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Research article

Synthesis and characterization of silver nanowires with high aspect ratio for transparent coating applications

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A B S T R A C T

In this study, the polyol method was used to synthesize AgNWs to prepare of transparent and conductive coatings. The aim is to synthesize silver nanowires with a one-dimensional morphology and a diameter of less than 100 nm and to formulate a conductive ink containing silver nanowires with high stability under environmental conditions and an easy synthesis method. The experimental design and determination of random samples were performed using Design Expert software. In general, three variables of polyvinyl pyrrolidone (PVP) in the range of 0.06–0.8 g, silver nitrate precursor in the range of 0.04–2.64 g, and the molar ratio of PVP to silver nitrate were selected, and the constants were reaction temperature, reaction time, solvent (EG), and mixing rate. Random samples, proposed by the software, were examined. The synthesized AgNWs were characterized and evaluated using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), scanning electron microscopy (SEM), and Fourier transform infrared analysis. FT-IR and DRS analysis used the Light transmittance coefficient. According to the results of XRD, FE-SEM, and SEM analyses, among the eight samples, S8 had a minimum diameter of 77.3 nm and an average length of 750 nm, and it was selected for further research. Then, the production of conductive ink was put on the agenda, eight conductive inks were made, and the optimal sample (S8) was identified at 3.75% by weight and the optimal molar ratio for ethanol and ethylene glycol solvents. The optimal ink was characterized and evaluated using visible-ultraviolet (UV-Vis), simultaneous thermal (TGA-DTA), and FE-SEM spectroscopic analyses. Conductive ink was then applied to the glass substrate. In addition, the EMI shielding efficiency in terms of dB using the surface electrical resistance of the conductive ink applied to the S5 sample was found to be 75.17 dB in the best case. Finally, the electrical resistance, transparency, and EMI shielding efficiency of the S8 sample were obtained as 2.8 Ω, 77% and 44.35 dB.

KEYWORDS

Silver nanowires
Polyol synthesis
One-dimensional nanomaterials
Transparent and conductive coatings
Electromagnetic interference shielding

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1. Introduction

One-dimensional nanostructures such as nanowires, nanorods, and nanotubes are crucial in creating nanoscale devices. [1]. As particles transition from the micro to nanoscale, there are significant alterations in their physical and chemical characteristics, driven by the increased surface area and quantum effects [2]. One-dimensional nanostructures like nanowires, nanorods, and nanotubes have been the research focus as potential materials for producing see-through electrodes. Typically, nanowires are structures with two dimensions ranging from 1 to 100 nm and one dimension on a larger scale. Because of this specific arrangement, they display distinct electrical, thermal, optical, and magnetic characteristics [3, 4]. Nanowires, alternatively, are wire formations with dimensions within the nanometer scale (1–100 nm).

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Because of the unique quantum mechanical characteristics they possess at this size, they are also referred to as quantum wires [5]. Silver metal possesses a broad range of properties across different wavelengths, which can be adjusted, enhanced, or created by regulating the particle shape at the nanoscale. With the highest thermal and electrical conductivity among metals, silver stands out as a viable option for electrical connections and flexible circuits. In this context, silver nanowires show great potential as conductive and see-through one-dimensional formations for producing thin films similar to indium tin oxide (ITO), a widely used material for this application [3–5].

Recently, various techniques such as chemical methods, polyol methods, and hydrothermal methods have been used to synthesize AgNWs. The polyol process, in particular, has emerged as a widely used method for producing AgNWs with consistent morphology. Despite its ability to create AgNWs with 30–50 nm diameters and an aspect ratio of about 1000, the polyol reduction process still presents certain limitations [6]. For example, during the synthesis process, various factors such as mixing rate, salt concentration, temperature, and reaction time greatly affect the shape of AgNWs, and therefore the experimental variables must be carefully controlled and optimized [4, 7]. Also, the advantages and disadvantages of using the polyol method for the synthesis of silver nanowires are listed in Table 1.

Typically, Sun et al.'s [8, 9] development of the polyol synthesis method for AgNWs represented one of the initial successful approaches for the large-scale production of metal nanowires. This method and its variations have since been extensively employed for the mass production of AgNWs used in transparent conductive (TC) layers. The process entails reducing silver ions with hot ethylene glycol (EG) in the presence of polyvinyl pyrrolidone (PVP), a polymeric capping agent. During the production of silver nanowires, ethylene glycol (EG) serves as the polyol, while polyvinyl pyrrolidone (PVP) acts as the capping agent and silver nitrate ($AgNO_3$) functions as the salt precursor. The method involves chemically reducing silver ions in the presence of a polymer coating agent. The addition of a small amount of appropriate salt can promote the formation of silver nuclei in the desired shape. Ethylene glycol (EG) is transformed into glycol aldehyde (GA), which acts as an agent for reducing silver ions [4].

Table 1. Advantages and disadvantages of using the polyol process to create silver nanowires.

Advantages	Disadvantages	Ref.
Ambient atmosphere	Relatively long reaction time	[1]
Simple process and no need for complex equipment	Production of nanoparticles as by-products	[5]
Easy purification and high yields	Extreme sensitivity to the concentration of substances added	[7]
Low cost	Relatively high temperature	[10]
Ability to adjust reaction conditions and achieve desired morphology	-	[11]
Commercialization	-	[12]

The growth rate and shape of silver nanowires can be influenced by the reaction temperature. Elevated temperatures generally lead to increased growth rates, but they may also cause irregular shapes. Numerous studies have demonstrated the significant impact of temperature on AgNWs due to the temperature-dependent oxidation of ethylene glycol, which serves as the reducing agent and converts to glycolaldehyde. Lower temperatures lack the necessary energy for the anisotropic growth of silver nanowires. Conversely, conducting the synthesis at 170 °C yields silver nanowires toward the end of the reaction. Mao et al. [13] noted that higher reaction temperatures result in a decrease in the diameter of AgNWs, while the highest aspect ratio is achieved at 170 °C.

The size and effectiveness of silver nanowires can be notably influenced by the levels of $AgNO_3$ and PVP. Also, the dimensions and structure of silver nano-forms have a substantial impact on key experimental factors including the concentrations of $AgNO_3$, PVP, and $CuCl_2$ salt. Studies have indicated that a low PVP concentration (50 mM), moderate $CuCl_2$ concentration (77 mM), and a heating time of three minutes are advantageous for producing silver nanorods and nanowires [4, 14–16].

In a study conducted by Wei et al. [17], they successfully produced high-purity silver nanowires (AgNWs) at varying reaction durations. The formation process of AgNWs was characterized using UV-vis absorption wavelengths at different time intervals. Generally, the duration of the reaction can impact the dimensions and production of nanowires - longer durations result in larger sizes and higher yields but may lead to impurity formation. Additionally, in a separate investigation on the consistent creation of silver nanowires, Sun et al. [8], demonstrated that nanowire growth escalates with prolonged reaction periods.

Through the manipulation of key factors in the polyol synthesis process, silver nanowires are rendered kinetically stable, resulting in their formation as the end product of the reaction. Proper stirring and thorough mixing of the solution ensures uniform length and diameter of the silver nanowires, minimizing the potential for silver atom accumulation and the formation of multiple particles. The mixing speed during the polyol reaction directly impacts the morphology and dimensional characteristics of the resulting silver nanowires. Moreover, when ethylene glycol is heated, it generates glycol aldehyde, which then transforms silver ions into silver atoms. As the nuclei grow, the energy required to alter their morphology exceeds the available thermal energy, leading to the nuclei getting stuck in a specific morphology. Generally, the use of nucleating agents and the regulation of their optimal conditions leads to spontaneous propagation, enabling twin growth to enhance the coverage of the lowest energy level of the (111) direction [18, 19].

Multiple factors influence the characteristics and shape of the produced AgNWs. Initially, the gradual introduction of silver nitrate solution is crucial to prevent excessively rapid development of oversaturated silver. Additionally, the reaction solution should produce Multiply Twinned Particles (MTP) in the shape of decahedrons with (111) orientations. The creation of these particles is directed by minimizing the surplus free energy on the surface. Once the MTPs are formed, their twin orientations create elevated local surface energy, attracting Ag atoms and facilitating the unidirectional growth of MTPs [5]. The concentration of PVP and silver nitrate is crucial because the PVP protective agent attaches to and shields the (100) direction, while the introduction of Ag promotes growth in the (111) direction, aiding in the

expansion of the length in the (111) direction [4, 7, 20]. Therefore, the quantities of PVP concentration and silver nitrate are also vital.

Another factor that affects the average diameter of silver nanowires is the molar ratio between the polymer (PVP) and the precursor salt ($AgNO_3$). The study demonstrated that as the molar ratio of PVP/$AgNO_3$ decreased from 9 to 3, the product composition changed from a rod to a nanowire. Conversely, increasing the molar ratio led to undesired formations in the product [21]. Moreover, a decreased proportion of PVP to $AgNO_3$ leads to insufficient coverage for both the rapidly expanding end surfaces and the side surfaces of each nanowire. Also, the inadequate PVP coating on the lateral surfaces fails to effectively protect these surfaces, resulting in an increase in the diameter of the nanowires due to lateral growth, as well as an increase in their length on the opposite side.

Several variables can influence the enhancement of AgNW performance and the regulation of AgNWs' shape. These variables include temperature, reactant concentration, reaction duration, solution acidity, reducing agent type, stirring rate, nucleating agents, PVP/$AgNO_3$ molar ratio, and PVP molecular weight [2–4, 6, 14]. The AgNWs obtained via heterogeneous nucleation offer greater control and uniformity compared to those obtained through homogeneous nucleation [4]. When heterogeneous nucleating agents such as AgCl suspension are present in the solution, silver atoms undergo a phase transition and nucleation takes place on the surface of these agents, resulting in the formation of quintuplet nuclei. In this study, silver chloride was caused within the reaction environment during the synthesis process.

