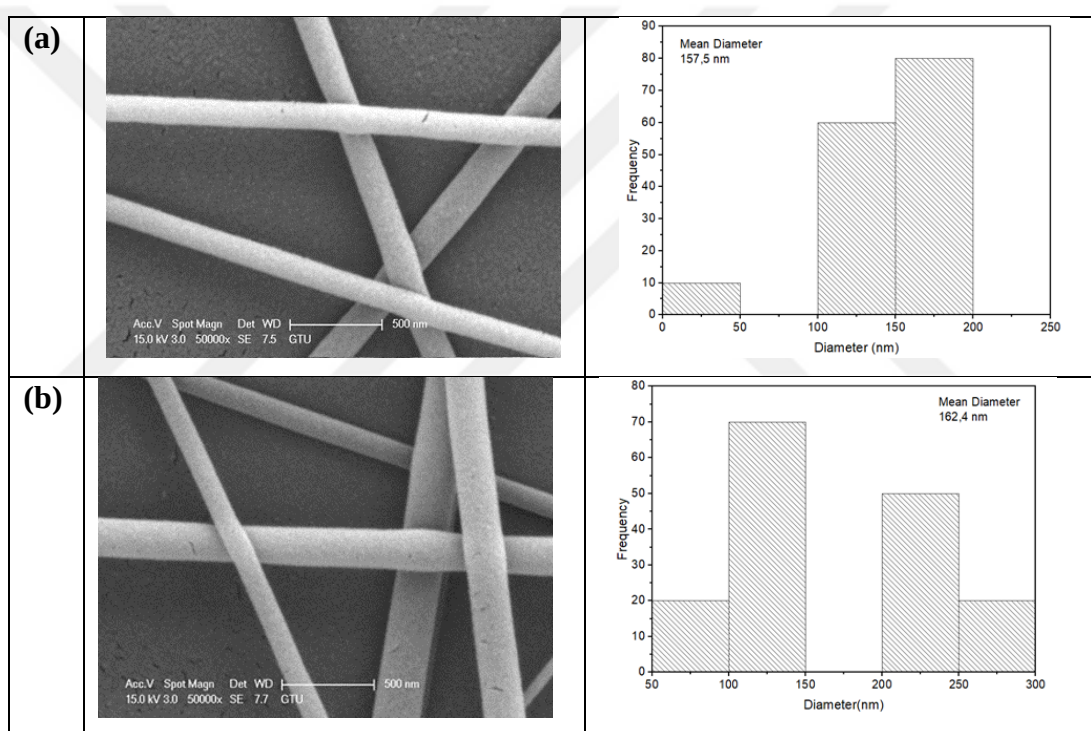


Figure 3.5: SEM image of TiO₂-PVP composite nanofiber for (a) 6,5% PVP concentration and histogram (b) 8,6% PVP concentration and histogram.

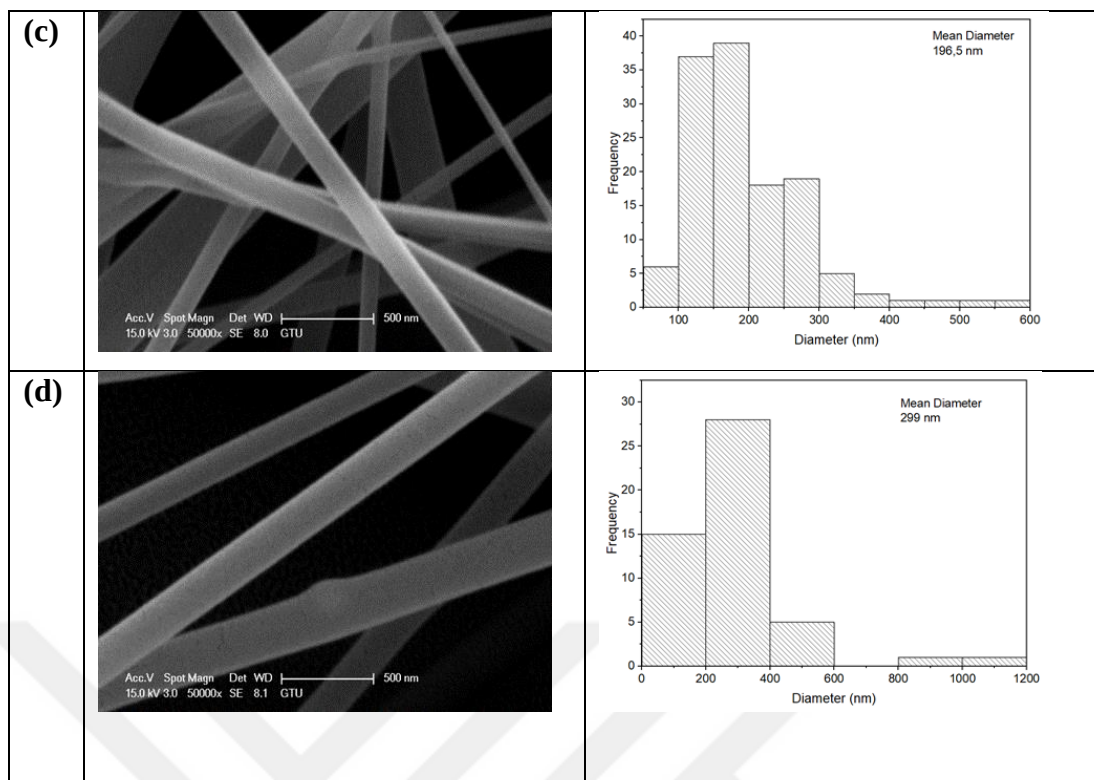


Figure 3.6 Continue: SEM image of TiO_2 -PVP composite nanofiber for (c) 9,7% PVP concentration and histogram (d) 15,8% PVP concentration and histogram.

The porosity of the fiber structure affects the perovskite layer's penetration depth into the fiber. If the space area is too low, the perovskite solution will not penetrate the fiber structure (Wang et al., 2017). The as-spun PVP- TiO_2 composite nanofibers on glass are shown in Figure 3.6. for (a) 5 min (b) 30 min deposition times.



Figure 3.7 The as-spun PVP- TiO_2 composite nanofibers on glass (a) 5min (b)30min deposition time.

3.3. Polymeric Nanofibers Conversion to Crystal TiO₂

Upon undergoing nano crystallization, TiO₂ exhibits favorable electrical conductivity. So, TiO₂ needs to be processed at a high temperature. for nanocrystal formation. TiO₂ has several phases; these are anatase, rutile, and brookite. The crystal structures and tetragonal unit cell are typical of TiO₂ phases. It composed of TiO₆ octahedra (Mohamad Noh et al., 2018). The anatase and rutile TiO₂ crystal structures representation is shown in Figure 3.7 (a) and (b), respectively (Hanaor & Sorrell, 2011).

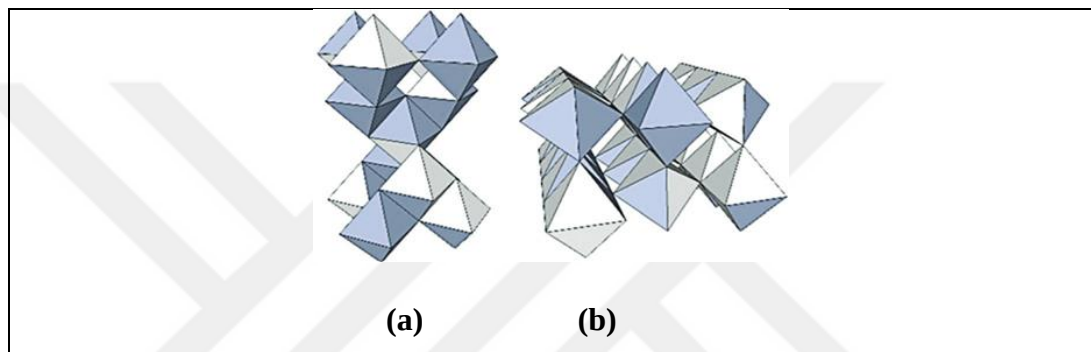


Figure 3.8: Diagram showing the (a) anatase and (b) rutile TiO₂ crystal structures. (Hanaor & Sorrell, 2011a).

Rutile structures lattice configuration that is compatible with a perovskite structure. As well as compared to anatase TiO₂ perovskite, rutile TiO₂ perovskite has shorter bond lengths, It indicates a shorter surface interaction between T TiO₂ and perovskite. These shorter lengths provide easier charge transfer. The nanofibers of spun PVP-TiO₂ composite were annealed at 120°C for 1 hour to dry and remove the solvents. After the nanofibers were calcinated at 500°C and 600°C for 3 hours separately to achieve the crystalline TiO₂. (3°C·min⁻¹ from RT to 250°C and 3°C·min⁻¹ from 250°C to 600°C/500°C) (Gonzalez-Abrego et al., 2017). The types of polymers and the solvents evaporated during the calcination process, causing the precursors to break down and causing a considerable drop in diameter. At the same time, nanosized grains started to grow. Because of the increased diffusion rate brought about by the higher calcination temperature, the nanograins merged with one another, producing a much greater proliferation of nanograins and a lower fiber diameter (Katoch et al., 2015) Figure 3.8 provides a schematic representation of how nanograins in NFs grow as the calcination temperature rises (Kim et al., 2018).

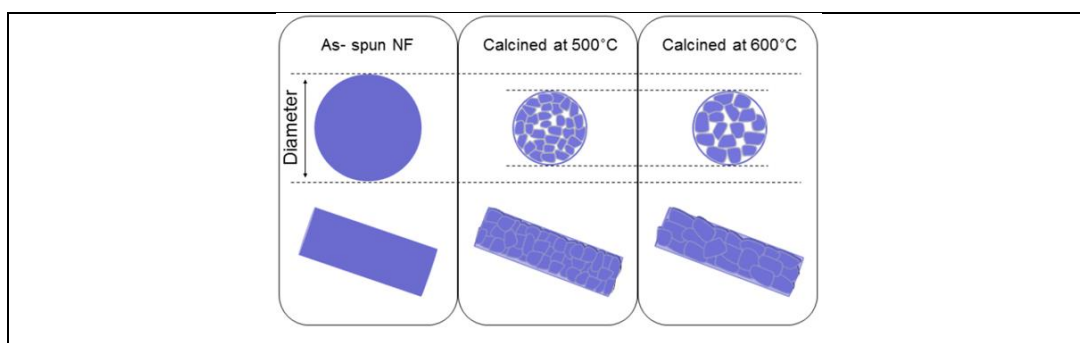


Figure 3.9: Diagrammatic representation of how nanograins form in NFs in relation to the calcination temperature(Kim et al., 2018).

The spun PVP-TiO₂ composite nanofibers prepared two different concentrations 9.7% and 15.8%. The diameters of these PVP- TiO₂ composite nanofibers are 196.5 nm and 299 nm, respectively. Figure 3.9 and Figure 3.10 shows the PVP-TiO₂ composite nanofibers SEM images before calcination and after calcination at 500°C and 600°C. ImageJ analysis software was used to measure the fiber occupied area from the SEM pictures. Table 3.2 shows the diameters of the fibers before and after calcination.

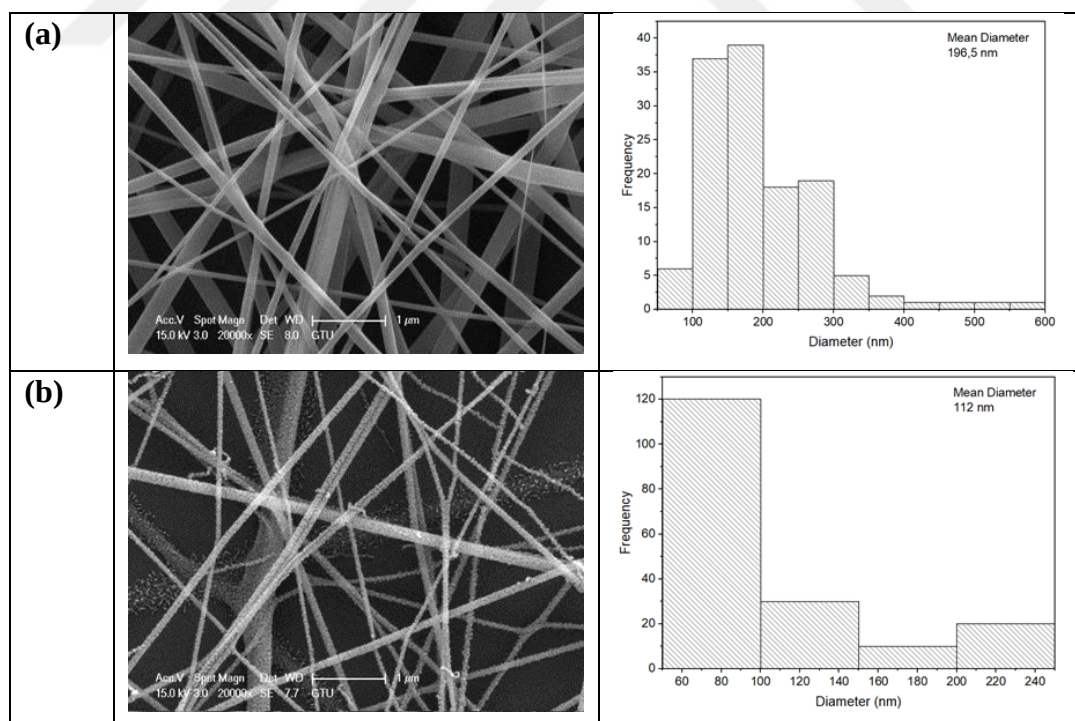


Figure 3.10: (a) 9.7% PVP concentration before calcination (b) after calcination at 500°C.

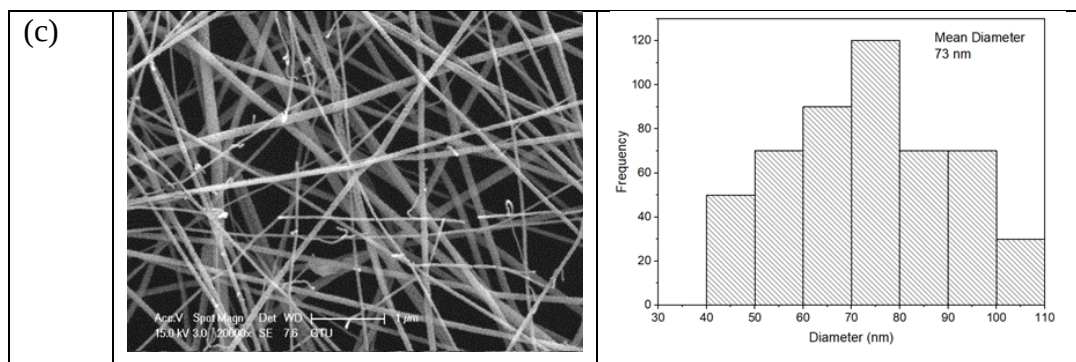


Figure 3.11 Continue: (c) 9.7% PVP concentration after calcination at 600°C.