To coat the substrate, researchers have explored numerous techniques such as spin coating [7], rod coating [3], spray coating [7], vacuum filtration [3], immersion coating [5], and plate coating [3]. Among these, spin coating, employed in this study, stands out as a widely favored solution-based deposition method for creating a consistent thin film on a flat substrate. This approach involves rotating the substrate at high speed (750 rpm), utilizing centrifugal force to evenly distribute the solution across the substrate's surface.

In this study, we produced silver nanowires measuring around 1.75 µm in length and 55 nm in diameter by introducing $CuCl_2$ salt, which boosts the formation of twin silver nuclei necessary for wire growth alongside single silver nuclei. Additionally, we fine-tuned the reaction time and temperature, as well as the concentrations of additives like silver nitrate and PVP. Subsequently, larger silver nanoparticles underwent Ostwald growth, where atom-to-atom dissolution (Ag^+ to Ag^0) and reattachment allowed them to evolve into uniform nanowires up to 5 µm long after initially forming nanorods or nanowires of consistent diameter during the ripening process. In this study, following the creation of silver nanowires using the modified polyol method, the preparation of a conductive ink using AgNWs and the production of the ink is carried out. Subsequently, the conductive ink, which is based on silver nanowires, is applied and layered onto the substrate, typically glass or PET.

2. Experimental

2.1. Materials used in the synthesis of silver nanowires

The reaction system includes silver nitrate as the silver precursor, polyvinyl pyrrolidone (PVP, average molecular weight 25,000) as a stabilizing agent, $CuCl_2$ as an external species to aid in the formation of silver nanowires, and ethylene glycol (EG) as both the solvent and the reducing agent for silver ions. Acetone, deionized water, and ethanol are used as solvents and for washing the silver nanowires during ultrasonic and centrifuge purification. All chemicals were purchased from Merck Chemical Company (Germany), and their purities were as follows: silver nitrate (≥99.0%), PVP (≥99.0%), $CuCl_2$ (≥98.0%), and EG (≥99.5%). Deionized water, acetone (≥99.5%), and ethanol (≥99.5%) were supplied by Sablan Company (Tehran, Iran) and were used without further filtration.

2.2. Silver nanowire synthesis

The first step is to prepare 3 separate solutions that must be prepared before starting the reaction. For this purpose, a solution of 0.18 M PVP in EG as the first solution, a solution of 0.8 mM $CuCl_2$ in EG as the second solution, and a solution of 0.214 M silver nitrate in EG is prepared as the third solution.

At the beginning of the reaction in the main vessel, 30 ml of pure ethylene glycol was heated to 170 °C for one hour, so that its EG was completely decomposed. Then, after stirring the solution for 60 minutes and breaking down ethylene glycol into glycol aldehyde (Eq. 1 [22]), the first solution (PVP) that has been prepared in advance is added to the main reaction vessel. Also, the following equation shows the conversion of EG to GA under a temperature of 170 °C.

$$2HOCH_2CH_2OH + O_2 \xrightarrow{170\ ^\circ C} 2HOCH_2CHO + 2H_2O \quad (1)$$

After 15 minutes of adding the first solution to the main reaction container, 0.8 cc of the second solution ($CuCl_2$) was added to the main reaction container and 30 minutes was given to the reaction until germination conditions were formed. After 30 minutes of the reaction time, the third solution (a solution of 0.214 M silver nitrate in EG) should be added drop by drop to the reaction vessel. During the reaction, the capacity of the Cu^{+2} ion is reduced by ethylene glycol, which absorbs atomic oxygen absorbed from the surface of AgCl nanoparticles. The reaction of this process is as follows [23]:

$$2HOCH_2CHO + CuCl_2 \rightarrow 2CH_2COOH + Cu^+ + 2HCl \quad (2)$$

$$Ag^+ + Cl^- \rightarrow AgCl \quad (3)$$

In the first step of the experimental procedure, copper chloride ($CuCl_2$) was added to the ethylene glycol solution as an external source of chloride ions. These chloride ions (Cl^-) then reacted with silver ions (Ag^+) in the solution to form silver chloride (AgCl), as shown in Eq 3. According to Eq. 3, the polyol synthesis involves the formation of AgCl seeds, which provide electrostatic stability to the reaction mixture. In addition, the primary AgCl seeds formed during the synthesis of copper chloride help reduce the concentration of free Cl- and Ag^+ ions in the solution by forming additional AgCl. Depending on the specific conditions of the reaction, such as temperature, the reaction typically requires between 1.5 and 2.5 hours to fully complete.

Meanwhile, ethylene glycol (EG) reduces silver chloride nanoparticles to metallic silver. During this process, EG is simultaneously oxidized to glycolaldehyde, as demonstrated in the following reaction (Eq. 4) [24]:

$$HOCH_2CH_2OH + 2AgCl \rightarrow HOCH_2CHO + 2Ag + 2HCl \quad (4)$$

Finally, the reaction solution is cooled to room temperature and prepared for washing. The final solution is poured into a separate container and washed three times with acetone, ethanol, and distilled

water, respectively. During this washing, the color of the solution has changed to gray, green, and deep gray respectively, and the top solution must be poured out. Then, the final solution was prepared in 4 falcons and washed three times each with ethanol, acetone, and distilled water through a centrifuge at 4000 rpm for about 4 minutes to remove impurities. Finally, the purified AgNWs were dispersed in ethanol for use in analysis and characterization.

Additionally, Fig. 1 illustrates a diagram depicting the various components used in the production of silver nanowires and the subsequent ink formulation.

2.3. Materials used in ink formulation based on silver nanowires

To create conductive inks using silver nanowires, the listed raw materials were used. Moreover, this formulation can be employed to produce conductive inks from silver nanowires using the aforementioned process, which can then be used to achieve a compatible, transparent, and conductive TC layer. Deionized water, isopropyl alcohol (IPA) as ink solvent, polyvinylpyrrolidone (PVP) as ink stabilizing agent, prepared solution of AgNWs (dispersed in ethanol), aniline as surface activating agent (interaction between AgNWs and substrate) increase, which improves the electrical properties of the conductive film based on AgNWs). All items have been purchased as before.

2.4. Formulation process

First, 0.2 g of silver nanowire powder is dissolved in 20 ml of isopropanol and double distilled water in a ratio of 1:2. Then the resulting solution is stirred for 10 minutes (at this stage, the prepared AgNWs solution can also be used). After that, 0.4 cc of aniline is added to it and dispersed for another 5 minutes. Finally, to stabilize the ink, 0.25 grams of stabilizer is added to it and it is given about 30 minutes to mix the desired solution completely. The important point here is that the formulation process should be done in the dark and away from light, and the reaction should be done at room temperature.

Also, in Fig. 1 (after centrifugation with red heaters), the formulation of conductive inks based on silver nanowires can be seen step by step.

2.5. Coating of silver nanowires

The first step in making a thin layer of silver nanowires is cleaning the substrate. At this stage, the substrate must be cleaned well, otherwise it can cause a short circuit of the prepared thin layer. In general, the presence of contamination on the surface of the address layer has a significant effect on conductivity and charge transfer. At first, glass slides and PET films are cut into 8 cm × 2 cm squares and cleaned in deionized water and ethanol for 3 minutes, respectively. Then the substrate is dried at 70 °C. In the next step, the prepared ink of AgNWs

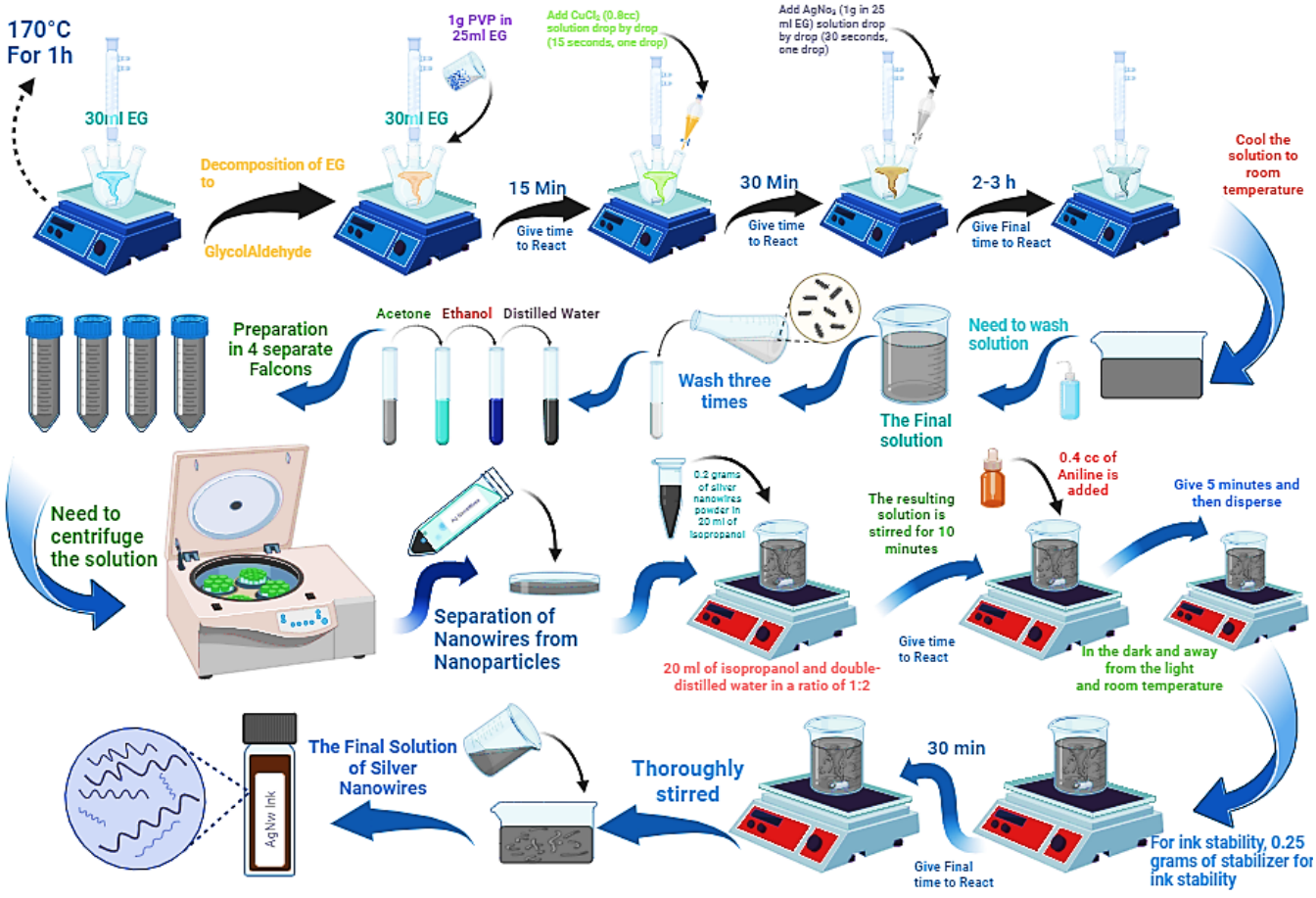

Fig. 1. A schematic of the synthesis of silver nanowires and then the formulation of the ink and finally its washing.