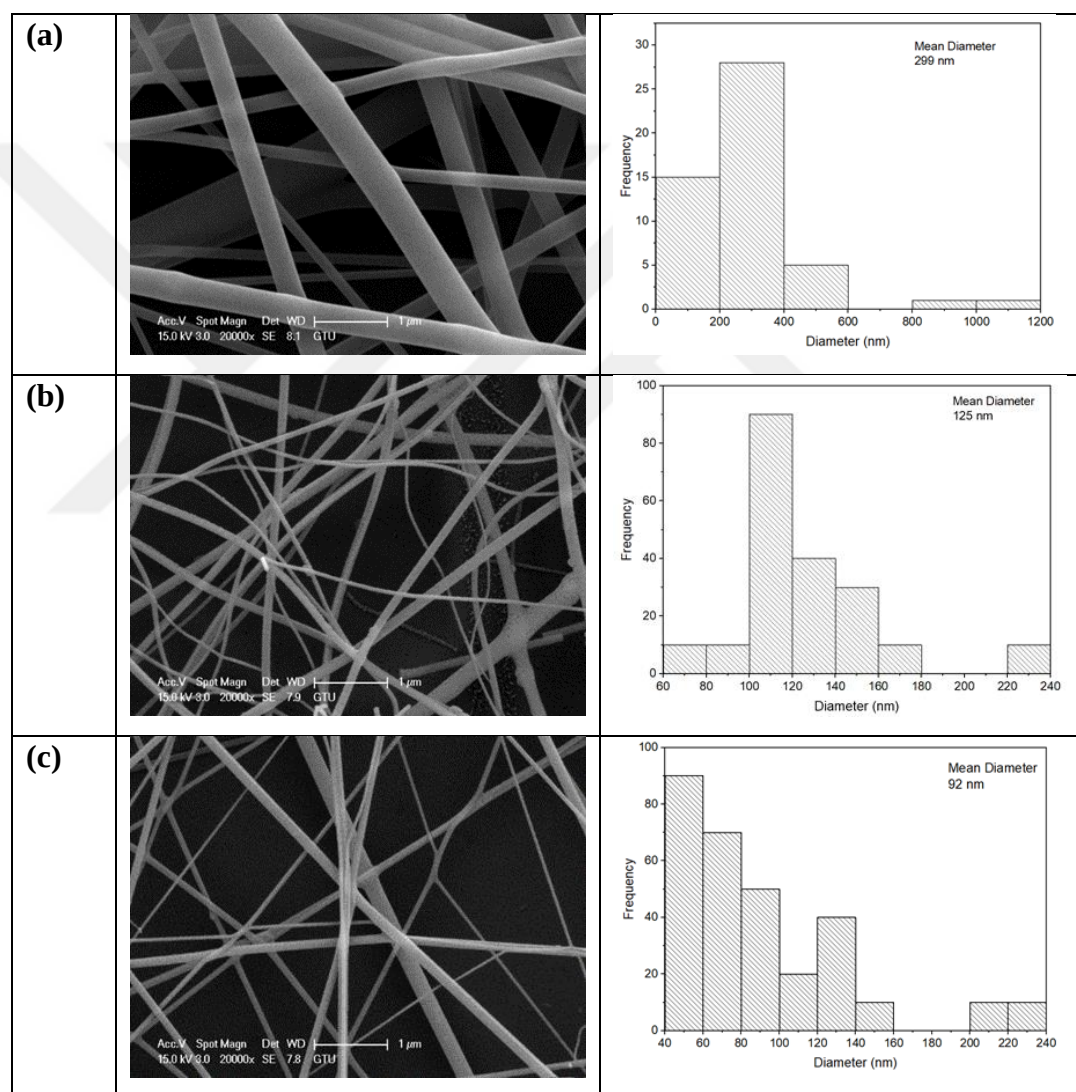
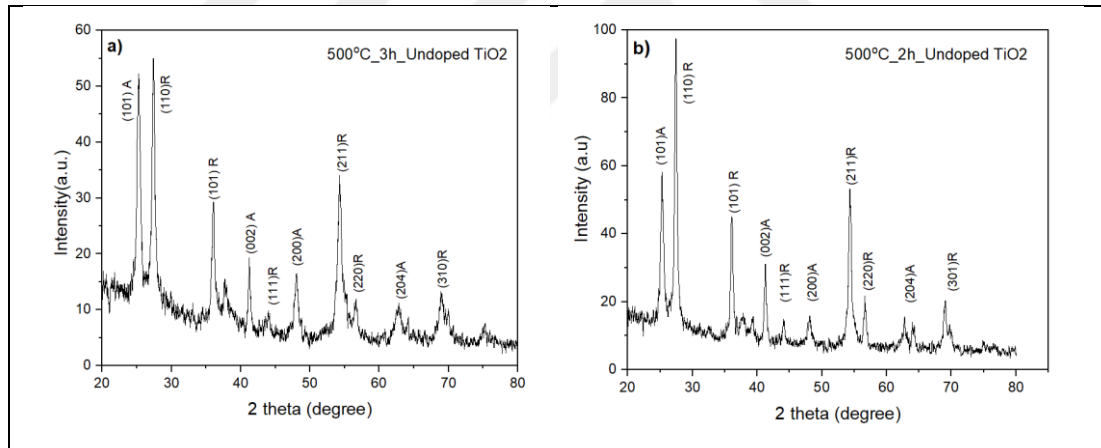


Figure 3.12: (a) 15.8% PVP concentration before calcination (b) after calcination at 500°C (c) after calcination at 600°C.

Table 3.2: As-spun nanofibers diameters before and after calcination.

Before calcination		After calcination at 500°C		After calcination at 600°C	
Fiber diameter (nm)	Fiber Area (%)	Fiber diameter (nm)	Fiber Area (%)	Fiber diameter (nm)	Fiber Area (%)
196	90	112	71	73	61
299	77	125	70	92	50

XRD techniques were used to examine the crystal structure and phase evolution of the electrospun TiO₂ nanofibers (Rigaku Slab Cu k-alpha 1.58Å Xray). Figure 3.11 shows the XRD patterns concede the phase transformation of the TiO₂ in nanofibers at 500°C. The as-spun nanofibers were amorphous. Well crystallized anatase-rutile TiO₂ nanofibers were achieved by 500°C heating of the as-spun fibers. Figure 3.12 shows the XRD pattern for TiO₂ at 600°C. The rutile phase's volume fraction increased as the annealing temperature raised. At 600°C the rutile phases are more significant.

**Figure 3.13:** Phase transformation of the TiO₂ in nanofibers **a)** at 500 °C_3h **b)** at 500 °C_2h

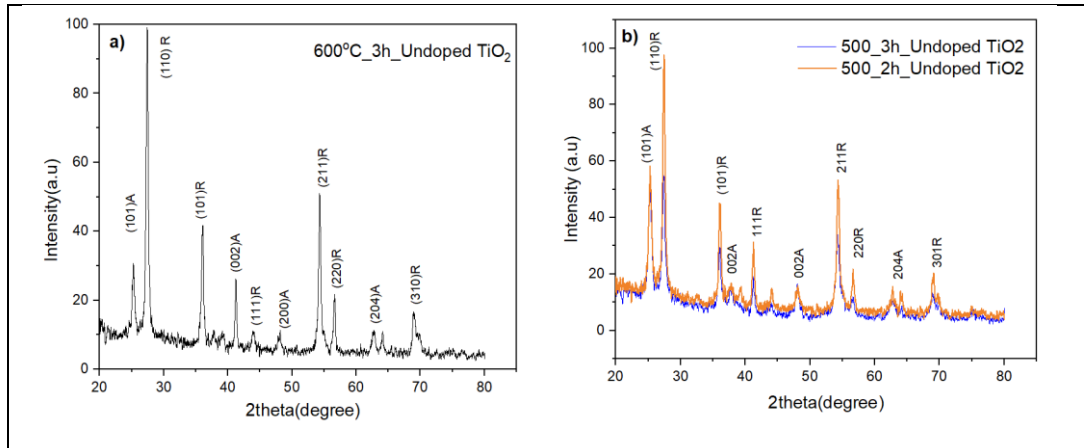


Figure 3.14: Phase transformation of the undoped TiO₂ in nanofibers at **a)** 600°C_3h. **b)** 2 h and 3 h comparison at 500°C.

When we compare 500°C_2h and 3h calcination times, for 2h hours calcination time rutile phase is more evident and crystal sizes are larger for 500°C_2h calcination time.

3.4. Ion Doping

By electrospinning a combination of TiO₂ solution and poly (vinylpyrrolidone) (PVP; Mw = 1 300 000, Sigma-Aldrich) polymer, TiO₂ nanofibers were created. Initially, 0.25g of titanium tetraisopropoxide Ti(OiPr)₄; 97%, Sigma Aldrich] was hydrolyzed with a solution of 1.4 mL 100% ethanol and 0.6 mL acetic acid to create the TiO₂ solution. The solution was stored in a dark medium for 48 hours without stirring. Next, separately, 0.46 g PVP dissolved in 2.75 mL of ethanol. and then different g of MgCl₂ added to the PVP solution for different concentrations of MgCl₂. Then TiO₂ solution added drop by drop to the MgCl₂ added PVP solution. The mixed precursor solution was stirred for half an hour to reach the necessary viscosity needed for electrospinning at ambient temperature. Next, the solution was put into a syringe that was attached to a 25-gauge stainless steel needle. A high voltage of 25 kV is supplied between the collector plate and the needle. 0.5 ml/hour feed rate was applied by using a syringe pump. Table 3.3 shows the MgCl₂ concentrations.

Table 3.3: MgCl₂ concentrations.

MgCl ₂ concentration (%)	MgCl ₂ (g)
2.5	0.12
1.0	0.047

For different doping concentrations, deposition time (t), Calcination Temperature (T), different nanofiber diameters (D) were obtained. Table 3.4 shows the summary of the parameters.

Table 3.4: Effect of MgCl_2 concentrations to the fiber diameter.

Sample name	MgCl_2 (%)	t (min)	D (nm)	T ($^{\circ}\text{C}$)	Shrinkage (%)
1	2.5	30	192	-	-
2	2.5	30	128	600	%33
3	1	30	166	-	-
4	1	30	91	600	%45

Figure 3.13 shows the SEM images and histograms of MgCl_2 doped TiO_2 -PVP composite nanofibers.

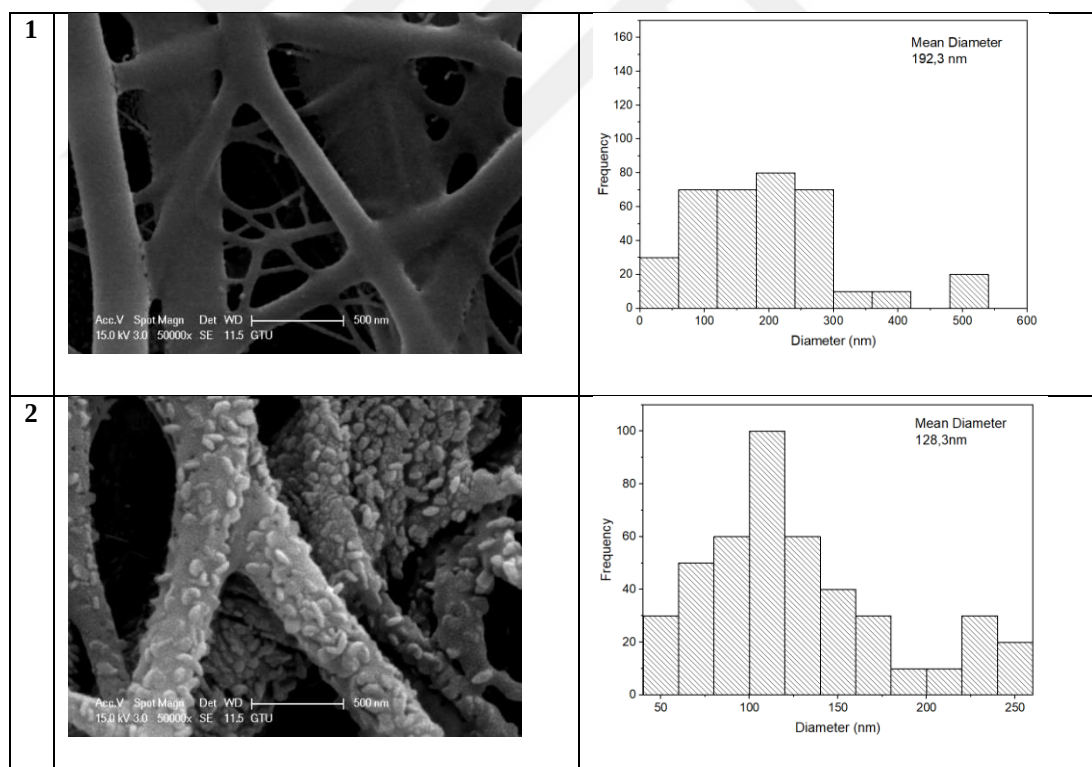


Figure 3.15: (1) 2.5% MgCl_2 doped TiO_2 nanofibers No Calcination (2) 2.5% MgCl_2 doped TiO_2 nanofibers 600 $^{\circ}\text{C}$ calcination.

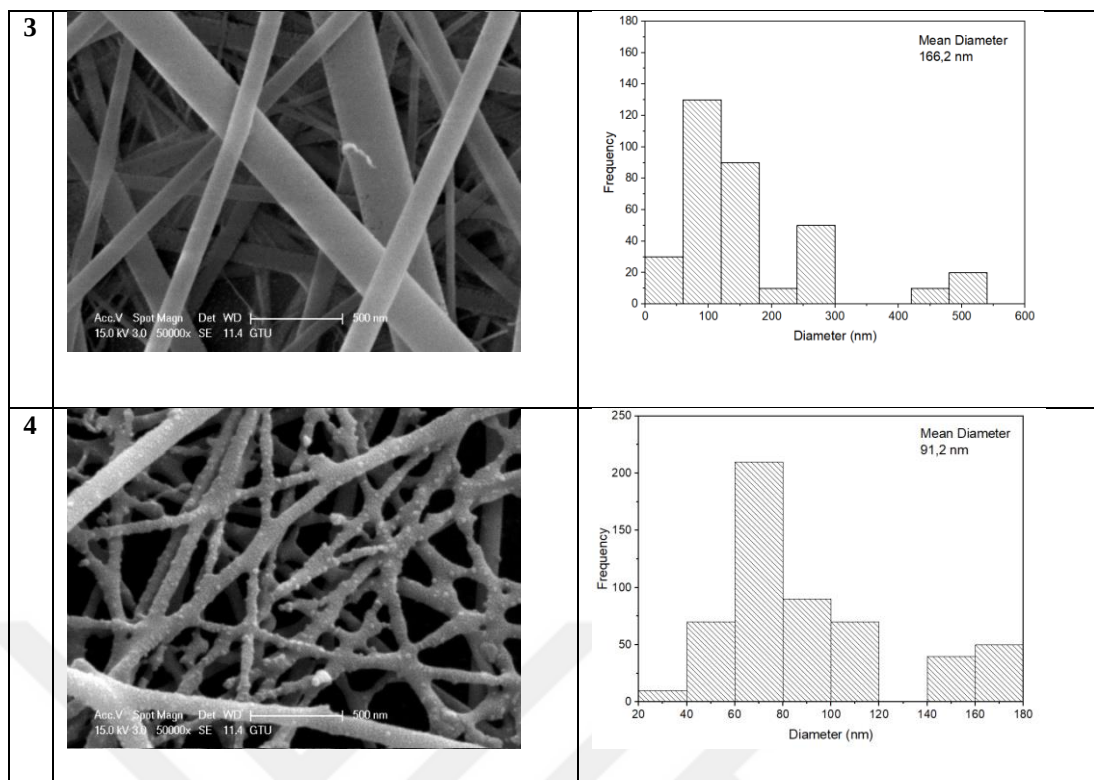


Figure 3.16 Continue: (3) 1%MgCl₂ doped TiO₂ nanofibers no calcination (4) 1%MgCl₂ doped TiO₂ nanofibers 600°C calcination.

For the %2.5 MgCl₂ doped TiO₂ sample 192.3 nm fiber diameter obtained before calcination, and after 600°C calcination fiber diameter decreased to 128.3nm, for the %1 MgCl₂ doped TiO₂ before calcination fiber diameter 166.2nm, and after calcination fiber diameter decreased to 91.2nm. In addition, as the MgCl₂ doped increases, the shrinkage rate decreases.

Table 3.5: Shows the EDS analysis of Mg doped TiO₂ nanofiber samples.

O K	30.42	43.74	660.1	0.01
NaK	11.53	11.54	573.4	0.01
MgK	5.32	5.03	368.03	0.02
AlK	1.32	1.12	98.14	0.04
SiK	36.24	29.69	2903.54	0
ClK	5.79	3.76	306.53	0.02
K K	0.5	0.3	22.72	0.21
CaK	5.98	3.43	225.67	0.03
TiK	2.9	1.39	85.94	0.07

1

O K	35.48	49.01	1026.16	0.01
NaK	12.9	12.4	750.05	0.01
MgK	6.13	5.57	492.29	0.01
AlK	1.33	1.09	114.95	0.04
SiK	33.74	26.55	3173.75	0
K K	0.43	0.25	24.07	0.2
CaK	5.83	3.21	269.26	0.02
TiK	4.16	1.92	149.35	0.04

2

Table 3.6 Continue: Shows the EDS analysis of Mg doped TiO₂ nanofiber samples.

O K	31.5	44.71	737.94	0.01	O K	38.23	51.71	1168.32	0.01
NaK	12.51	12.36	642.81	0.01	NaK	13.41	12.63	770.16	0.01
MgK	3.99	3.73	282.13	0.02	MgK	3.21	2.85	253.09	0.02
AlK	1.31	1.1	101.2	0.05	AlK	1.03	0.83	90.91	0.05
SiK	39.08	31.59	3236.12	0	SiK	35.9	27.66	3407.85	0
ClK	2.15	1.38	116.14	0.05	K K	0.37	0.21	20.38	0.23
K K	0.54	0.31	25.3	0.22	CaK	6.43	3.47	291.29	0.02
CaK	6.4	3.62	249.5	0.03	TiK	1.41	0.64	49.91	0.12
TiK	2.52	1.19	76.85	0.08					
3					4				

For the 2.5% and 1% doped samples Mg amount is so excessive, I tried to obtain less Mg concentrations. For new doping concentrations, MgCl₂ doped TiO₂ nanofibers obtained. Table 3.6 shows the summary of the parameters. Figure 3.14 shows SEM images and histograms of the nanofibers.

Table 3.7: Effect of MgCl₂ concentrations to the fiber diameter.

Sample name	MgCl ₂ (%)	t (min)	D (nm)	T (°C)	Shrinkage (%)
A	0.1	10	249	-	-
B	0.1	10	80	500	%68
C	0.5	10	262	-	
D	0.5	10	133	500	%50

As can be seen from table 3.6 fiber diameters for samples A and C without calcination were 249 and 262 nm, respectively. The higher amount of Mg-doped in sample C led to a slight increase in fiber diameter. On the other hand, after the calcination process for samples (b) and (d), the fibers shrank and a significant decrease in diameter was observed. The diameters of samples (b) and (d) were measured as 80 nm and 133nm, respectively. The shrinkage percentages of samples with 0.1% and 0.5% MgCl₂ are 68% and 50%, respectively. However, it can be concluded that a higher amount of Mg restricted the shrinkage percentages. The insertion of dopants into the TiO₂ lattice, which may result in lattice and volume expansion, is responsible for this phenomenon (M.Çalışır, 2020).

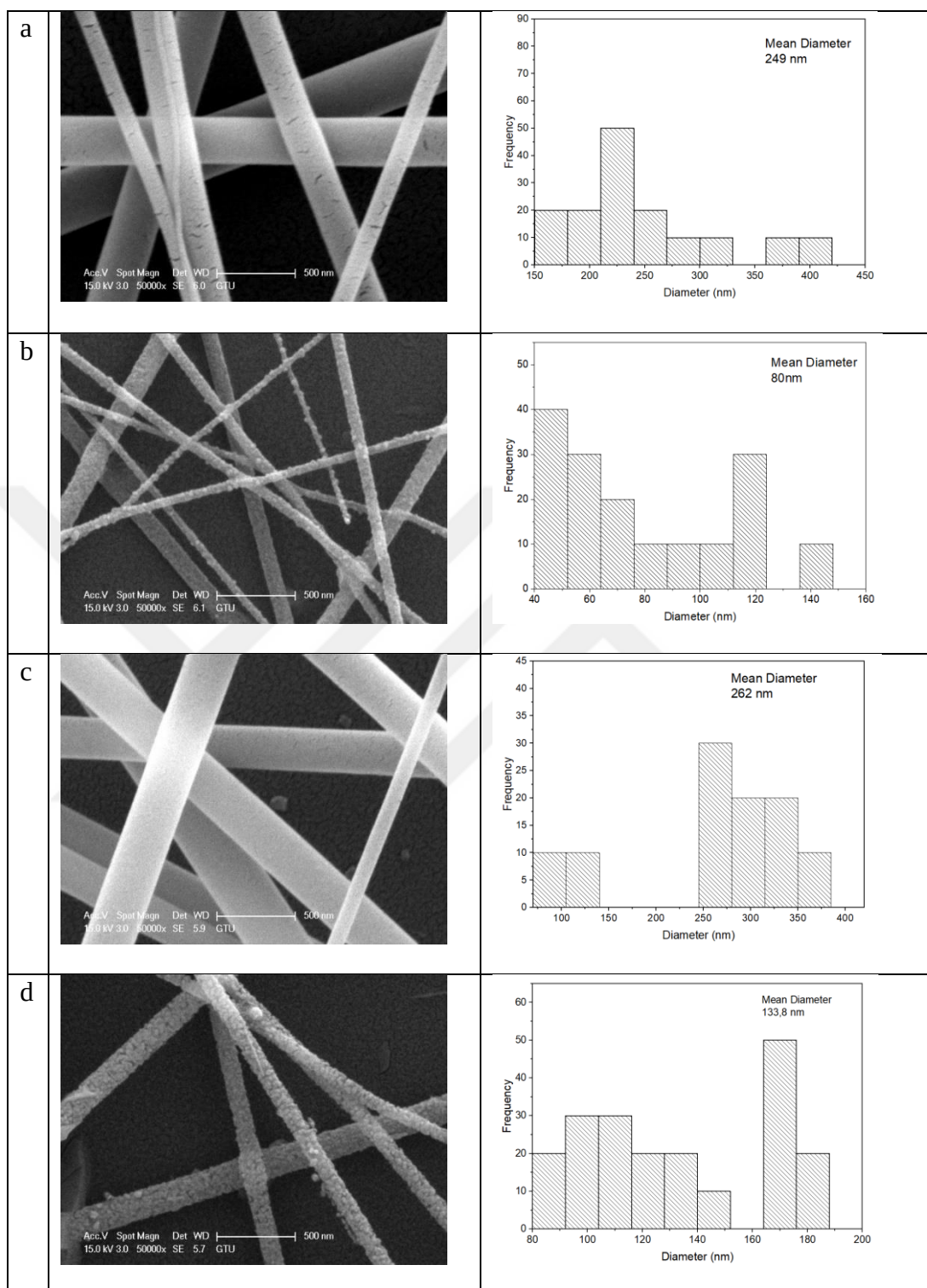
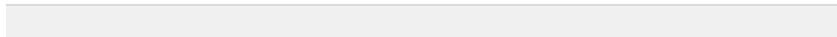


Figure 3.17: a) 0.1% MgCl₂ doped TiO₂ no calcination b) 0.1% MgCl₂ doped TiO₂ 500°C calcination c) 0.5% MgCl₂ doped TiO₂ no calcination d) 0.5% MgCl₂ doped TiO₂ 500°C calcination.

Table 3.7 shows the EDS analysis of the doped nanofibers. For 0.1% MgCl_2 doped nanofibers Mg weight% 49.52 and for the 0.5% MgCl_2 doped nanofibers Mg weight % 45.41 obtained.

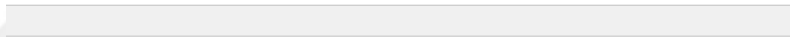
Table 3.8: EDS analysis for **(b)** 0.1% MgCl_2 doped TiO_2 500°C calcination and **(d)** for 0.5% MgCl_2 doped TiO_2 500°C calcination.

(b)



Element	Weight %	Atomic %	Net Int.	Net Int. Error
MgK	49.52	65.9	330.86	0.01
TiK	50.48	34.1	146.48	0.05

(d)



Element	Weight %	Atomic %	Net Int.	Net Int. Error
MgK	45.41	62.11	470.21	0.01
TiK	54.59	37.89	253.57	0.02

Well crystallized anatase-rutile TiO_2 and MgCl_2 doped TiO_2 nanofibers were produced by raising the as-spun fibers' temperature to 500°C. Figure 3.15 shows the XRD patterns for MgCl_2 doped Ti nanofibers for different calcination times.

The EDX elemental mapping used to determine the homogeneous distribution of the Mg element is shown in Figure 3.15. Before and after the calcination process, Mg element mapping showed a uniform distribution in the nanofibers. These images indicate that Mg doping was achieved throughout the nanofibers. The cross-section view of the nanofibers after calcination can be seen in Figure 3.15c.

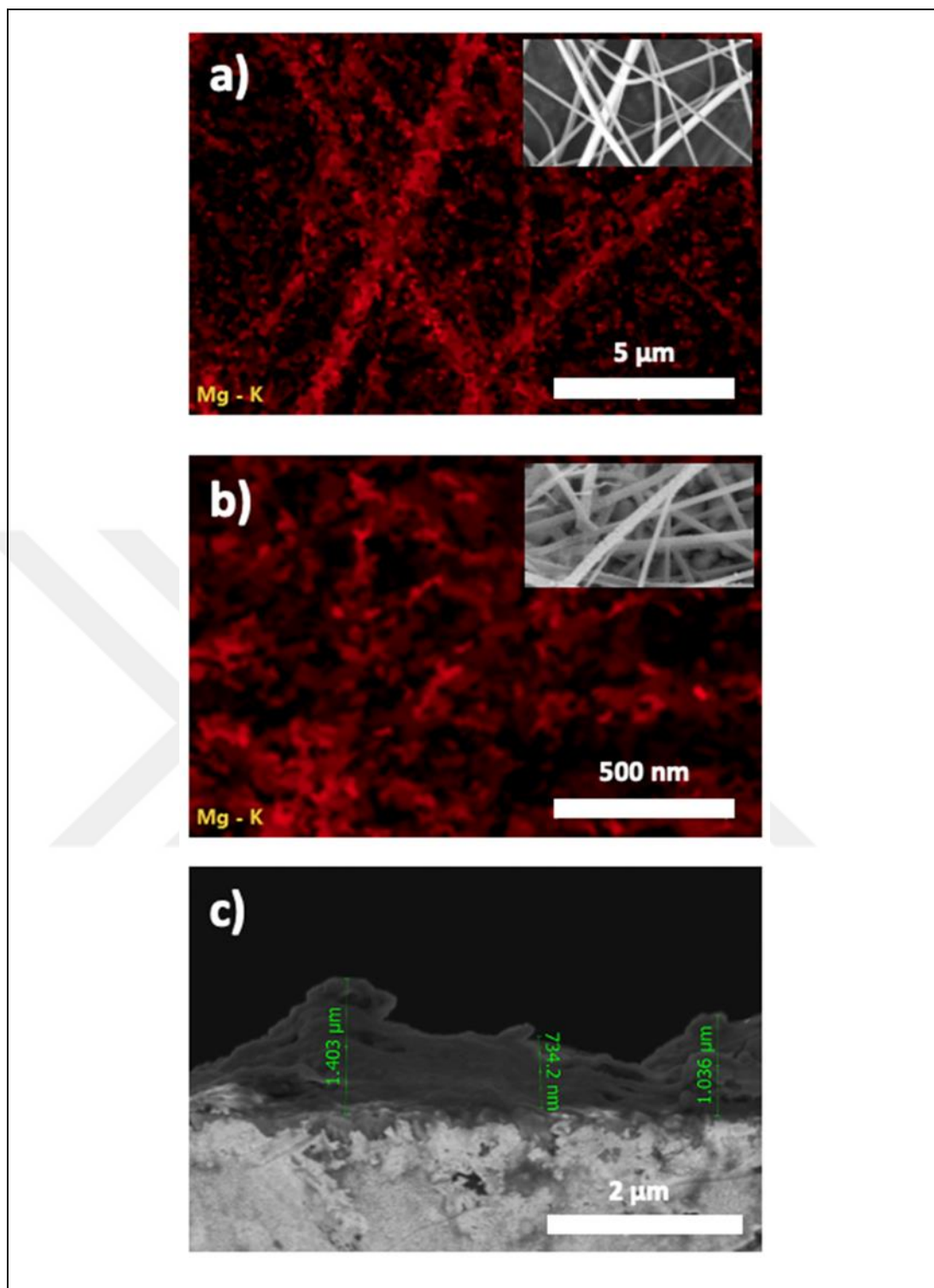


Figure 3.18: Images of SEM/EDX elemental mapping of Mg-doped fibers **(a)** Before calcination and **(b)** After calcination; the insets are the corresponding field emission SEM images. **(c)** Cross section of the nanofibers after calcination.

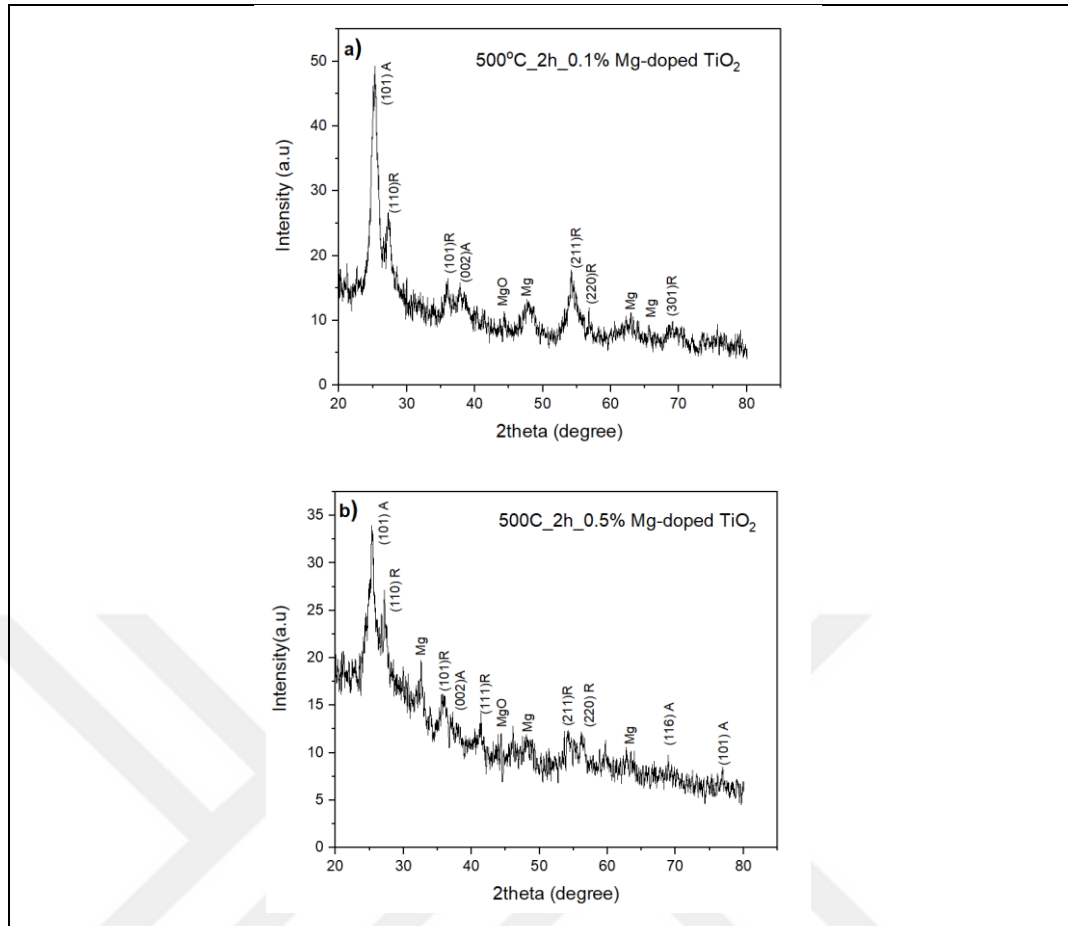


Figure 3.19 XRD patterns for 500°C_2h **a)** 0.1% MgCl₂ doped TiO₂ nanofibers **b)** 0.5% MgCl₂ doped TiO₂ nanofibers.