with a concentration of about 0.5 mg/ml, which has been prepared before, is coated on a single layer on the surface of the substrate, which is completely dry and free of any contamination, through plate coating according to the following process. After drying, TC based on AgNWs can be prepared for analysis and relevant characterization. In addition, the significant point of this method is that increasing the number of coating repetitions improves the conductivity, but its transparency decreases. Also, a schematic of the process of coating silver nanowires on glass can be seen in Fig. 2.

Further increasing the baking temperature up to 160 °C resulted in the melting of several thin nanowires. Moreover, it is observed that PVP is not completely removed even after washing the AgNWs with ethanol, which is responsible for the low conductivity of TCE. Finally, by performing several modifications and optimizations in the synthesis and fabrication process, TC based on AgNWs can potentially replace TC based on ITO.

2.6. Characterization

The morphology of silver nanostructures was investigated using the FESEM of the TESCAN Company and the MIRA III device model. Crystallinity was investigated using XRD with Cu-Ka source and manufacturer company PHILIPS and device model PW173 with a voltage of 40 kV and current of 30 mA. The transparency of TCEs was analyzed by UV-vis absorption spectroscopy and DRS (device model: SCINCO DRS S_4100, SCINCO company). Then, to check the morphology and size of the nanowires, they were examined and analyzed by SEM (TESCAN VEGA3), and imaging was carried out at a 20 kV acceleration voltage. Finally, a four-point probe was used to check the electrical resistance for the electrical resistance measurement test.

3. Results and discussion

3.1. Chemical reactions and analysis

The process of creating silver nanowires involves several important chemical processes that affect the result. Silver ions (Ag^+) are reduced to metallic silver (Ag^0) in the presence of ethylene glycol (EG), which acts as both a solvent and a reducing agent. The entire reaction can be described as follows:

$$Ag^+(aq) + EG(l) \rightarrow Ag^0(s) + GA(l) \quad (5)$$

PVP is a stabilizing compound that prevents silver particles from aggregating and promotes the development of nanowires. $CuCl_2$ helps develop silver nanowires by increasing nucleation sites and modifying their shape. Furthermore, the oxidation of ethylene glycol can yield glycolaldehyde and other byproducts, which can influence the reaction kinetics and morphology of silver nanowires. These procedures rely heavily on reaction temperature. Higher temperatures can speed up the reduction of silver ions and the oxidation of ethylene glycol, resulting in various nanowire shapes and growth rates.

In the reaction system, silver ions (Ag^+) and chloride ions (Cl^-) undergo a precipitation reaction to form silver chloride (AgCl). This reaction can be represented as follows:

$$Ag(aq) + Cl(aq) \rightarrow AgCl(s) \quad (6)$$

Silver ions, usually delivered into the process as silver nitrate ($AgNO_3$), easily interact with chloride ions in the solution. The chloride ions could come from an additional chloride source, such as copper chloride ($CuCl_2$) or sodium chloride (NaCl). When silver and chloride ions combine, they precipitate as silver chloride (AgCl), an insoluble white solid under typical circumstances.

This precipitation is critical because AgCl is used as a precursor in the polyol synthesis of silver nanowires. The produced AgCl particles act as nucleation sites, and when exposed to a reducing agent such as ethylene glycol, they can be reduced further to metallic silver (Ag). The creation of AgCl is also an important step in influencing the growth and morphology of the resultant silver nanowires because it affects the concentration of free silver ions in the reaction media. Silver chloride (AgCl) is created by an ionic exchange of positively charged silver ions (Ag^+) and negatively charged chloride ions (Cl^-). This mechanism is initiated by the poor solubility of AgCl in aqueous solutions, which causes fast precipitation.

During the polyol process, the following reaction can be used to convert AgCl into silver nanoparticles:

$$AgCl(s) + EG(l) \rightarrow Ag(s) + HCl(g) + Glycolaldehyde(l) \quad (7)$$

This reaction is important in the production of silver nanowires because it demonstrates how silver chloride (AgCl) nanoparticles can be converted to metallic silver. The resulting metallic silver can then grow into nanowires depending on the reaction parameters, such as temperature, concentration, and the presence of stabilizing compounds like PVP. The equation also underlines ethylene glycol's dual role in the polyol approach as a solvent and reducing agent, both of which are necessary for successful silver nanowire synthesis.

3.2. Investigating the synthesis of silver nanowires

As seen in Fig. 3, this image shows the initial success in producing

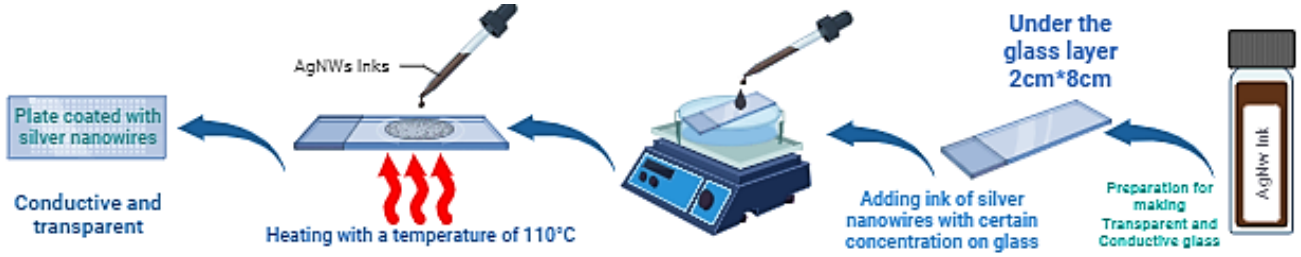

Fig. 2. Summary of the fabrication process of transparent and conductive TC based on silver nanowires.

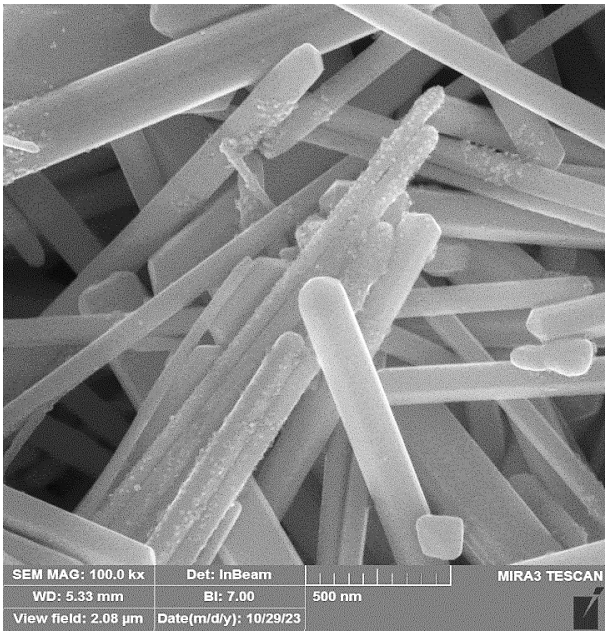

Fig. 3. FE-SEM image of silver nanowires, image of the sample synthesized at 170 °C.

silver nanowires. Of course, to further examine the produced nanowires and obtain their characteristics, SEM and FE-SEM analyses were carried out.

For this purpose, a specific amount of silver nanowire solution dispersed in ethanol was placed on a thoroughly clean aluminum foil, free of any contaminants, and the sample was then photographed and analyzed. The length and diameter of the nanowires in all experiments were measured using SEM and FE-SEM images with the aid of ImageJ software. The measured dimensions of the nanowires were an average diameter of 55 nm and a length of 1.75 µm. As shown in Fig. 3, the high density of silver nanowires, with a significant number of connections and a well-formed crystal structure between them, is evident. This structural arrangement significantly enhances the electrical conductivity of the sample.

Fig. 4 shows how differing response times (2.5 hours and 1.5 hours) affect the microstructures of silver nanowires. After 2.5 hours of reaction, the nanowires become longer and more uniform, with fewer flaws and a well-developed crystal structure. At 1.5 hours, however, the nanowires seem shorter, with more apparent flaws and less homogeneity. Higher PVP/$AgNO_3$ ratios and longer reaction times lead to better crystal formation and uniform nanowire diameters, improving overall product quality and electrical conductivity.

3.3. Effect of temperature

The reaction temperature has a considerable effect on the growth rate and form of silver nanowires. Higher temperatures often result in higher development rates, but they may also produce non-uniform forms. Some investigations have shown that temperature is critical in the synthesis of AgNWs, owing to the temperature-dependent oxidation of ethylene glycol into glycolaldehyde, which serves as the reducing agent. At higher temperatures, this oxidation process intensifies, directly altering the quality and uniformity of the nanowires [25].

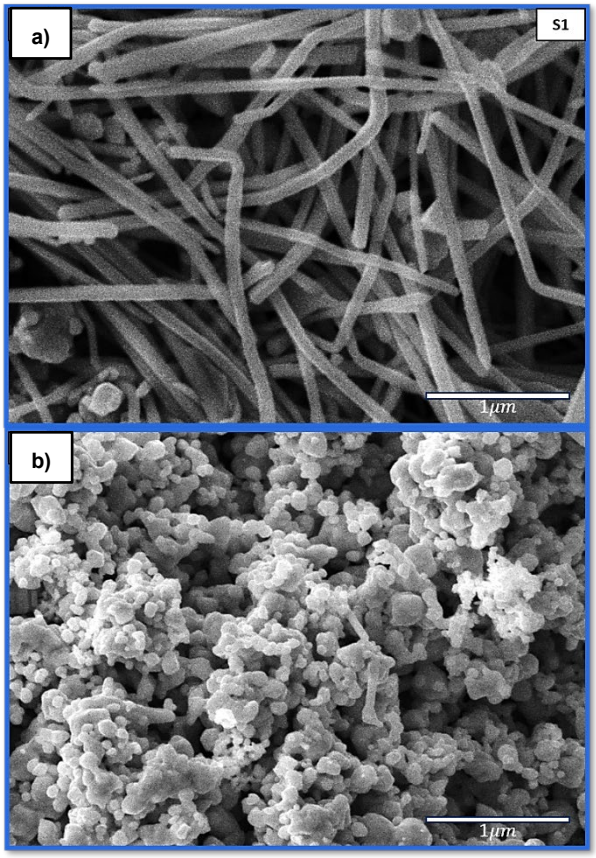

Fig. 4. SEM images of samples with reaction times of a) 2.5 and b) 1.5 hours, respectively, showing the influence of reaction time and PVP/$AgNO_3$ ratio on the microstructures of the silver nanowires.

In the initial stage, most of the synthesis reactions have been done at 160 and the reaction time is about one hour. The length of most AgNWs decreased dramatically when the temperature was higher or lower than 160 °C. For example, in Fig. 5a, we can see that no AgNWs were formed in the experiment conducted when the temperature was set to 100 °C.

When the temperature is below 110 °C, no nanowires are formed. SEM images show that the products obtained at 100 °C are composed of silver nanoparticles with different morphologies and sizes. Some of these nanoparticles can be converted into nanorods/nanowires after preparing the solution (prepared at 100 °C) and then at 160 °C for one hour. Also, Fig. 5b shows the scanning electron microscope of silver nanowires grown at a temperature of 185 °C. These nanowires had an average diameter of 45 nm. The number of these nanowires was significantly increased (about 90%) compared to the sample synthesized at 100 °C.

On the other hand, lower temperatures lead to smaller nanowires, while higher temperatures lead to longer nanowires. This is because lower temperatures limit the diffusion of silver ions and the growth of nanowires, while higher temperatures accelerate the process. Also, temperature affects the aspect ratio. In general, the aspect ratio is the ratio of the length of a nanowire to its diameter. Higher temperatures typically result in nanowires with higher aspect ratios. This is because higher temperatures promote the growth of nanowires along their longitudinal (111) axis instead of their two lateral axes.

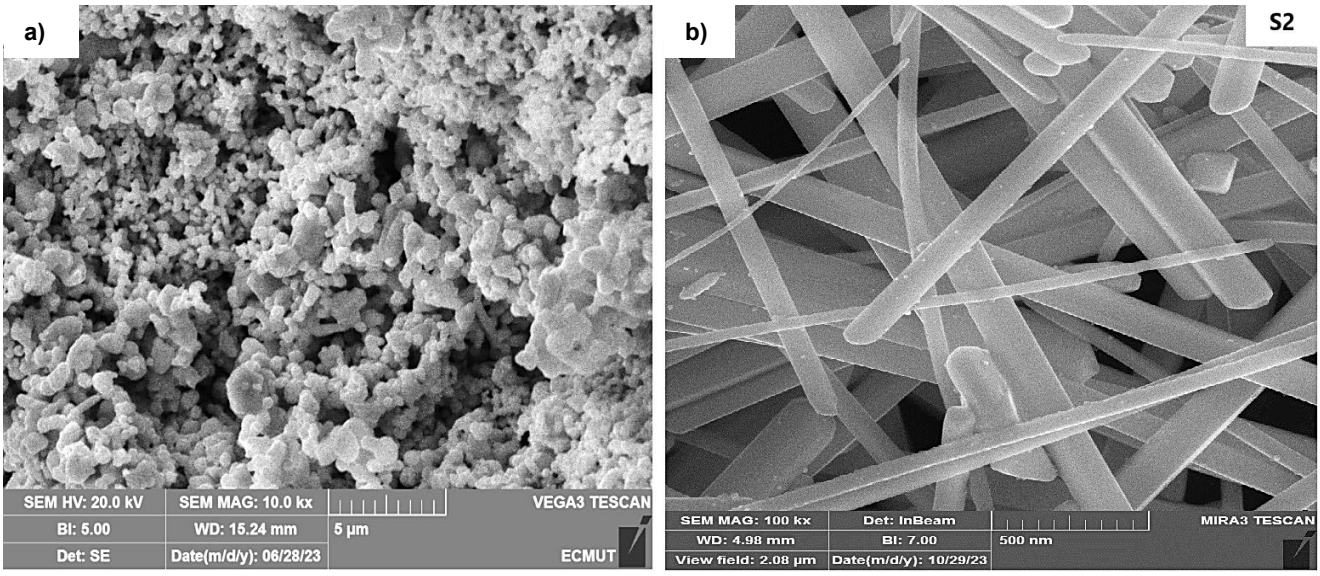

Fig. 5. FE-SEM image of the silver nanowires synthesized at a) 100 °C and b) 170 °C with an aspect ratio of ~1000.

Fig. 5b shows the image of silver nanowires synthesized at the optimized temperature of 170 °C. In general, there is an optimal temperature range for the synthesis of silver nanowires, which is usually between 120 and 180 °C. Temperatures outside this range can lead to lower efficiency due to factors such as incomplete reduction of silver ions or excessive accumulation of nanowires. Finally, it can be concluded that by carefully controlling the reaction temperature, the morphology, size, aspect ratio, and efficiency of nanowires can be

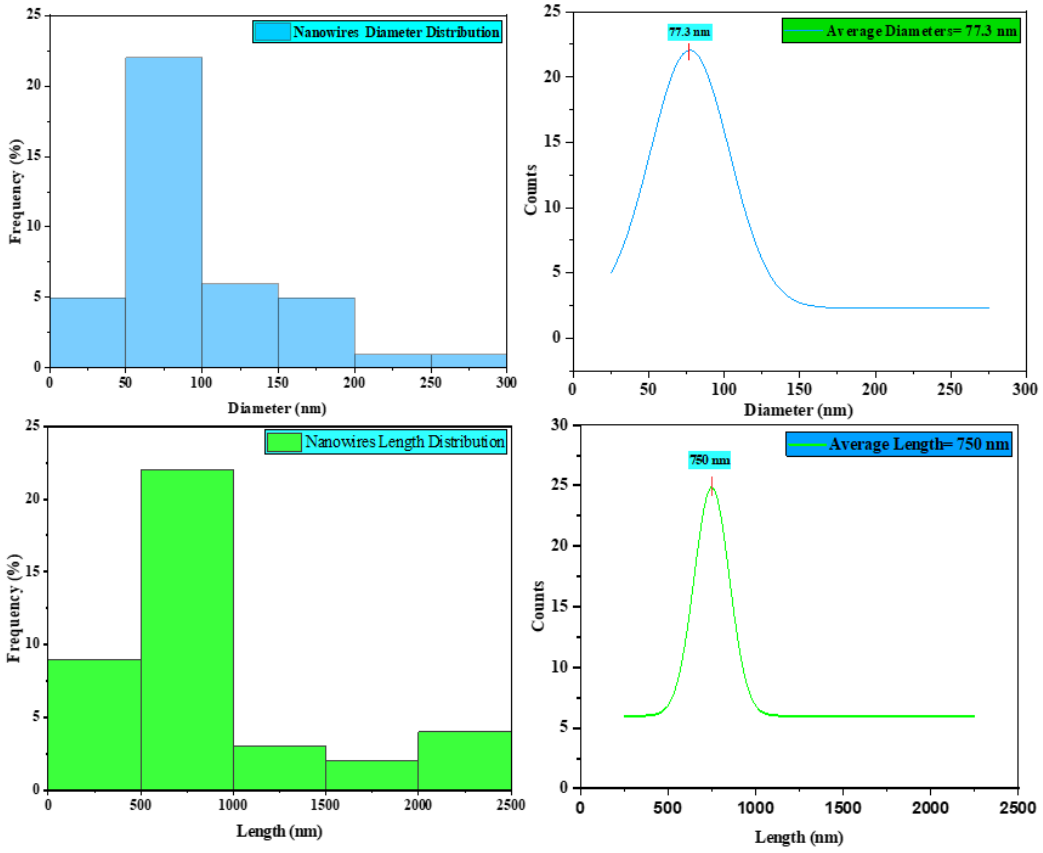

Fig. 6. Size distribution of silver nanowires with a diameter of 77.3 and a length of 750 nm obtained at a temperature of 170 °C.