When we doped the TiO₂ nanofiber with MgCl₂ at XRD analyze we saw Mg peak coherent with literature (Yuniar & Yufita, 2020).

Table 3.8 shows the Crystallite sizes calculated from Scherrer's equation (nm) of Anatase and rutile phases of TiO₂ for different doping concentrations. Using the Debye-Scherrer formula $D = k\lambda/(\beta \cos \theta)$, where k is constant (0.9), λ is the x-ray wave length (0.154 nm), β is the FWHM value, and θ is the reflection angle, we may also calculate the crystals size (D) from the XRD results (Yuniar & Yufita, 2020). From the literature, when compared with pure Ti %10 wt MgO doped to TiO₂ the bandgap energy decreased and 20%wt ion doped TiO₂ the band gap energy increased (Yuniar & Yufita, 2020).

Table 3.8: Crystal sizes of Rutile and Anatase Phases for 500°C.

Annealing Temperature_time_Phase	2 θ	Crystal Size	Average Crystal Size
500°C_3h_Rutile	27.37	10.67	14.11
	36.07	13.54	
	41.24	23.10	
	54.31	9.34	
	56.59	22.09	
	69.18	5.91	
500°C_2h_Rutile	27.42	15.55	17.80
	36.07	17.99	
	41.25	22.17	
	54.34	15.80	
	56.65	26.28	
	69.19	9.03	
500°C_3h_Anatase	25.25	9.22	12.23
	37.77	19.51	
	48.03	17.39	
	55.05	2.83	
500°C_2h_Anatase	25.30	10.69	14.48
	36.07	16.60	
	48.08	15.81	
	62.77	14.84	
500°C_2h_Rutile_0.1%Mg Doped	27.24	6.65	6.82
	54.43	3.93	
	56.91	12.45	
	69.82	4.26	
500°C_2h_Anatase_0.1%Mg Doped	25.25	6.61	4.06
	37.82	3.51	
	47.99	4.37	
	62.46	1.76	
500°C_2h_Rutile_0.5%Mg Doped	26.09	3.38	6.25
	35.94	10.10	
500°C_2h_Anatase_0.5%Mg Doped	25.29	10.86	4.00
	37.54	0.68	
	49.66	0.45	

As shown in Table 3.8 when the amount of doping is increased there is a small reduction in the size of the crystal structure. Because some of the Mg dopant ions do not get into the TiO_2 lattice and instead remain on the surface, creating grain boundaries. This can impact the growth of the crystal structure, resulting in a smaller crystal size as the doping concentration increases. However, if the amount of doping is increased too much, it can inhibit crystal growth and increase the number of grain boundaries. This can have a negative impact on the performance of the material as a photo-anode (Shakir et al., 2018). In addition, the smaller crystal sizes reduced defects and generally result in a larger surface area and higher porosity, which can improve the contact between the ETL and the perovskite layer, leading to improved device performance. Figure 3.16 shows the XPS analysis.

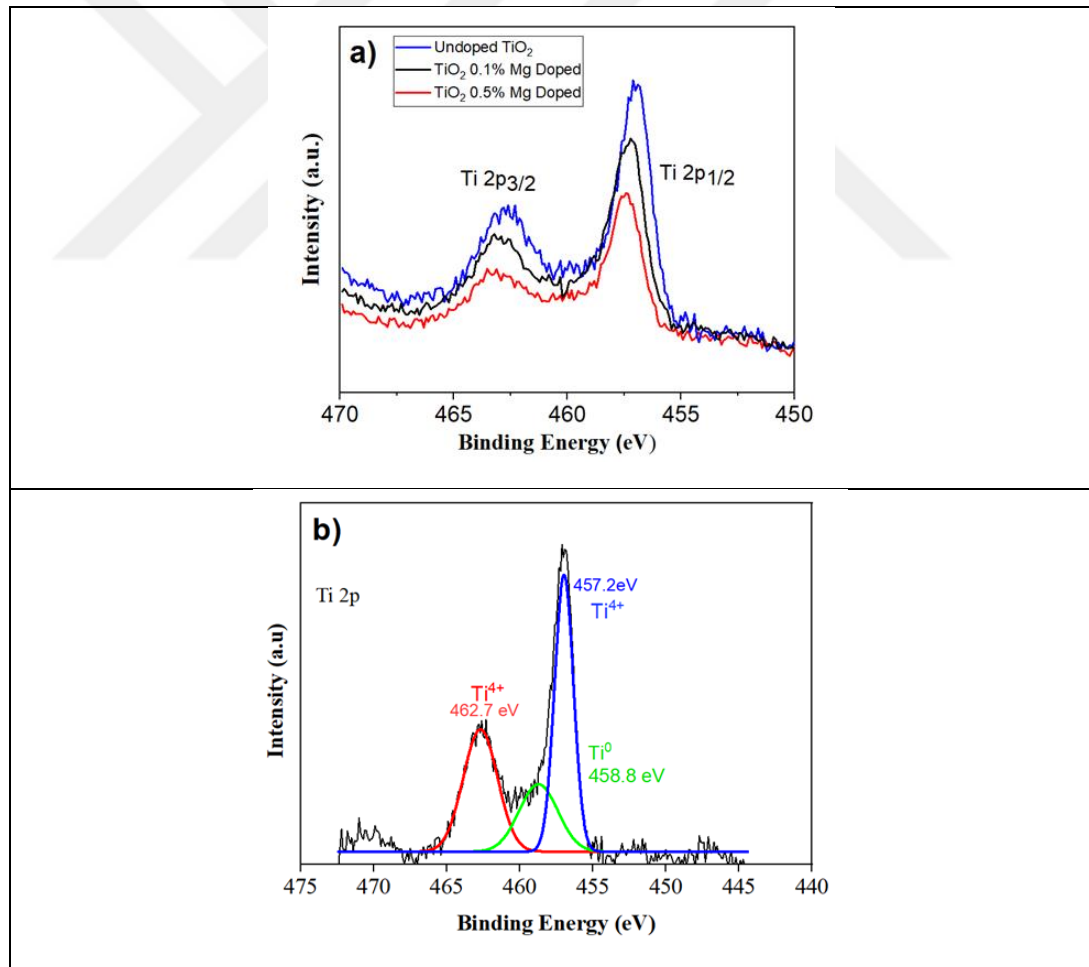


Figure 3.20: XPS analyses of the Ti 2p for (a) non-doped TiO_2 , 0.1% Mg doped TiO_2 , and 0.5% Mg doped TiO_2 nanofibers. (b) Non-doped TiO_2 fitting for

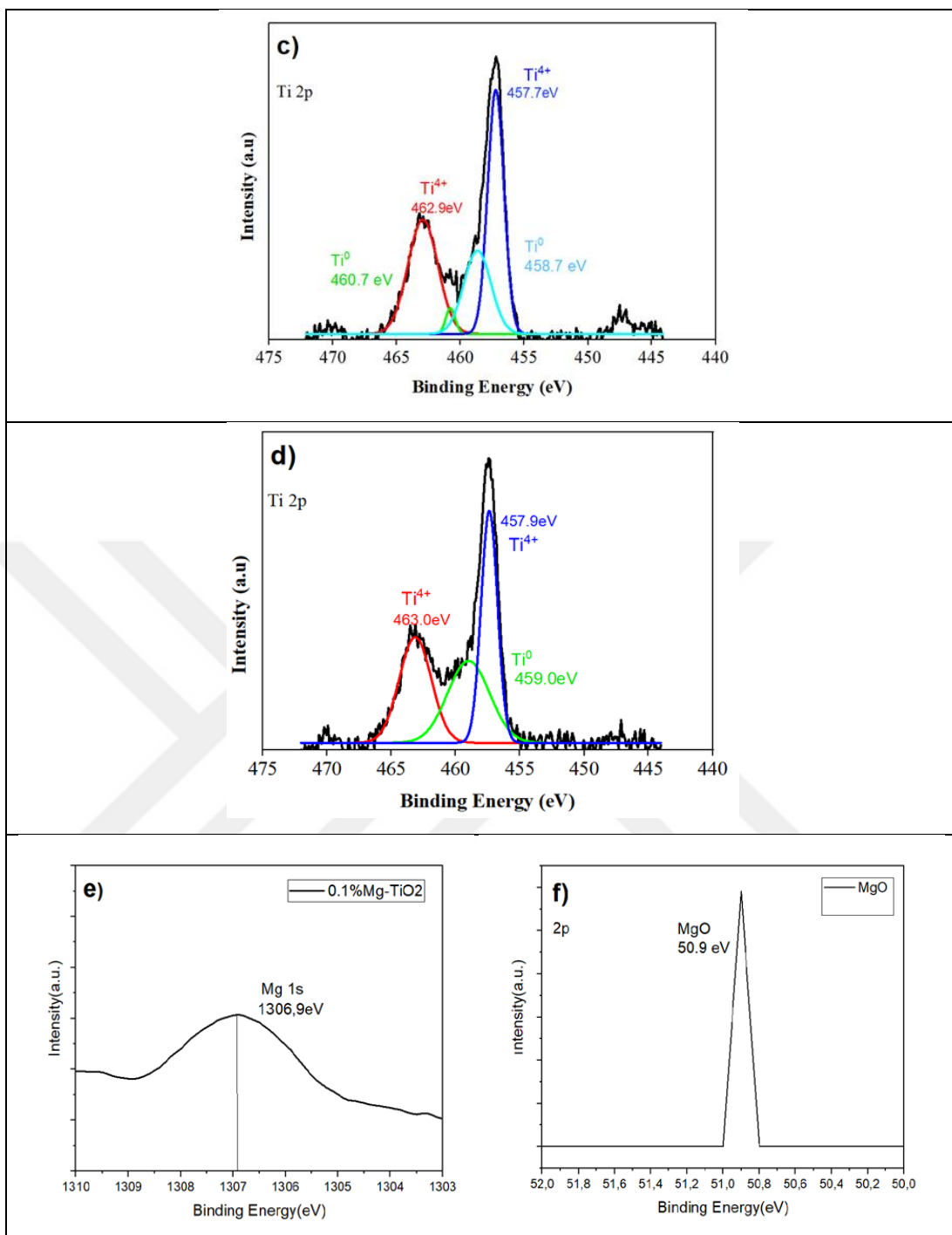


Figure 3.21 Continue: XPS analyses of the Ti 2p for (c) 0.1% Mg doped TiO₂ and (d) 0.5% Mg doped TiO₂. (e) Mg 1s binding energy for 0.1% Mg doped TiO₂ and (f) Mg 2p MgO binding energy for 0.1% Mg doped TiO₂.

Absorbance Wavelength spectra and PL Spectra shown in figure 3.17a and b respectively. The optical properties of pure TiO₂ and Mg-doped TiO₂ nanofibers were characterized by UV-Vis spectrometer. The optical responses of these samples are displayed in Figure 6. The compact layer was used as a base measurement. The results show that samples with nanofibers have a higher absorbance in UV and VIS regions.

This is the reason for the interaction of light with a higher surface area of nanofibers. Among samples with nanofibers, the absorption coefficient of Mg-doped TiO₂ nanofibers is less than that of undoped TiO₂ nanofibers from 200 to 1100 nm. This absorption capability is reported in the literature (Manju & Jawhar, 2018). It is a conclusion of Mg doping that shifts the absorption edge from visible to UV region. It can be stated that the substitution of Mg in Ti sites and the formation of Mg-Ti mixed oxides can enlarge the band gap. Therefore, Mg doping will enhance the absorption of light by the perovskite layer with the improved J_{sc} when the incident light passes through the ETM layer. Upon adding 0.1% and 0.5% of Mg doping, the light absorption before the 320 nm region showed significant enhancement due to better crystallinity. However, the light absorption of 0.5% MgCl₂ doped films deteriorated, which is attributed to the crystal size.

Photoexcited electron-hole pair recombination rate in semiconductor materials can be effectively studied using photoluminescence (PL) technology. The PL spectrum is a result of the irradiative recombination of photoexcited electron and hole, thus lower PL intensity indicates a lower electron-hole recombination rate. Figure 3.17b indicates that the intensity of Mg-doped TiO₂ is lower than those of pure TiO₂. This behavior implies that for the Mg-doped sample, the electron-hole recombination rate is much lower and separation efficiency is much higher. Conversely, however, the suppression of electron hole recombination is critical for the energy-level alignment at the interface of TiO₂ and perovskite layers. When the CBM of the TiO₂ is lower than that of the perovskite (cliff structure), the interface recombination becomes dominant, and the V_{oc} declines. When the CBM of the TiO₂ is higher than that of the perovskite (spike structure), the interfacial recombination is largely cut off, and an increase in the V_{oc} of the solar cells is achieved (Sabbah, 2022). The wider band gap that occurred in Mg-doped TiO₂ nanofibers is due to an ascending shift of CBM (Rafieh et al., 2019). With the Mg doping, the cliff structure will be minimized that will suppress the electron-hole recombination and increase the efficiency of the perovskite cells.

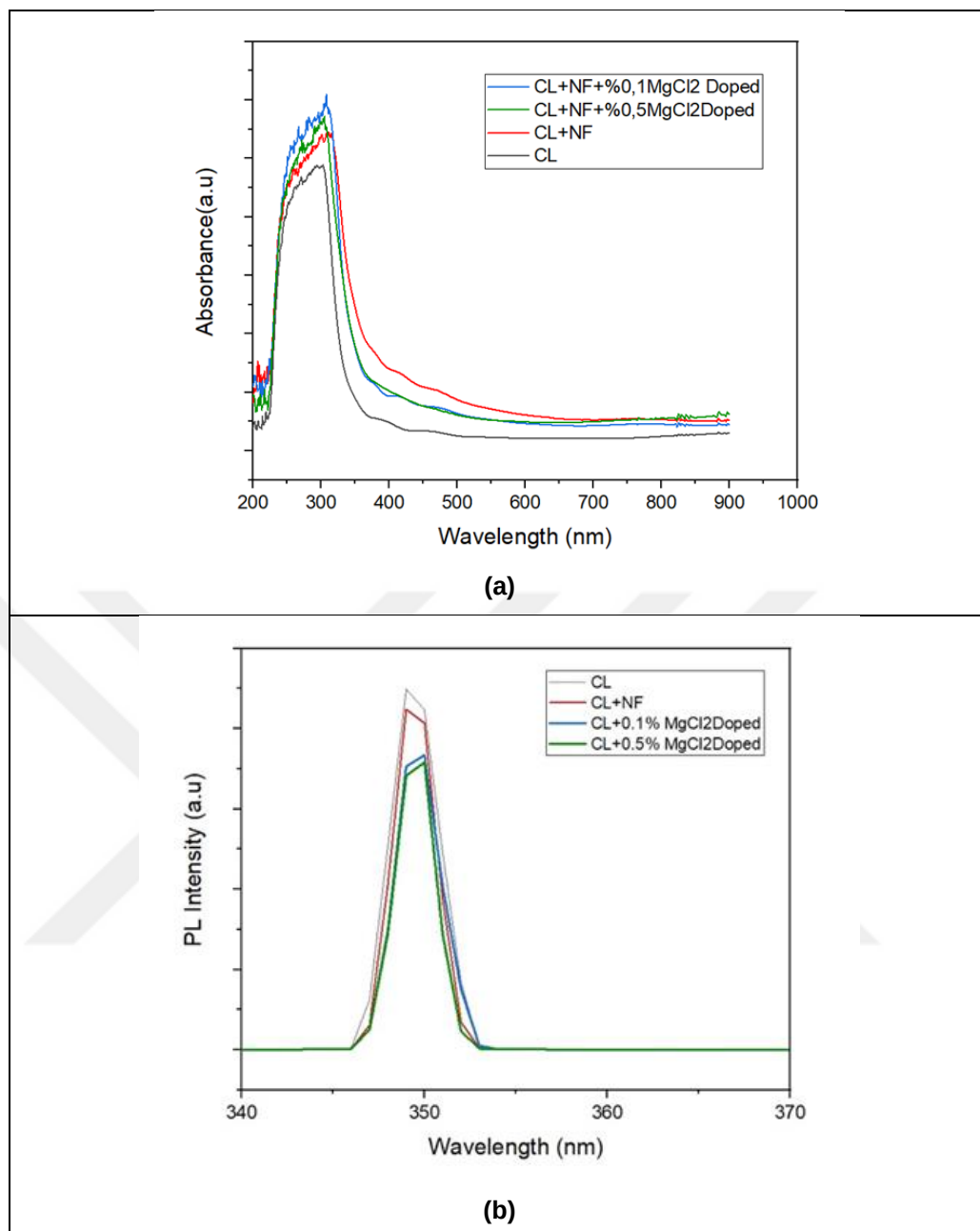


Figure 3.22: (a) Absorbance wavelength spectra (b)PL wavelength spectra.