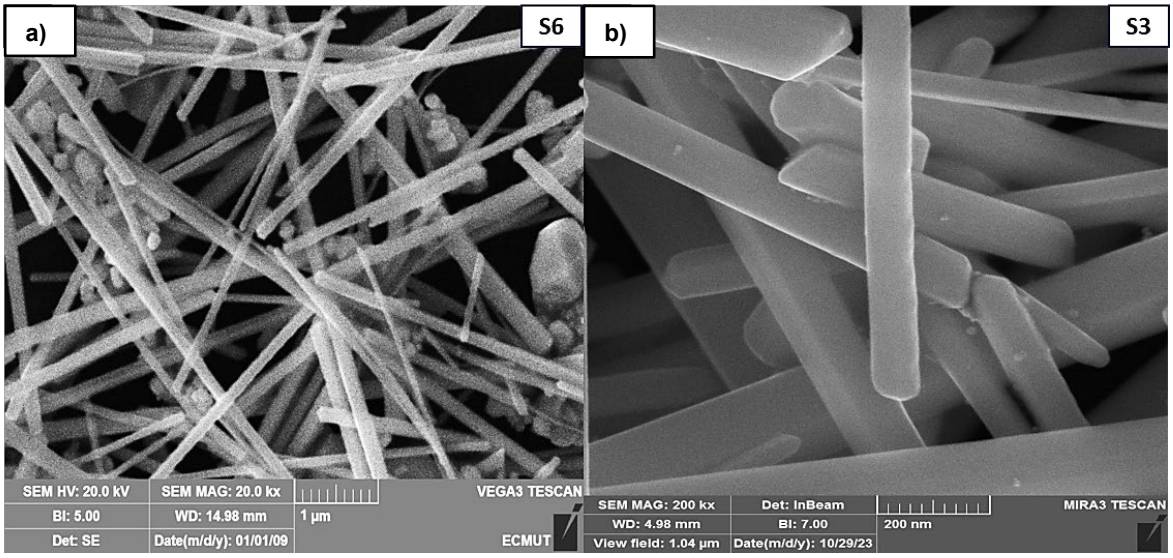

Fig. 7. a) SEM image with 110 mM $CuCl_2$ concentration and b) FE-SEM image of silver nanowires synthesized with a concentration of 48 mM in 10 ml of $AgNO_3$.

optimized and the production of nanowires with desirable properties for various applications can be made possible. Also, the size distribution of nanowires in Fig. 6 shows that they have an average diameter of 77.3 nm and an average length of 750 nm, so the optimized temperature is 170 °C.

3.4. Effect of concentration of reactants

The concentration of $CuCl_2$ and sodium chloride can affect the synthesis of silver nanowires. The presence of cations and anions including Cu(II) and Cl^- in the synthesis process affects the shape of silver. Generally, $CuCl_2$ and NaCl are intermediate agents added to facilitate the growth of silver nanowires. Higher concentrations of $CuCl_2$ can lead to longer nanowires, while lower concentrations can lead to shorter nanowires. It can be seen in the SEM image in Fig. 7a that at an excessively high concentration of $CuCl_2$ (110 mM), in addition to one-dimensional products (nanorods and nanowires), amorphous silver chloride particles also appear.

Increasing the concentration of $AgNO_3$ generally leads to the formation of silver nanowires with a larger diameter and a higher aspect ratio. This is because the higher concentration of Ag^+ ions provides more materials for the growth of nanowires and the excessive concentration of $AgNO_3$ can also increase the formation of spherical nanoparticles and agglomerates due to the nucleation and rapid growth of nanowires. As seen in Fig. 7b, $AgNO_3$ concentration can affect the size and efficiency of silver nanowires. In addition, the shape and size of silver nanostructures strongly affected experimental variables such as PVP and $CuCl_2$ concentration, and AgNWs were synthesized. Researchers have stated that low concentrations of PVP (50 mM), medium concentration of $CuCl_2$ (77 mM), and heating time of one hour and 30 minutes are favorable for the formation of silver nanorods and nanowires.

3.5. Effect of time reaction

In general, the reaction time can affect the size and yield of nanowires, longer times lead to larger sizes and higher yield, but it causes the

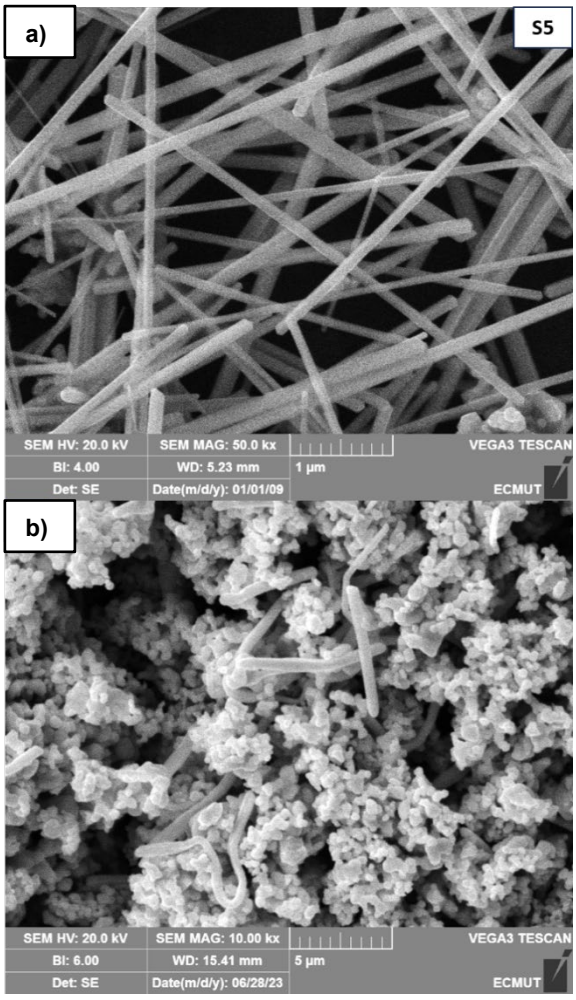

Fig. 8. a) SEM image of sample A (reaction time: 2.5 h, 750 rpm) and b) FE-SEM image of sample B (reaction time: 1.5 h, 1200 rpm)

formation of impurities. In a 2002 study on the uniform synthesis of silver nanowires Sun et al. [8] showed that the growth of nanowires increases with increasing reaction time.

As shown in Fig. 8, nanowire length and diameter increase with reaction time. This is because longer response times allow for more nanowire nucleation and development. Reaction time generally influences three stages: nucleation, growth, and final structure development. Sample A (S5) was prepared with a 2.5-hour reaction period, producing larger and longer nanowires. Sample B was made with a 1.5-hour reaction time, yielding smaller and thinner nanowires. Sample B is mixed at a higher rate of 1500 rpm, which affects nanowire uniformity and alignment. The rate of nucleation is regulated by several parameters, including reactant concentration, temperature, and the presence of stabilizing agents. The silver nanowires' length and thickness increase in proportion to the processing time. Therefore, an ideal reaction time is critical for reaching the necessary nanowire dimensions. The optimal reaction time for sample A (S5) is 2.5 hours, and for sample B it is 1.5 hours. The higher mixing rate of 1500 rpm was applied.

3.6. Effect of mixing rate

Stirring and final mixing of the solution make the length and diameter of silver nanowires uniform and reduce the possibility of accumulation of silver atoms and multiple particles. Fig. 9 shows the scanning electron microscope images of the synthesized silver nanostructures at different mixing rates of the polyol reaction. As can be seen, when the

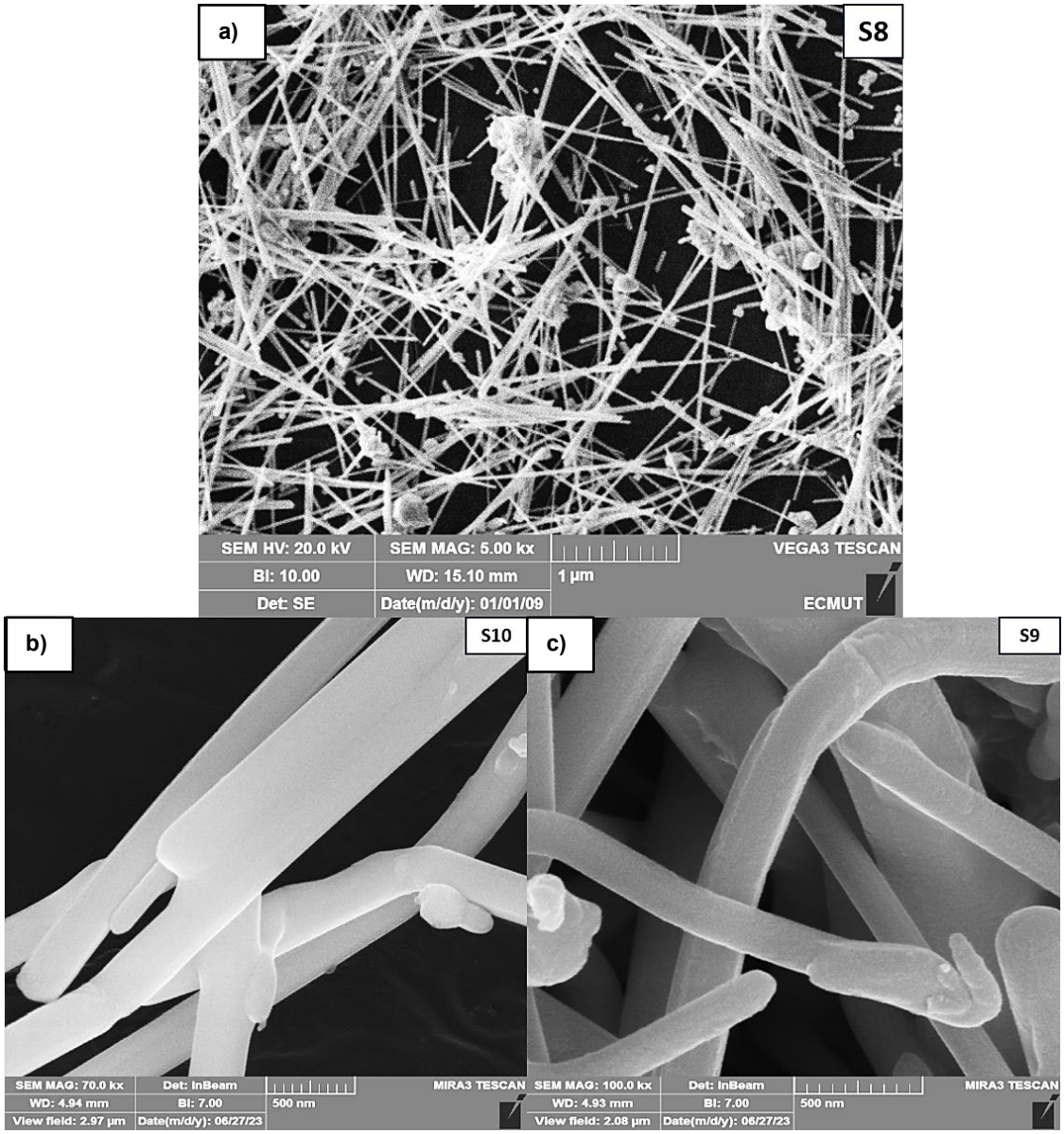

Fig. 9. a) Scanning electron microscope (SEM) image and b & c) field emission scanning electron microscope (FE-SEM) images of silver nanowires synthesized under different mixing rates of polyol reaction at different magnifications: a) 750, b) 1200, and c) 1500 rpm.

reaction was carried out under a stirring rate of 300 rpm, silver nanowires with an average diameter of about 100 nm were synthesized. Such nanowires also had the lowest amount of nanoparticles. As seen in Fig. 9b & c, with the further increase of the solution mixing rate, the final synthesized product does not contain only silver nanowires. Also, by performing the polyol reaction at a high mixing rate (1200 and 1500 rpm), the size and shape of the synthesized nanostructures are different. As can be seen in Fig. 9b, individual silver nanowires do not have the same size and have variable diameters in different parts of their length. The size of one-dimensional nanostructures resulting from a high mixing rate is also shown in Fig. 9c.

The mixing rate also affects the growth rate of silver nanowires. As shown in Fig. 10, the slow mixing rate due to the limited diffusion of reactants can lead to the formation of shorter and thicker nanowires. Conversely, rapid mixing due to enhanced diffusion and uniform growth conditions leads to the formation of longer and thinner nanowires.

3.7. Effect of nuclear factors

The concentration, size distribution, and crystal structure of the salt nuclei used in this research, the effect of AgCl plays a special role. Its function is to promote heterogeneous nucleation and control the growth process. In general, heterogeneous nucleation occurs when silver (Ag^+) ions, instead of forming new nuclei in the solution, sit on the surface of existing AgCl nanoparticles and nucleate. This mechanism leads to the formation of silver nanowires with a uniform size distribution. Fig. 11 shows an FE-SEM image of spherical silver chloride samples, which are essential for the growth of silver nanowires before the reaction. Due to the effect of AgCl suspension on heterogeneous nucleation, the final morphology of nanocrystals can be changed.

3.8. Conductive ink and coating of silver nanowires

After synthesizing silver nanowires and obtaining an optimal sample (S8), it was used to produce ink and coating. AgNWs were deposited on a glass substrate to fabricate transparent conductive electrodes with high transmittance of 77% and very low conduction resistance using spin coating at moderate temperatures. The properties of fabricated TC were optimized by changing the concentration of AgNWs solution.

After the synthesis of silver nanowires, the synthesized AgNW is then dispersed in a solvent to form a stable ink. The solvent and dispersing agents used are very important to achieve high ink stability, printability, and electrical conductivity. The prepared coating solutions included amounts of 35 , 28 , 15 , 10 , 40 , 25 , 35 , and 20 cc of ethanol, respectively, which resulted in a decrease in the density of silver nanowire and therefore in the amount of transmission and surface resistance. Examples are effective. The different densities in the coatings obtained from solutions with different concentrations of silver nanowire inks are evident in the field emission scanning electron microscope images given in Fig. 12.

Before focusing on the final products, the growth behavior of AgNWs is first investigated. Fig. 13 shows the graph of Ag^+ concentration in the reaction system at different reaction times. Before the formation of these three phases, there is an important stage called supersaturation. This step of increasing the temperature of the solution causes the dissolution of larger amounts of raw materials in it. Supersaturation can be created by dissolving certain amounts of the precursor in the desired solvent. For this purpose, the temperature of the solvent can be increased so that more quantities of the precursor can be dissolved in it.

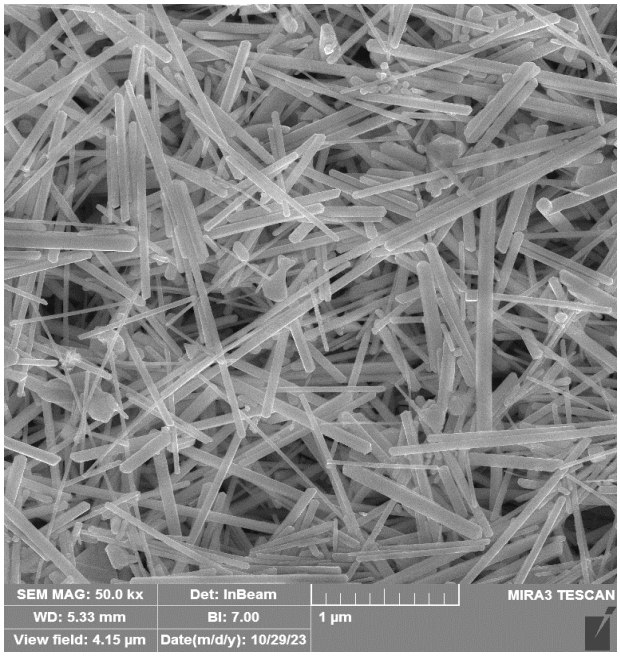

Fig. 10. FE-SEM image of silver nanowires synthesized at a mixing rate of 770 rpm.

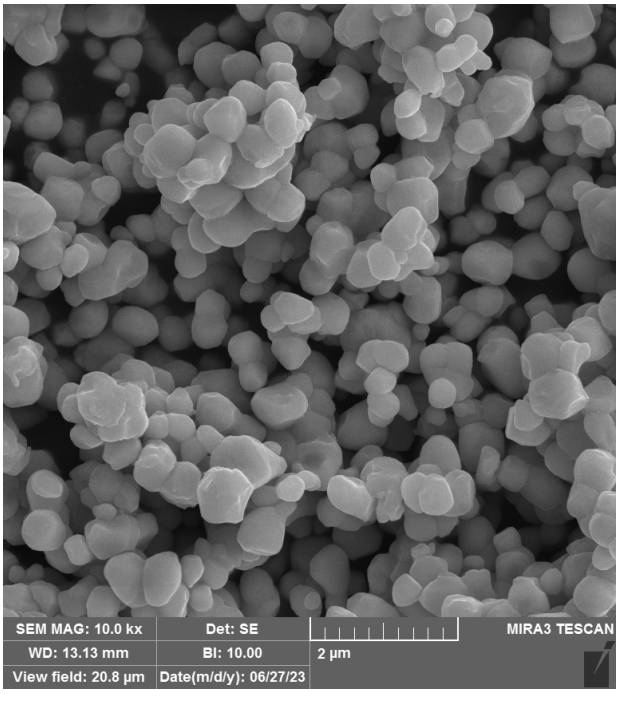

Fig. 11. An image of AgCl particles as nucleating particles.

After the pre-supersaturation stage, it is time for nucleation. For nucleation, it is necessary to leave the solution in the supersaturated state. Getting out of supersaturation can be done in several ways. One of them is to increase the precursor concentration beyond the supersaturation concentration and the other is to decrease the temperature after reaching supersaturation. Because the solubility is lower at a lower temperature, and thus the solution leaves the supersaturated state as the temperature decreases. The first phase (0–60 minutes) is the nucleation process and the evolution of the nucleus to the seed. If the temperature decreases, the solution leaves the

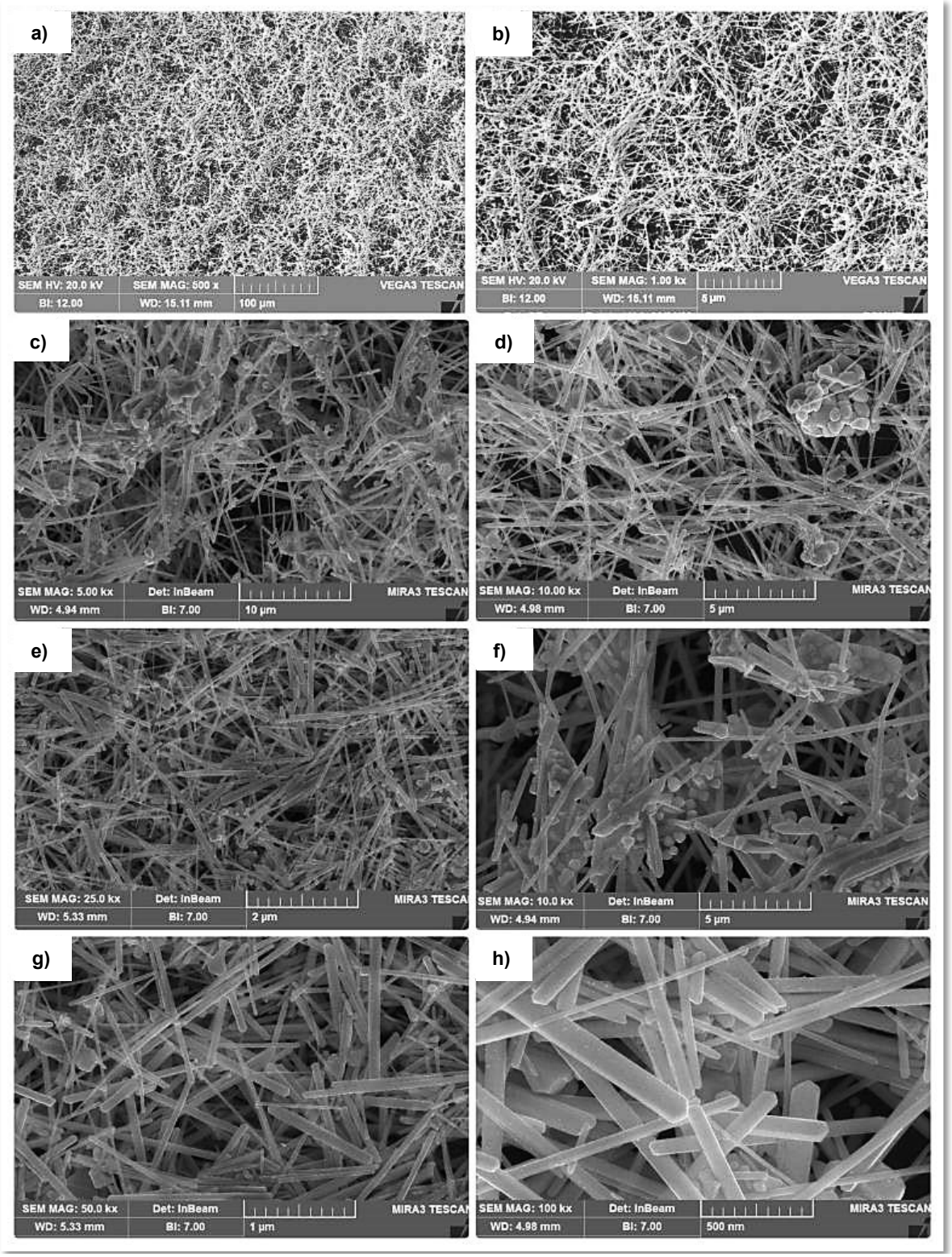

Fig. 12. FE-SEM images of coated all samples.