Bandgaps of the samples calculated from absorbance wavelength spectra Figure 3.18 shows the bandgap graphs for samples.

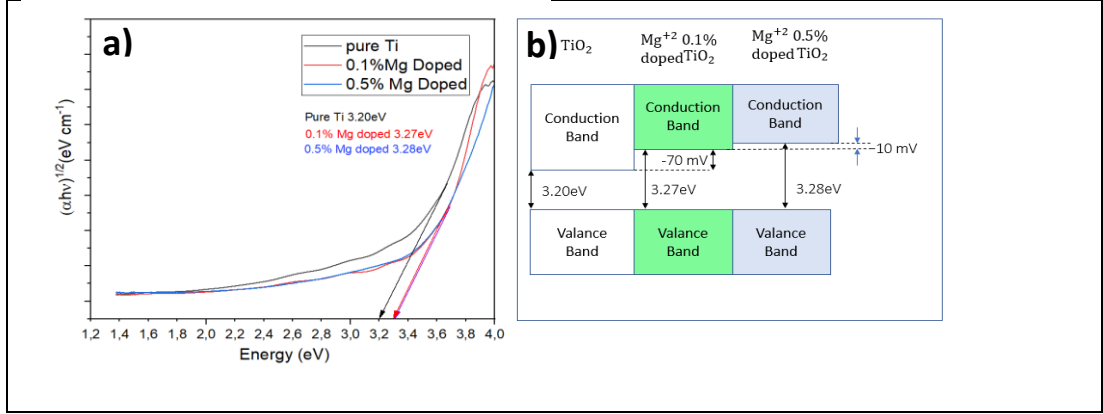


Figure 3.23: (a) The band gap of Pure TiO_2 nanofiber, 0.1% MgCl_2 doped TiO_2 nanofiber and 0.5% MgCl_2 doped TiO_2 **(b)** Schematic representation of the bands.

The optical band gaps were derived from the Tauc plot (reference). The Tauc relation is given as:

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g)$$

where α is the absorption coefficient, A is the absorption constant, E_g is the band gap and $h\nu$ is the photon energy; and h is Planck's constant, and ν is the frequency of light. The measured band gaps of undoped TiO_2 , 0.1% Mg-doped TiO_2 , and 0.5% Mg-doped TiO_2 nanofiber films were presented in Figure 7 (a–d). Mg- TiO_2 showed a band gap value of 3.27 eV consistent with the value reported in the literature (C. Zhang et al., 2011). Pure TiO_2 nanofiber's band gap is 3.20 eV and doping 0.1% Mg, the band gap is shifted to smaller values, from 3.20 eV to 3.27 eV. When the Mg doping quantity increased to 0.5% band gap value increased to 3.28 eV. The changes in absorption and band gap tuning that occur are linked to the creation of trapping states and intermediate sources that can transport electrons. The addition of Mg as a dopant result in the formation of oxygen vacancies and localized trap states, which help to transport electrons. Therefore, the vacancies generated by these dopant atoms are highly effective for adjusting the material's optoelectronic properties. The introduction of Mg as a dopant changes the structure of the material by rearranging the atoms into their respective lattice positions. As a result, the low bandgap energy of the Ti nanofibers is likely due to the larger average crystal size. When Mg is added to TiO_2 nanofiber films, the crystal size decreases, and the band gap shifts. This reduction in the band gap between the conduction and valence bands is anticipated to improve the injection of charges from the perovskite layer to the ETL.

4. ALTERNATIVE METHOD FOR ETL : SEQUENTIAL INFILTRATION SYNTHESIS

An innovative technique called sequential infiltration synthesis (SIS) is used to fabricate hybrid organic–inorganic and inorganic nanostructures by growing inorganic components in polymers during the vapor phase. Over the past ten years, the number of SIS applications has been steadily increasing. To apply SIS to other chemistries and advance beyond thin film polymer templates, however, a fundamental knowledge of precursor-polymer interactions is required (Weisbord et al., 2020).

In the Sequential Infiltration Synthesis method, with the partial pressure increase due to dosing times, the precursor molecules TTIP (Titanium IV isopropoxide) and H₂O will penetrate into the polymer. Because PMMA or PVP polymers have carbonyl groups, precursor molecules can form covalent bonds with the polymer and titania can infiltrate into the polymer. For this, the premise cylinder temperature was set to 80°C and in the first step of the process, N₂ gas was sent to the system at a rate of 100 sccm and waited for 30 minutes. Afterwards, the nitrogen flow was stopped and after a waiting period of 30 s, the chamber valve was closed, waiting for 1 s and the TTIP precursor was sent to the chamber with a pulse of 0.15 s. After waiting for 100 s, the chamber valve was opened, N₂ gas was sent at a rate of 100 sccm and waited for 10 s. Then, nitrogen flow was stopped and waited for 3s and TTIP precursor was sent to the structure and 10 cycles were repeated in this way. Then, the chamber valve was closed and after a waiting time of 1s, the H₂O precursor was sent to the chamber with 0.04s pulses, and after a waiting period of 100 seconds, the chamber valve was opened and nitrogen flow was provided at 100 sccm rate for 100 seconds. This recipe is repeated for 4 different situations:

- i. 4 cycle 135°C,
- ii. 4 cycle 185°C,
- iii. 8 cycle 135°C,
- iv. 8 cycle 185°C.

Figure 4.1 a and b show the SEM images for 132 nm fibers after SIS treatment and after polymer etching, respectively, for 4 cycles at 135°C, while in 1 (c) and (d) 177nm diameter fibers are post SIS treatment and after polymer etching, respectively. SEM pictures are shown.

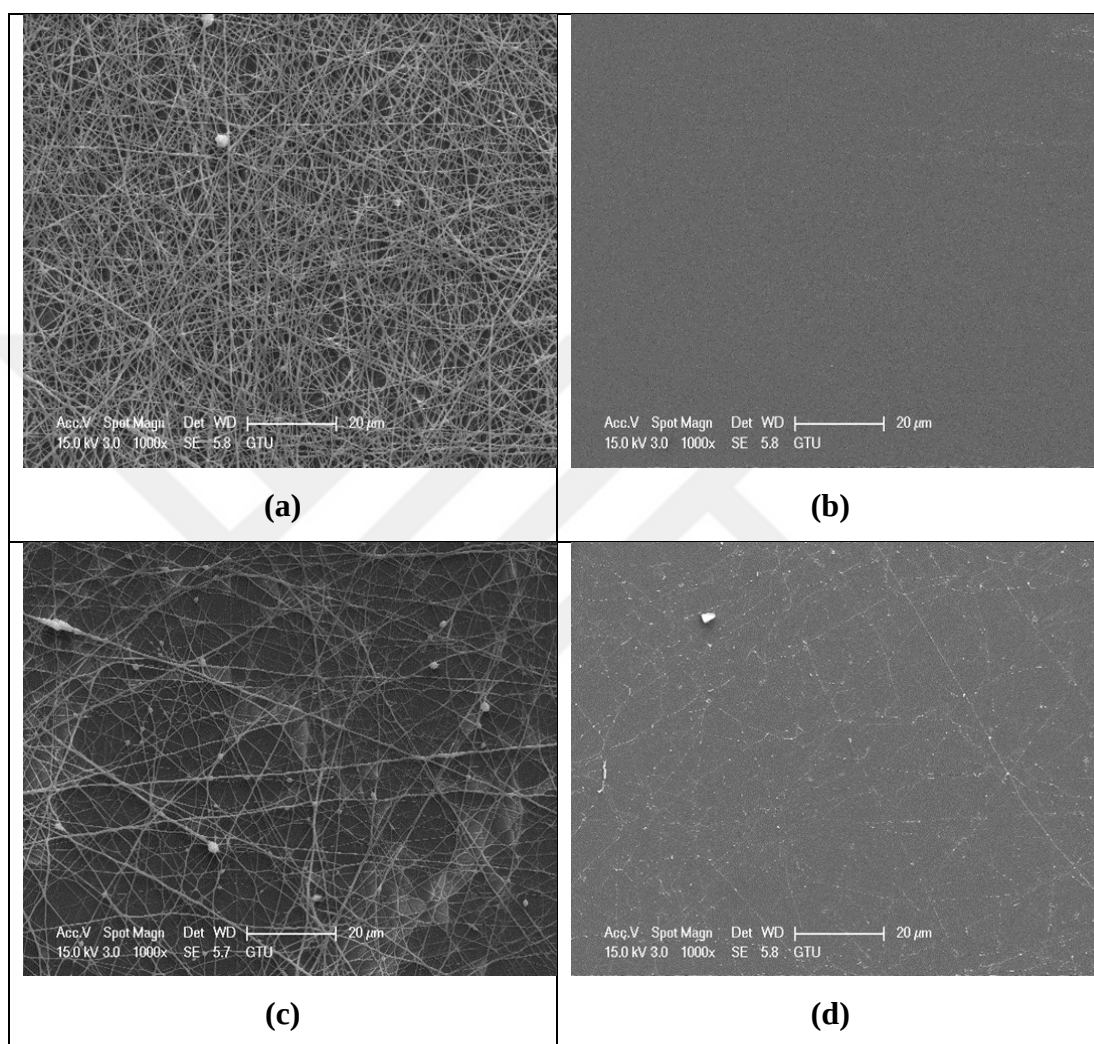


Figure 4.1: 4 cycle 135°C **(a)** 132 nm diameter fiber for SIS **(b)** 132 nm fiber etched **(c)** 177 nm diameter fiber for SIS **(d)** 177 nm diameter fiber etched.

Figure 4.2 a show the EDS graphic and table 4.1 shows elemental analysis for 132 nm fibers at 135°C for 4 cycles. While the EDS graphic and elemental analysis after polymer etching for 177 nm diameter fibers shown in figure 4.3 and table 4.2 respectively.

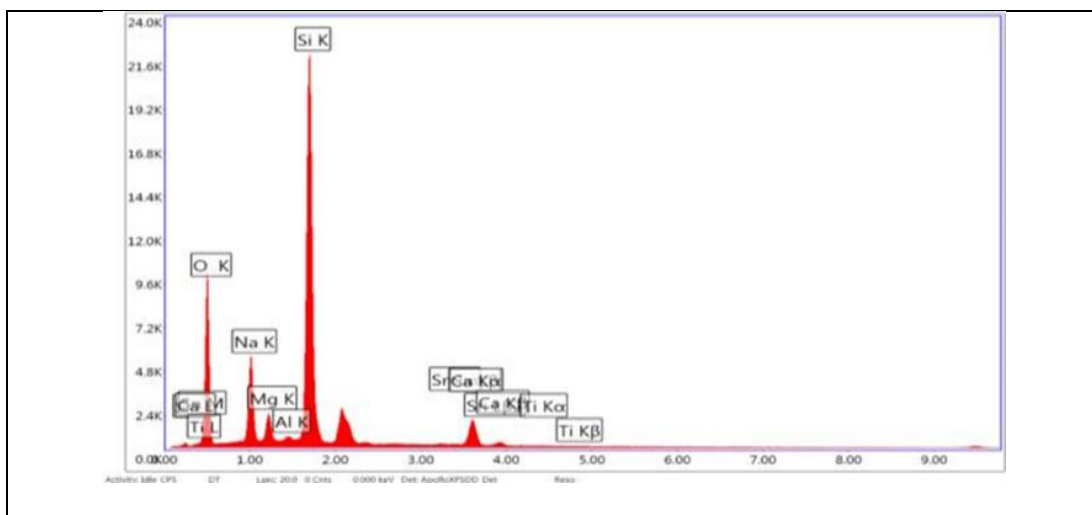


Figure 4.2: 4 cycle 135°C after polymer etched 132 nm fibers EDS graph.

Table 4.1: 132 nm fibers element analyze table.

Element	Weight %	Atomic	Net Int.	Net Int. Error
O K	37.19	50.83	2750.34	0
NaK	12.02	11.43	1653.93	0.01
MgK	3.2	2.88	615.96	0.02
AlK	0.8	0.65	171.4	0.04
SiK	38.91	30.29	8913.8	0
SnL	1.02	0.19	54.94	0.2
CaK	6.74	3.68	725.64	0.02
TiK	0.11	0.05	9.28	0.55

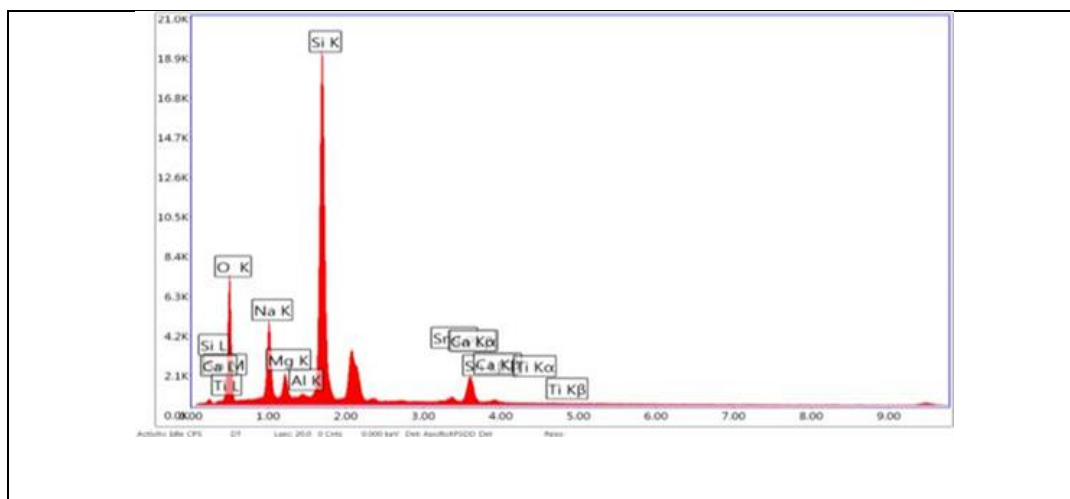


Figure 4.3: 177 nm fibers EDS graph.

Table 4.2: 177 nm fibers element analyze table.

Element	Weight %	Atomic	Net Int.	Net Int. Error
O K	32.44	46.41	1930.31	0.01
NaK	12.42	12.37	1439.85	0.01
MgK	3.15	2.97	508.7	0.02
AlK	0.73	0.62	130.13	0.06
SiK	40.06	32.64	7742.34	0
SnL	3.67	0.71	167.21	0.13
CaK	7.47	4.26	681.28	0.02
TiK	0.06	0.03	4.09	0.57

Figures 4.4 a and b shows the SEM images after SIS treatment and after polymer etching for 132 nm fibers, respectively, for 4 cycles at 185°C, while in 3 (c) and (d), after SIS treatment and polymer etching for 177nm diameter fibers, respectively. SEM pictures are shown.