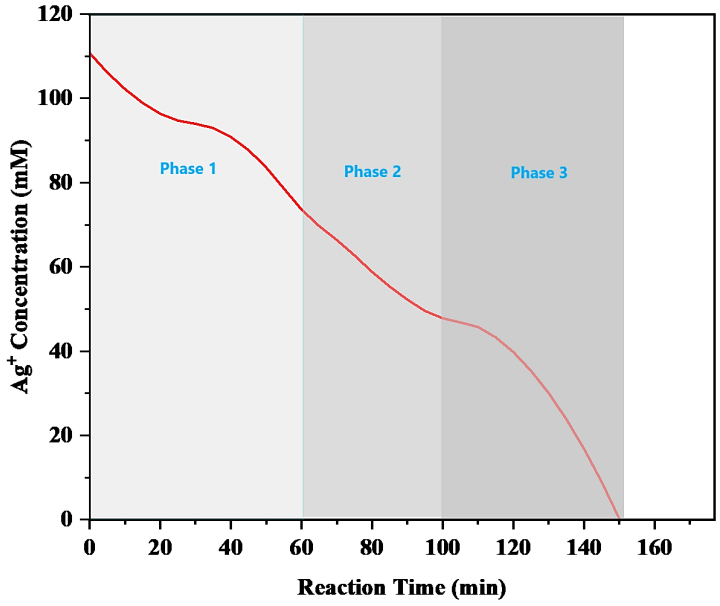

Fig. 13. Evolution trend of Ag^+ concentration with reaction time. The first phase nucleation process, the second phase evolution of the nucleus to grain and the formation of silver nanowires, and the third phase growth of silver nanowires.

supersaturated state and nucleation begins. Thermodynamically, the solution no longer tends to keep the precursor in solution and tends to turn it into a solid. The second phase (60–100 minutes) is the initial formation process of silver nanowires. This stage is the evolution of kernel to seed. At this stage, the buds grow and become nanoparticles. The third phase (100–150 minutes) is the growth of nanoparticles with a preferred direction (111) (Fig. 14). At this stage, if the created buds remain stable, other atoms or molecules in the solution will join the buds and make them bigger, and the nanoparticles will grow according to the Fig. 14, they will grow in the (111) direction of the particles and two other directions. (110) and (100) are limited and primary nanowires grow exactly after the end of the reaction and cooling of the solution.

Repeating the synthesis experiment of silver nanowires with different

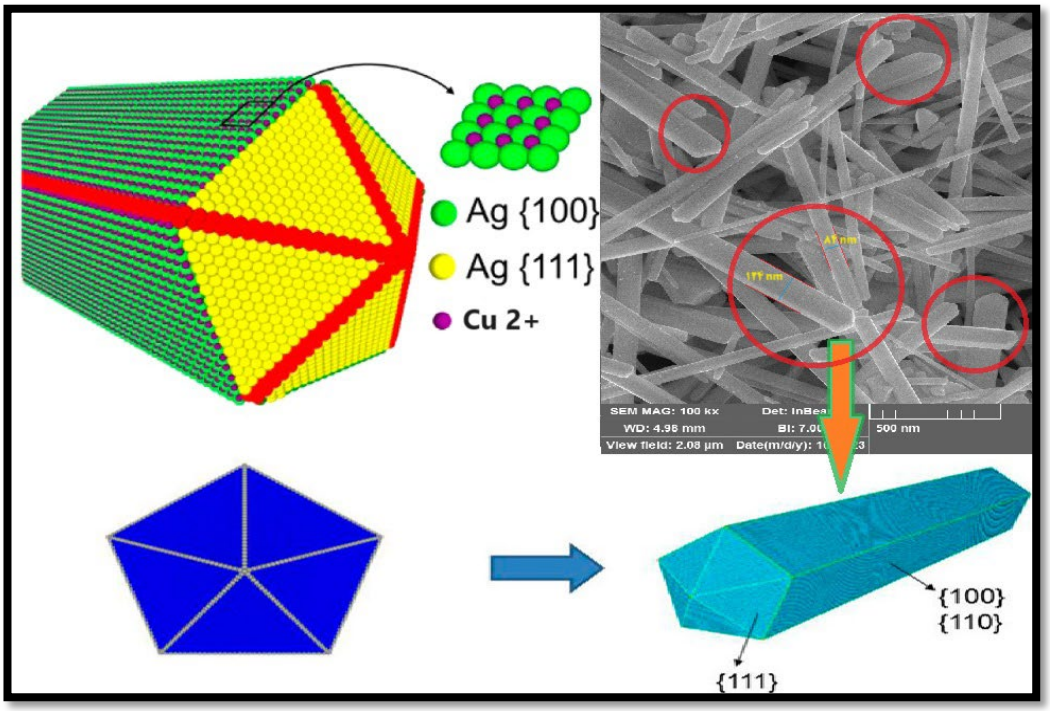

Fig. 14. Evolution of a nanowire from a silver twin nanoparticle (MTP) in FE-SEM image and a schematic of its growth mode and direction.

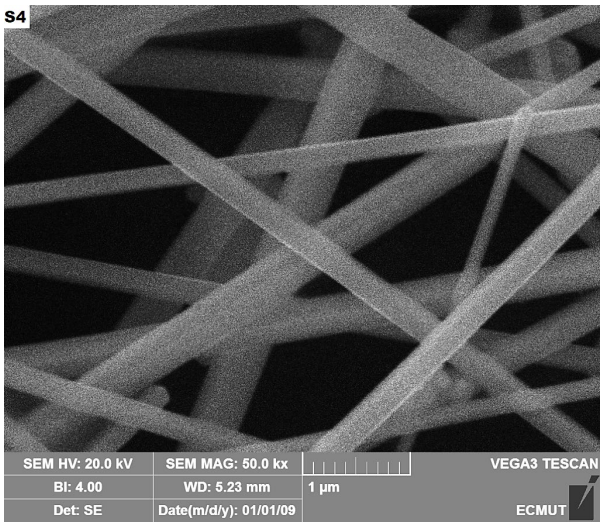

Fig. 15. SEM image of silver nanowires synthesized in sample S4.

molarity values of $CuCl_2$ showed that the concentration of copper chloride is important, that is, in low and high molarities, either the number of nanowires is small compared to the particles, or the length of the nanowires is short, and the optimal concentration can be found. Table 2 shows the results of changes in the molarity of $CuCl_2$. As it can be seen with 114 molarity, it meets the optimal conditions, that is, the long length of the nanowires and the low ratio of particles compared to the silver nanowire, which can be seen in their images (Fig. 15).

3.9. Characterization of AgNWs

Fig. 15 shows the SEM image of the produced silver nanowire sample. As can be seen, this image confirms the formation of nanowires. Nanowires have average lengths ranging from 4.48 µm and their average diameter is less than 0.197 µm. At first, nanowires are formed from the initial germination of silver grains. After that preferential growth, they can become nanowires. Cubic particles indicate preferential unsuccessful growth under experimental conditions.

As stated, one of the problems of the synthesis of nanowires by the polyol method is the inevitable formation of particles that not only do not help to reduce the surface resistance of the sample but also cause a decrease in the transparency of the sample. Trying to reduce and eliminate these particles has been one of the basic issues in making silver nanowires.

Table 2. The results of the synthesis of silver nanowires with different concentrations of $CuCl_2$.

Sample code	Concentration of $CuCl_2$	Visible results are seen with a microscope
S1	114 mM	Only AgNWs
S2	87 mM	Only AgNWs
S3	95 mM	Only AgNWs
S4	90 mM	Only AgNWs
S5	80 mM	Mostly AgNWs
S6	110 mM	A mixture of silver nanowires with nanoparticles
S7	134 mM	Mostly AgNWs
S8	77 mM	Mostly AgNWs

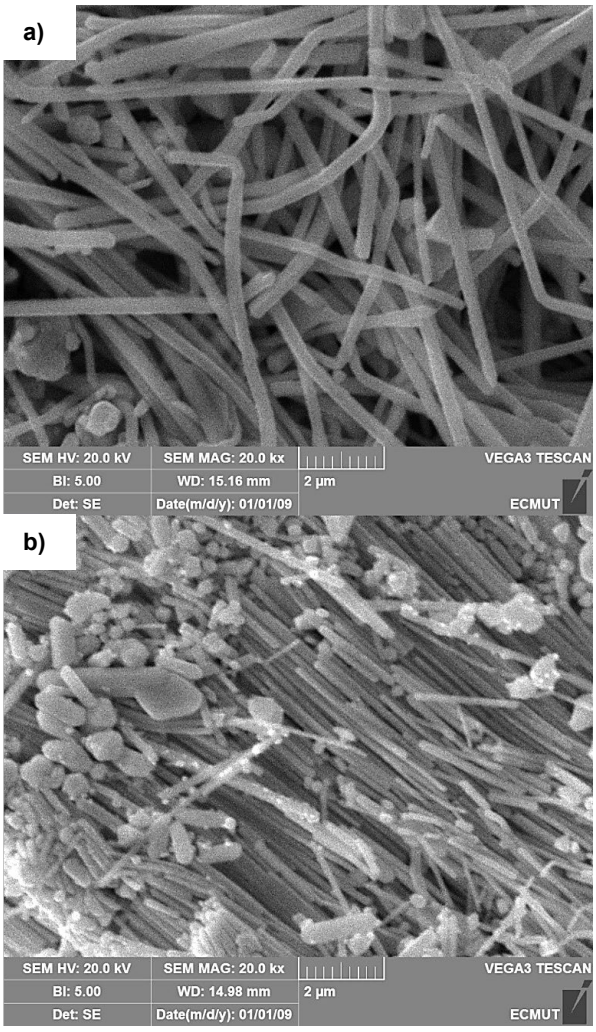

Fig. 16. Scanning electron microscope image of the sample a) after the purification operation and b) before the purification process.