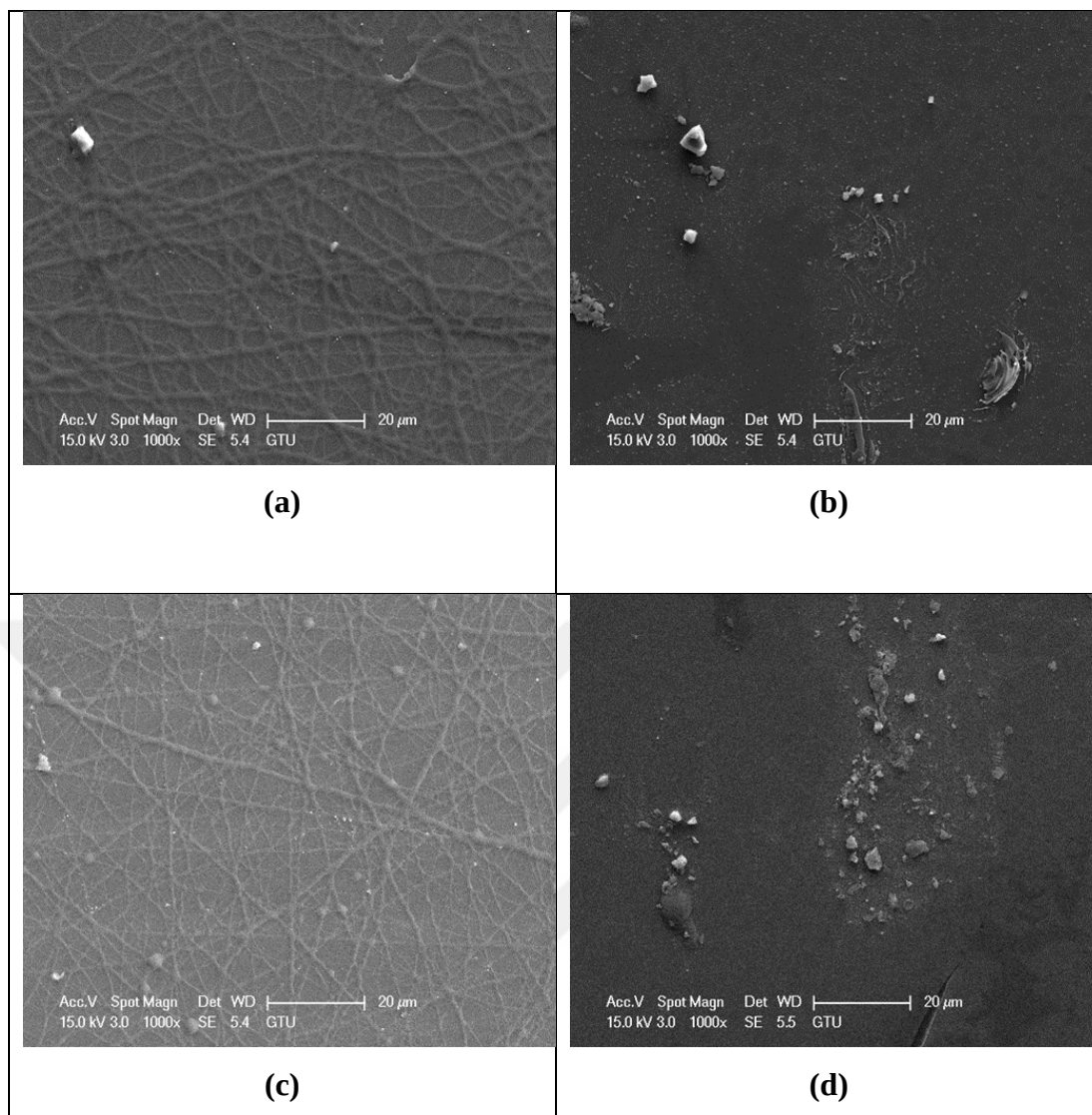


Figure 4.4: 4 cycle 185°C (a) 132 nm diameter fiber for SIS (b) 132 nm fibers etched (c) 177 nm diameter fibers for SIS (d) 177 nm diameter fibers etched.

Figure 4.5 and b show the SEM pictures after SIS treatment and after polymer etching for 8 cycle of 132 nm fibers at 135°C, respectively, while in 4.5 (c) and (d) 8 cycles of 135°C at 177 nm diameter fibers are shown after SIS treatment and SEM pictures are shown after the scraping of the polymer.

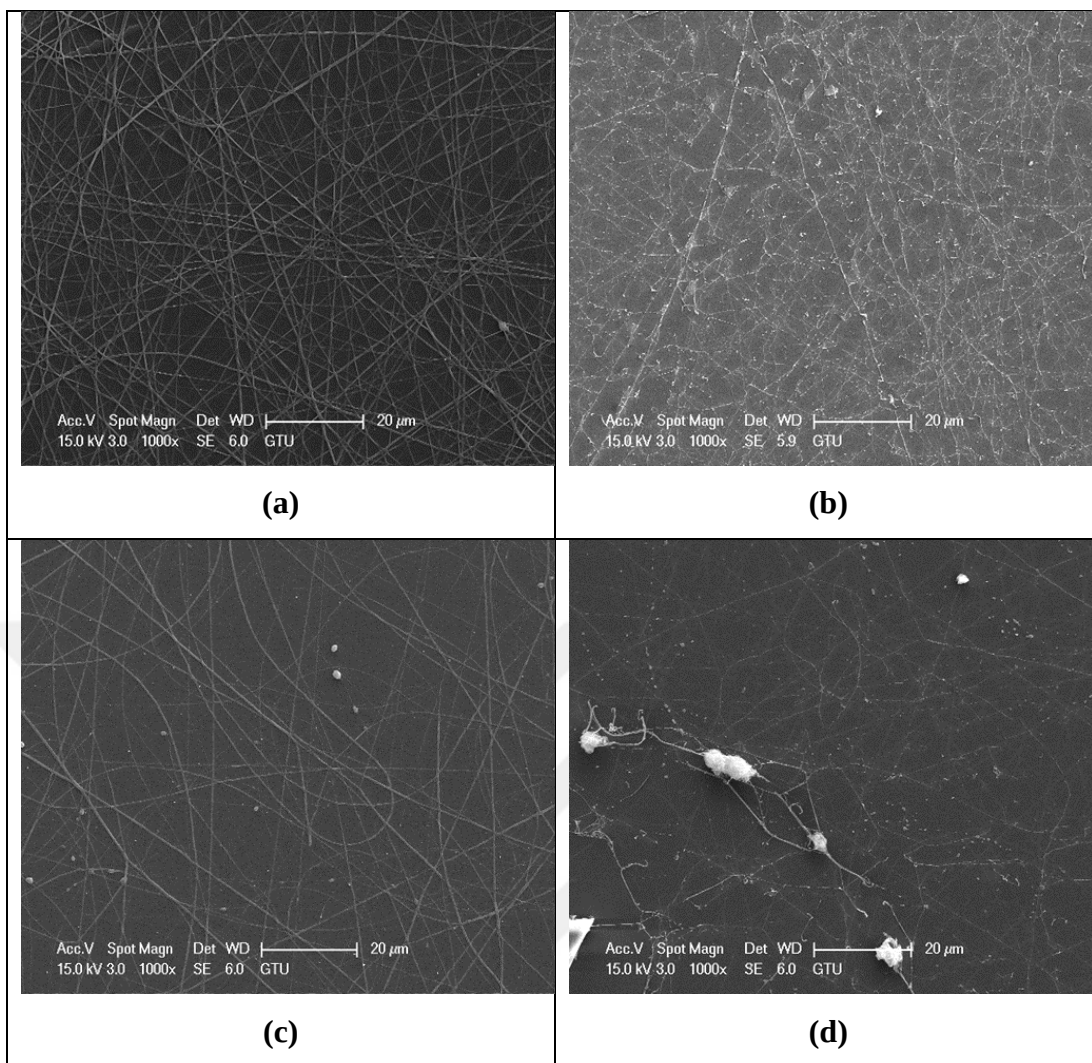


Figure 4.5: 8 cycle at 135°C **(a)** SIS for 132 nm diameter fiber **(b)** 132 nm fiber etched **(c)** SIS for 177 nm diameter fiber **(d)** 177 nm diameter fiber etched.

In Figure 4.6 and Table 4.3, 8 cycles at 135°C for 132 nm fibers EDS graphic and elemental analysis table after polymer etching process. While in Figure 4.7 and Table 4.4, 8 cycle at 135°C for 177 nm fibers EDS graphic and elemental analysis table after polymer etching process.

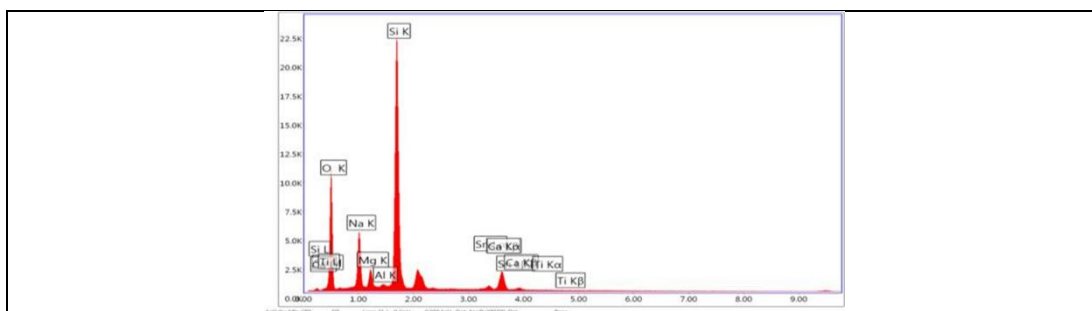


Figure 4.6: 8 cycles 135°C after polymer etched 132 nm fibers EDS graph.

Table 4.3: 8 cycle 135°C after polymer etched 132 nm fibers element analyze table.

Element	Weight %	Atomic	Net Int.	Net Int. Error
O K	36.94	51.33	2795.75	0
NaK	12.09	11.69	1631.28	0.01
MgK	3.08	2.82	585.32	0.02
AlK	0.68	0.56	145.43	0.04
SiK	36.83	29.16	8474.56	0
SnL	3.57	0.67	195.34	0.09
CaK	6.73	3.73	737.33	0.02
TiK	0.09	0.04	7.37	0.56

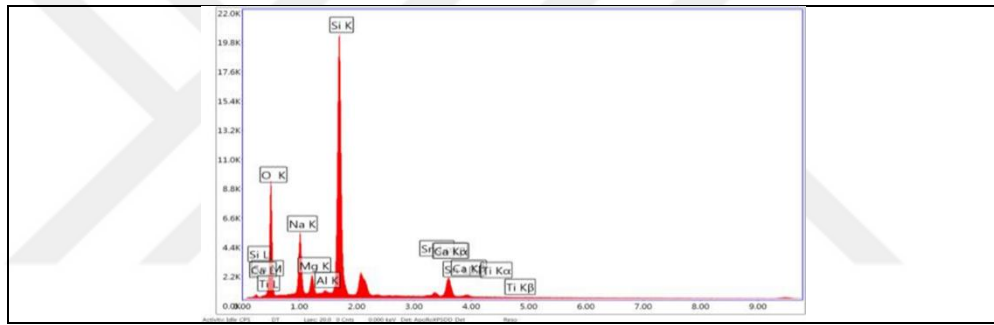


Figure 4.7: 8 cycle 135°C after polymer etched 177 nm fibers EDS graph.

Table 4.4: 8 cycle 135°C after polymer etched 177 nm fibers element analyze table.

Element	Weight %	Atomic	Net Int.	Net Int. Error
O K	35.74	50.02	2533.2	0.01
NaK	12.44	12.12	1601.16	0.01
MgK	3.12	2.87	562.11	0.02
AlK	0.74	0.61	148.07	0.05
SiK	37.47	29.88	8154	0
SnL	3.65	0.69	188.67	0.11
CaK	6.74	3.77	698.5	0.02
TiK	0.1	0.05	8.14	0.57

Figure 4.8 and b show the SEM pictures after SIS treatment and after polymer etching for 8 cycles of 132 nm fibers at 185°C, respectively, while in 7 (c) and (d), after SIS treatment and after polymer etching for 177nm diameter fibers, respectively. SEM pictures are shown.

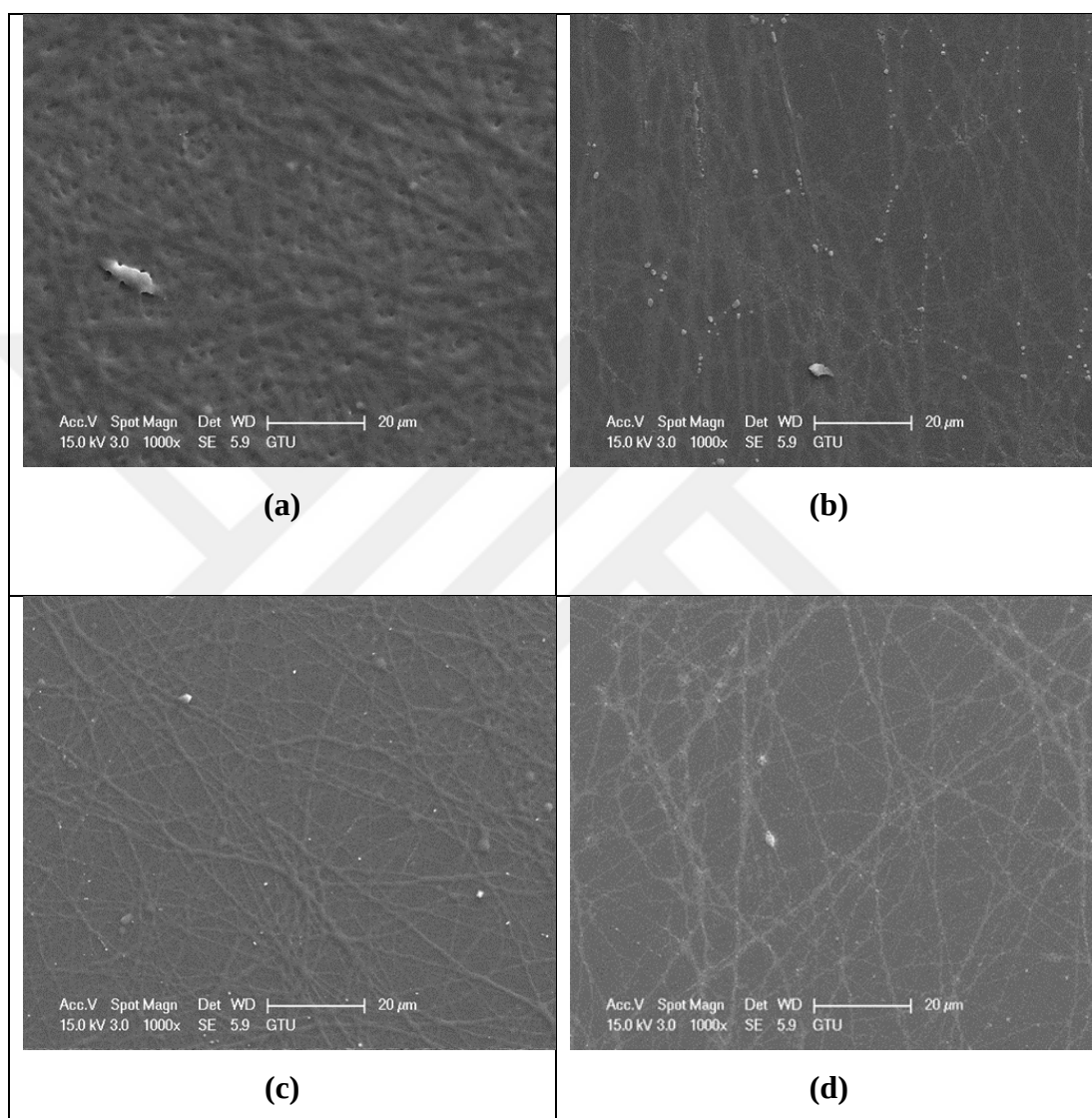


Figure 4.8: 8 cycle at 185°C (a) SIS for 132 nm diameter fiber (b) 132 nm fiber etched (c) SIS for 177 nm diameter fiber (d) 177 nm diameter fiber etched.

Figure 4.9 and Table 4.5 shows the EDS graphic and elemental analysis table after the polymer etching process for 132 nm fibers at 185°C for 8 cycles.

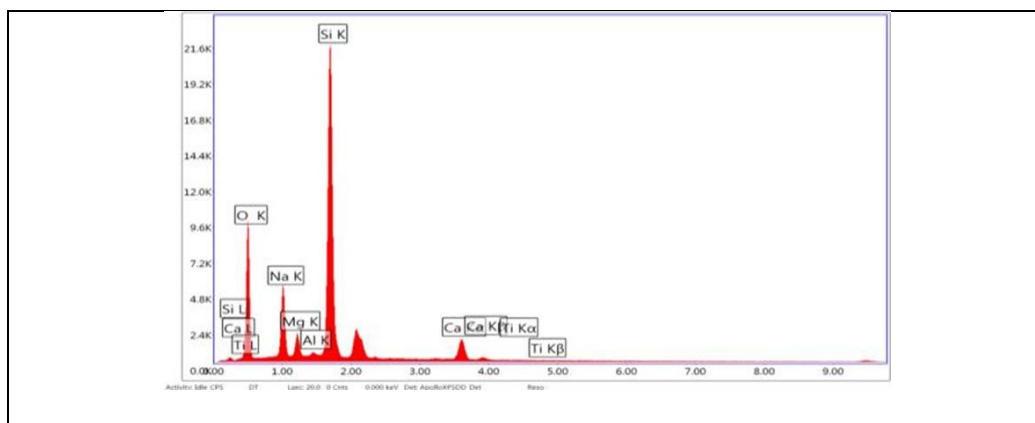


Figure 4.9: 8 cycle 185°C after polymer etched 132 nm fibers EDS graph.

Table 4.5: 8 cycle 185°C after polymer etched 132 nm fibers element analyze table.

Element	Weight %	Atomic	Net Int.	Net Int. Error
O K	37.84	51.29	2720.13	0.01
NaK	12.17	11.48	1658.77	0.01
MgK	3.1	2.76	587.56	0.02
AlK	0.73	0.59	154.12	0.04
SiK	38.64	29.83	8746.78	0
CaK	7.41	4.01	786.42	0.01
TiK	0.11	0.05	9.24	0.56

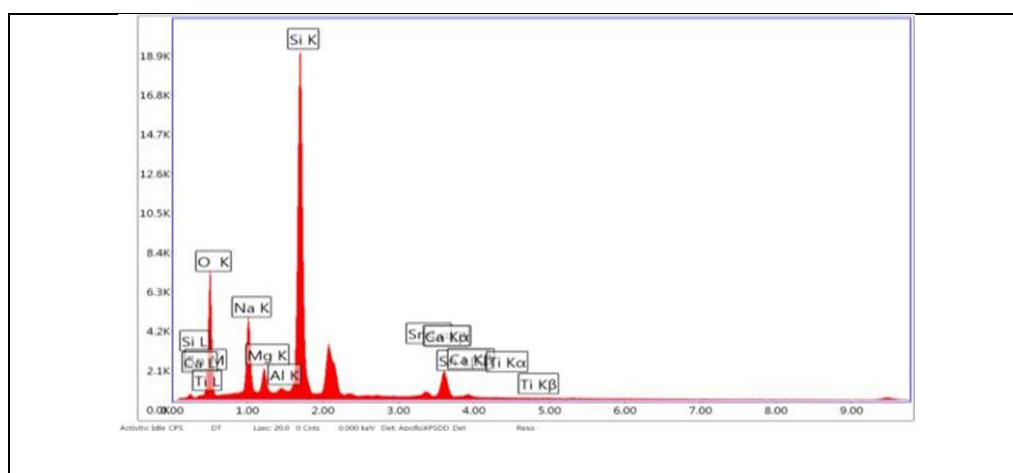


Figure 4.10: 8 cycle 185°C after polymer etched 177 nm fibers EDS graph.

Table 4.6: 8 cycle 185°C after polymer etched 177 nm fibers element analyze table.

Element	Weight %	Atomic	Net Int.	Net Int. Error
O K	32.56	46.57	1927.53	0.01
NaK	12.41	12.35	1423.89	0.01
MgK	3.21	3.02	512.29	0.02
AlK	0.82	0.7	145.74	0.05
SiK	39.71	32.36	7601.79	0
SnL	3.79	0.73	171.67	0.13
CaK	7.39	4.22	669.12	0.02
TiK	0.12	0.06	8.26	0.56

For the SIS process, a new solution was prepared using LiCl salt, which has a high solubility in DMF. For this, 0.012 g of LiCl salt, 0.45 g of PMMA polymer were weighed sequentially in a vial on a precision balance and the solution was completed to 3 g by adding DMF solvent. A solution of 0.4% LiCl, 15% PMMA polymer-salt-DMF by weight was prepared. The solution was stirred for 24 hours on a magnetic stirrer at 1000 rpm until a homogeneous mixture was obtained. For the new experiment to be made, the applied volt value was adjusted to be 10 kV, the flow rate was 0.2 mL/h, and the distance between the needle tip and the collector plate was 15 cm in order to increase the fiber density. An average fiber diameter of 248 nm was obtained using a 20 gauge needle tip. The SEM picture and histogram of the obtained fibers are shown in Figure 4.11.

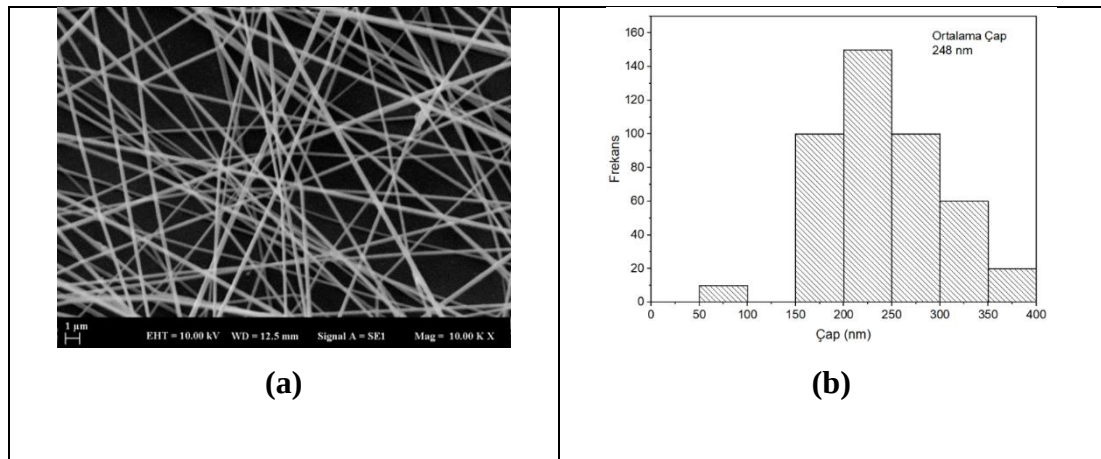


Figure 4.11: 248 nm diameter fiber (a) SEM picture (b) Histogram.

In order to observe the effect of the fiber diameter on the SIS process when the fiber diameter thickens, 0.4% LiCl, 15% PMMA polymer-salt-DMF solution by weight was prepared again, and the solution was mixed for 24 hours on a magnetic stirrer at 1000 rpm until a homogeneous mixture was obtained. However, this time, the applied voltage was increased to 12kV, the flow rate was increased to 0.4ml/h, and the distance between the needle tip collector plate was increased to 17 cm, and fibers with an average diameter of 311 nm were obtained. The SEM picture and histogram of the obtained fibers are shown in figure 4.12 During both electrospinning, the ambient temperature was 26.5°C and the humidity was 53%. The deposition time is 30 min to obtain dense fibers.

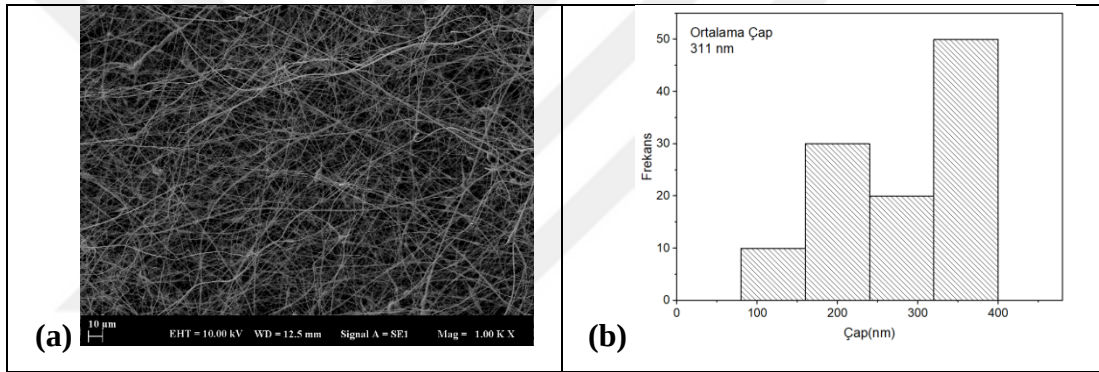


Figure 4.12: 311 nm diameter fiber (a) SEM picture (b) Histogram.

The SIS process was repeated for 8 and 12 cycles at 135°C for different fiber diameters. In Figure 10 and b, SEM images after SIS treatment and after polymer etching are shown for 8 cycles of 248 nm fibers at 135°C, respectively.

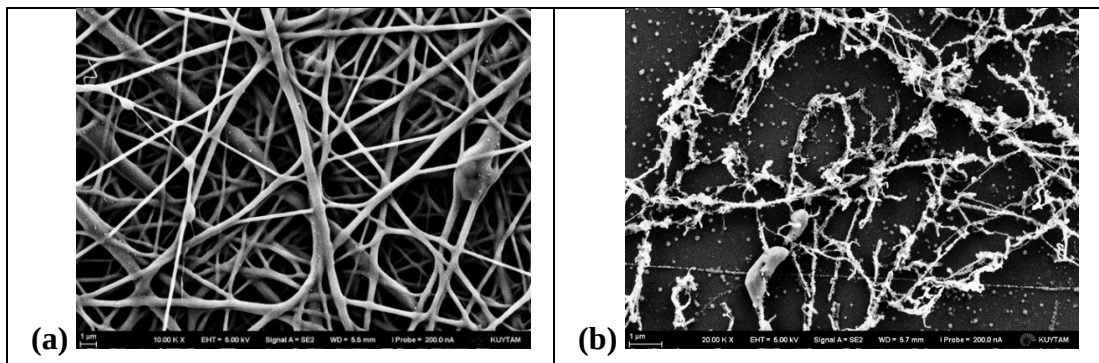


Figure 4.13: 8 cycle 135°C (a) 248 nm diameter fiber for SIS (b) 248 nm fibers etched.

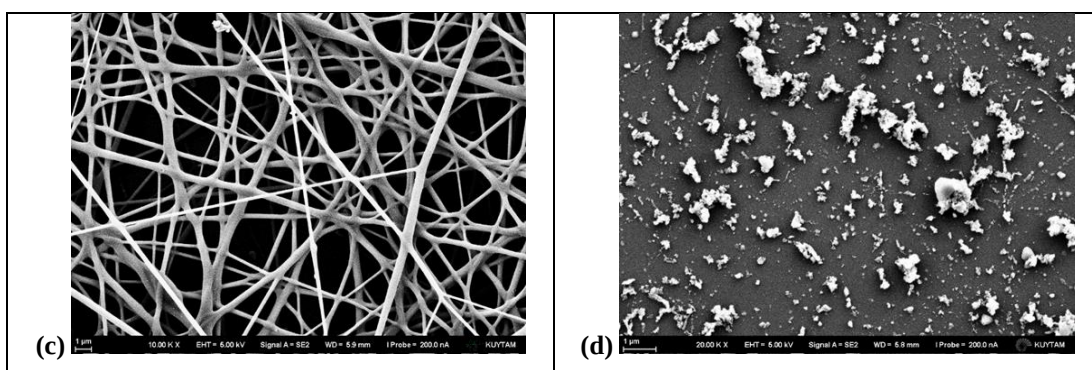


Figure 4.14 Continue: 8 cycle 135°C (c) 311 nm diameter fiber for SIS (d) 311 nm diameter fibers etched.

The EDS graph and table obtained without etching after the SIS process for 8 cycles of 135°C 311 nm fibers are shown in Figure 4.14

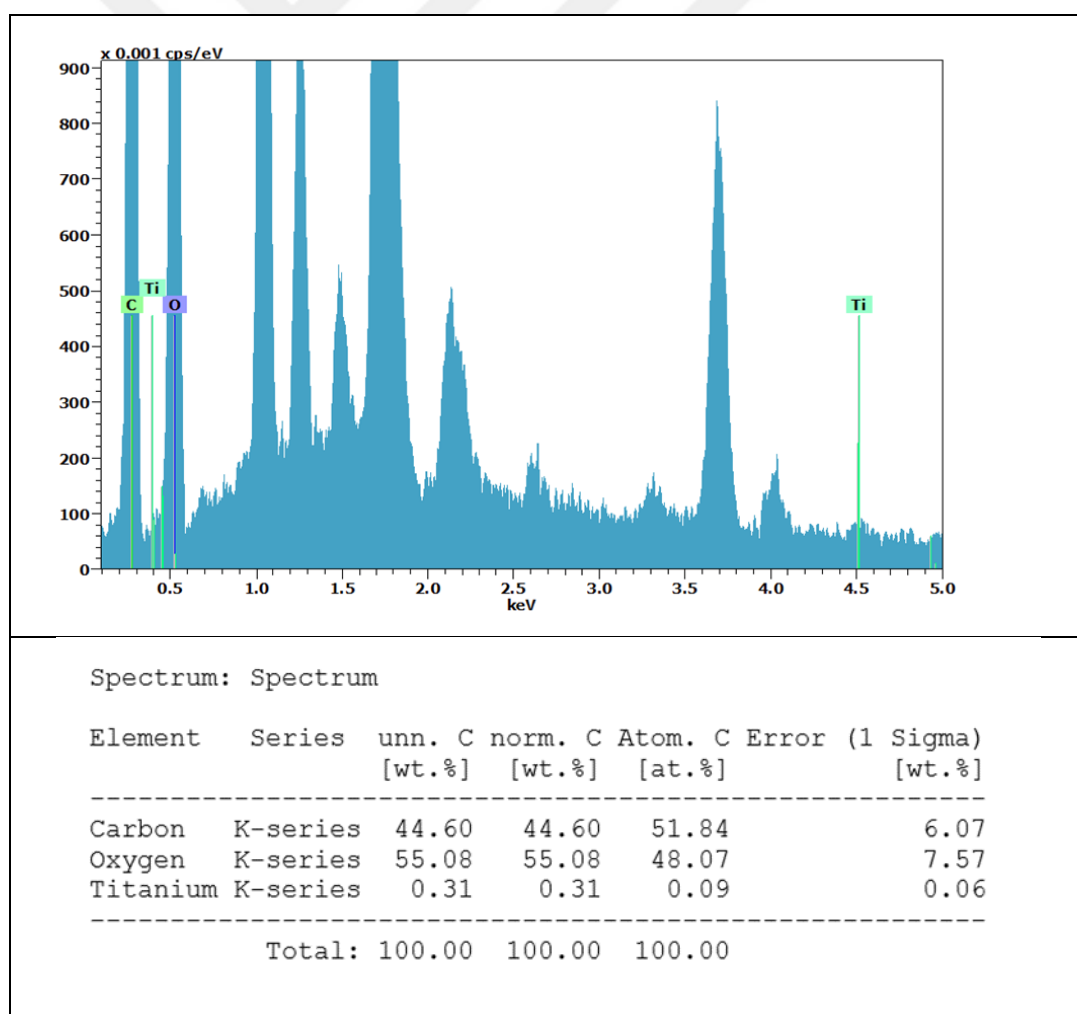


Figure 4.15: 135°C 8 cycle EDS graph and elemental analysis table obtained without etched the polymer for 311 nm fibers.

Figures 4.15 a and b show 12 cycles at 135°C for 248 nm fibers after SIS treatment and after polymer etching, while SEM images after SIS treatment and after polymer etching are shown for 311 nm diameter fibers in 4.15 c and d, respectively.

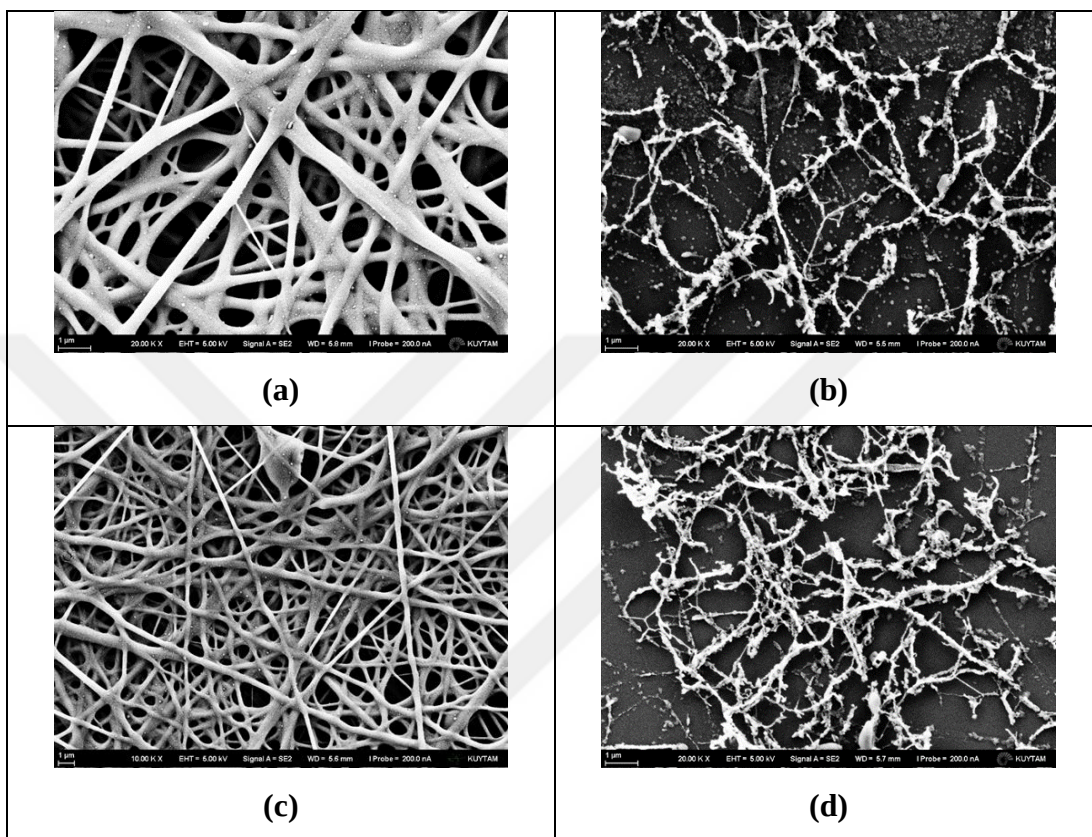


Figure 4.16: 12 cycles at 135°C (a) SIS for 248 nm diameter fiber (b) 248 nm fiber etched (c) SIS for 311 nm diameter fiber (d) 311 nm diameter fiber etched.

Figure 4.16 shows the EDS graph and table obtained after etching after the SIS process for 12 cycles of 248 nm fibers at 135°C.

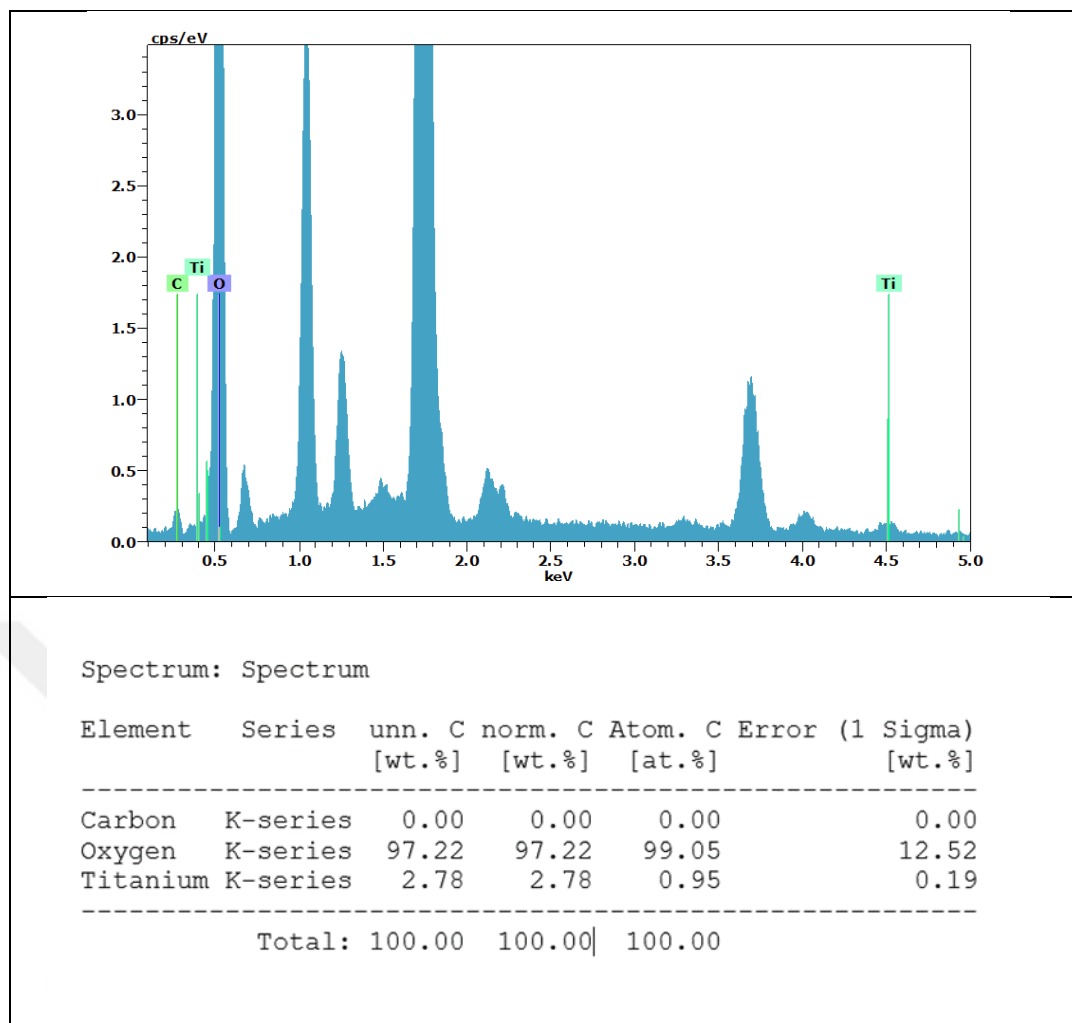


Figure 4.17: 135°C 12 cycle 248 nm fibers for SIS process after etching i EDS graph and table.

The samples obtained as a result of the SIS process, which was carried out as 12 cycles at 135°C, were found suitable. In addition, the most Ti presence from the EDS analysis was detected at 135°C for 12 cycles for 248 nm fibers.

Photoelectrochemical measurements were carried out by recording photocurrent density (J) across a linear voltage sweep from -0.2 V to 1.2 V with a potentiostat/galvanostat instrument upon irradiation with a high-pressure Hg arc lamp connected to a monochromator. In all electrochemical measurements, Platinum (Pt) was used as the counter electrode and Ag/AgCl was used as the reference electrodes and N₂ gas was purged to the cell. Scan rate 10mV/s and electrode system light distance 22 cm. The electrodes were immersed in 0.5M NaOH solution. The intensity of the light was adjusted to be 100 mW/cm². The setup is shown in figure 4.17.

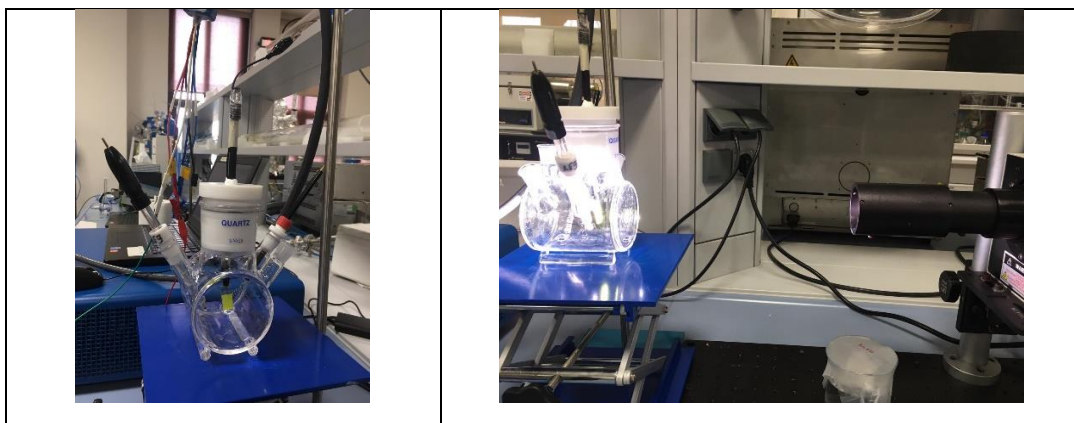


Figure 4.18: Photoelectrochemical system setup.

As shown in figure 4.18 the current density was obtained as $1.9\mu\text{A}/\text{cm}^2$ after SIS treatment and etched process on 248 nm diameter nanofiber and the current density was obtained as $5.83\mu\text{A}/\text{cm}^2$ after SIS treatment without etching process. A higher current density was obtained for the P2 sample, because some Titanium remaining on the surface when etched was lost from the structure with etching. Structures dependent on current density summarized on table 4.7.

Table 4.7 Structures (P1 and P2) dependent on current density.

Sample	Structure	J ($\mu\text{A}/\text{cm}^2$)
P1	FTO Glass/NF/SIS/ETCH	1,90
P2	FTO Glass/NF/SIS	5,83

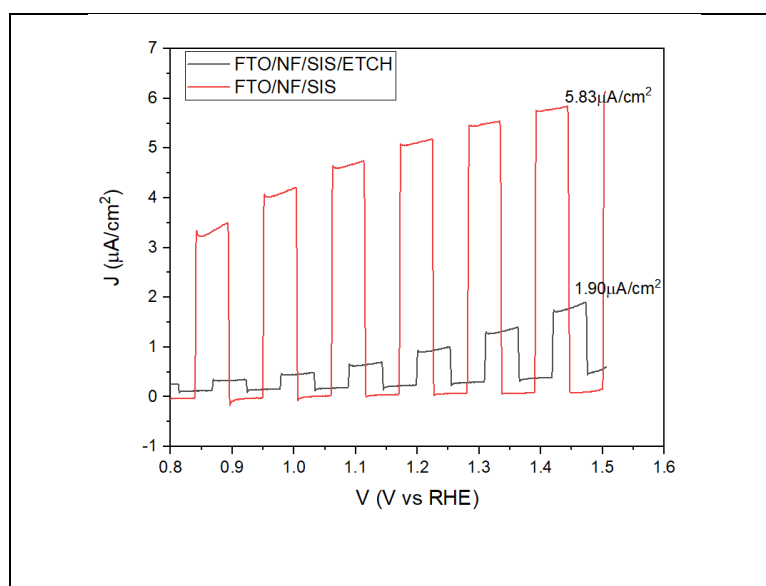


Figure 4.19: Photoelectrochemical measurements current density Voltage graph for FTO/NF/SIS/ETCH and FTO/NF/SIS samples.

5. CONCLUSIONS

In conclusion, electrospinning was used to create TiO₂ nanofibers, which were then annealed at 500°C, 2 hours. From XRD patterns the TiO₂ anatase and rutile phases of the fibers was successfully obtained at temperature 500°C. It is important to obtain the rutile phase because it is compatible with the Perovskite structure, and it is possible to increase the efficiency of the cell with this structure. According to SEM analysis, nanofiber diameters reduced during calcination. TiO₂ nanoparticles lattice structure, shape, and particle size are all impacted by doping. These modifications would lessen surface states and trap locations. EDS confirms the presence of Mg, Ti and O, additionally from the XPS spectrum's shifting Ti2p peak positions also shows the Mg doping. The Mg²⁺ doped TiO₂ 's conduction band shifted negatively by roughly 70 mV in comparison with the TiO₂ sample, it's also decreasing the resistivity of the TiO₂ film. As a result, carrier transport velocity can be increased. The CBM of TiO₂ was positioned higher after adding Mg to the blocking layer, which improved the Voc. Additionally, a small layer of magnesium hydroxide and oxide formed at the HBL's surface, which could further increase Voc by suppressing recombination at the surface of compact TiO₂. Better yet, high Jsc and FF were attained since the CBM's higher lying location would not impede the electron transfer between the perovskite and the two TiO₂ layers. Recombination of photo-excited electrons and holes produces PL emission intensity; hence, a lower PL intensity denotes a lower rate of electron-hole recombination. The rate of electron and hole recombination is decreased by Mg doping. Adding 0.1% and 0.5% of MgCl₂ absorption in the 300–400 nm region showed significant enhancement. The light absorption intensities of films with MgCl₂ were gradually enhanced due to better crystallinity. However, the light absorption of 0.5 MgCl₂ doped films was deteriorated, which is attributed to the crystal size. The TiO₂ mesoporous layer's porosity and particle size are crucial components in the production of the perovskite crystal, which is crucial for charge carrier extraction and light harvesting efficiency. At this study fiber area obtained approximately 70% of the sample. The remaining amount of space is sufficient for perovskite to fill the structure. By developing inorganic components in polymers during the vapor phase, a novel method known as sequential infiltration synthesis (SIS) is employed to construct hybrid organic-inorganic and inorganic nanostructures. SIS process, which was carried out as 12 cycles at 135°C, were found suitable, the most Ti presence from the EDS

analysis was detected at 135°C for 12 cycles for 248 nm fibers. In future studies, different amounts of additives can be tried by calculating cell efficiency.



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BIOGRAPHY

Kübra Erdoğan completed her undergraduate education at Yıldız Technical University, Department of Physics. After completing her master's degree in Materials Science and Engineering at Gebze Technical University, she worked as a physics teacher in various institutions for a while. She enrolled in Gebze Technical University at Physics PhD program in February 2019.



PUBLICATIONS AND PRESENTATIONS FROM THE THESIS

Erdogor, K., Yucel, O., & Oruc, M. E. (2023). Investigation of Structural, Morphological, and Optical Properties of Novel Electrospun Mg-Doped TiO₂ Nanofibers as an Electron Transport Material for Perovskite Solar Cells. *Nanomaterials*, 13(15), 2255.