As it is clear in the SEM images, the samples made in this research also need to reduce these particles or in other words these aggregates. One of the methods used to reduce this, as mentioned in the previous chapters, is done just before centrifugation, the controlled selective sedimentation method, which is as follows. The process simply involves slowly adding acetone to a mixture of the final reaction solution and water. Since the silver nanowires were covered with PVP and PVP is not soluble in acetone, the silver nanowires accumulated and settled at the bottom of the container. After adding 15 cc of acetone to the sample, there was a change in the color of the solution from green to yellow, the precipitate was gray and the upper solution was green. Fig. 16 shows the scanning electron microscope images of the sample before and after the purification operation. Fig. 16 is related to the prototype without particle cleaning, and as can be seen, a large amount of silver particles has been created. In Fig. 15, which is related

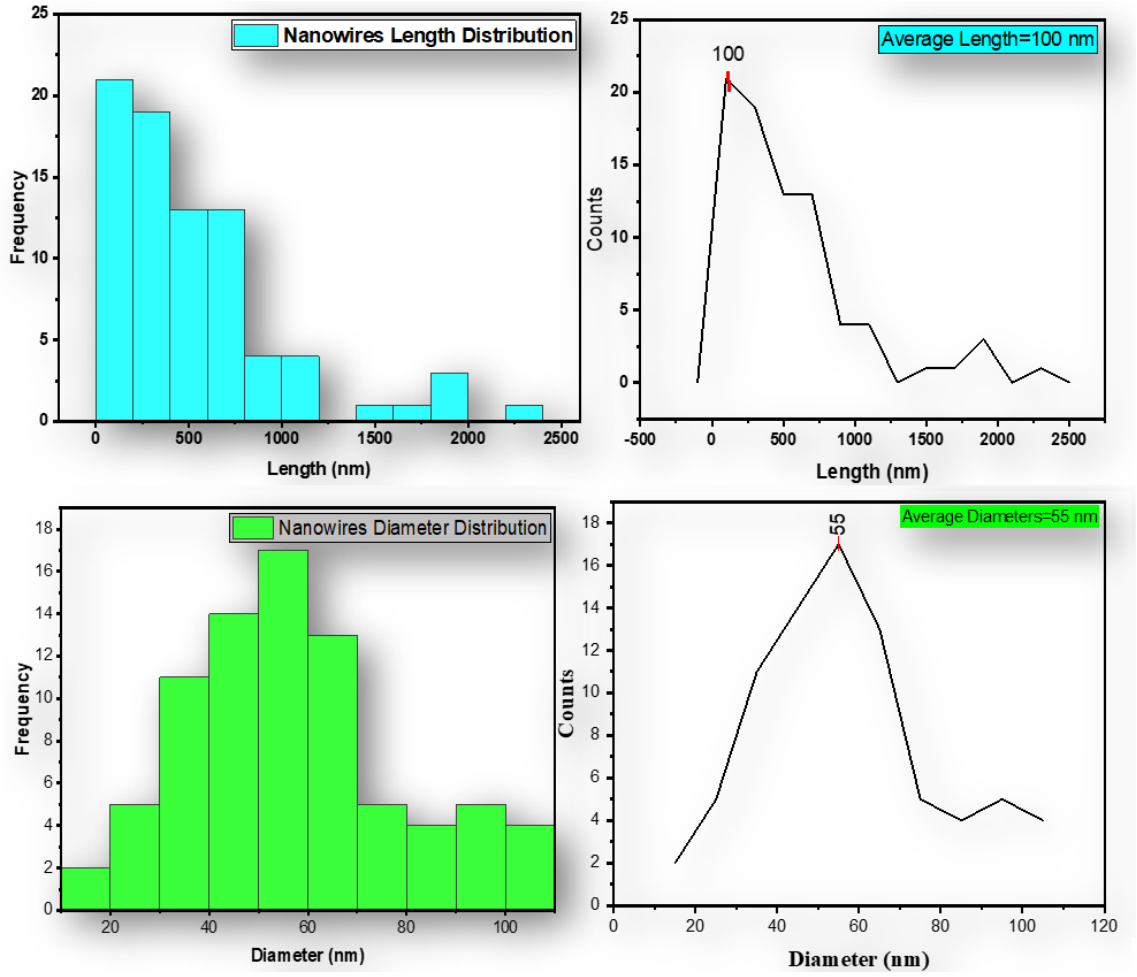

Fig. 17. Size distribution of silver nanowires and average length of 100 nm nanowires and size distribution of silver nanowires and average diameter of 55 nm nanowires.

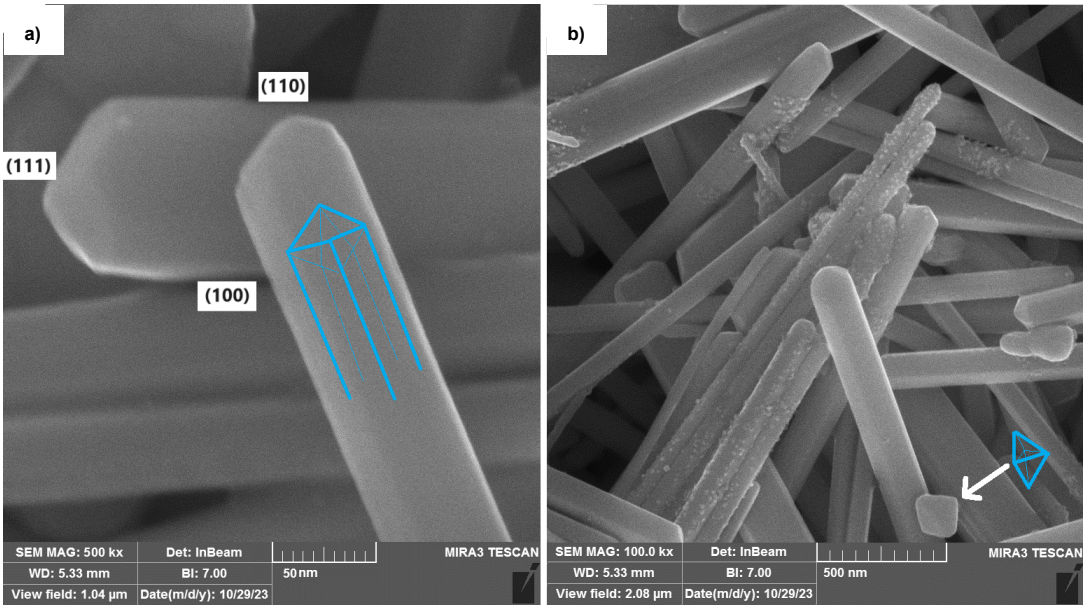

Fig. 18. a) FE-SEM image of silver nanowires of sample S7 and confirmation of the pentagonal nanostructure and its respective directions and b) FE-SEM image of silver nanowires of sample S7 with different magnification and primary particle (MTP) observation.

to obtaining the same concentration, 10 cc concentration (TC4 sample), and the same purification method is used, it can be seen that the particle size has decreased significantly, which can have a positive effect. To have an example of the level of transparency, the optical transmittance of the sample is measured, showing a noticeable increase in transparency compared to samples with larger particle sizes.

Fig. 17 displays SEM images that illustrate the size distribution of silver nanowires. By utilizing ImageJ software (v. 1.52), the size distribution of these nanowires was determined. In Fig. 16, it is apparent that the average length of the silver nanowires measures 100 nm, while the average diameter is 55 nm. In general, it should be noted that silver nanowires grown on a substrate with a high surface energy have a smaller diameter than silver nanowires grown on a substrate with a lower surface energy.

Fig. 18 shows the quintuplet structures of silver nanowires grown from (MTP) state with 134 mM and the same reaction time. In this image, the ends of these nanowires are terminated with the (111) direction, and the side surfaces are bounded by the (110) and (100) directions. PVP has a strong interaction with the (100) direction and a weak interaction with the (111) direction. Moreover, the interaction between PVP and the (110) and (100) directions should be very weak so that the two ends of the nanowire can grow continuously during Ostwald ripening. As a result, once the initial wire structure is formed, it can easily grow and become a long nanowire because its lateral surfaces are strongly constrained by PVP. In Fig. 18, only one purification was done and sampling was done.

Using the images obtained from silver nanowires in Fig. 19d, the size distribution of silver nanowires was calculated using ImageJ software (v. 1.52), and according to Fig. 19, the average diameter was 0.05 µm and according to the length size distribution. The nanowires were obtained in the form of an average length of 1.75 µm.

In general, the length and diameter of silver nanowires have a significant effect on their properties. Longer and larger-diameter (thicker) nanowires exhibit higher electrical conductivity and lower transparency, while shorter, smaller-diameter (thinner) nanowires exhibit lower electrical conductivity and higher transparency. In

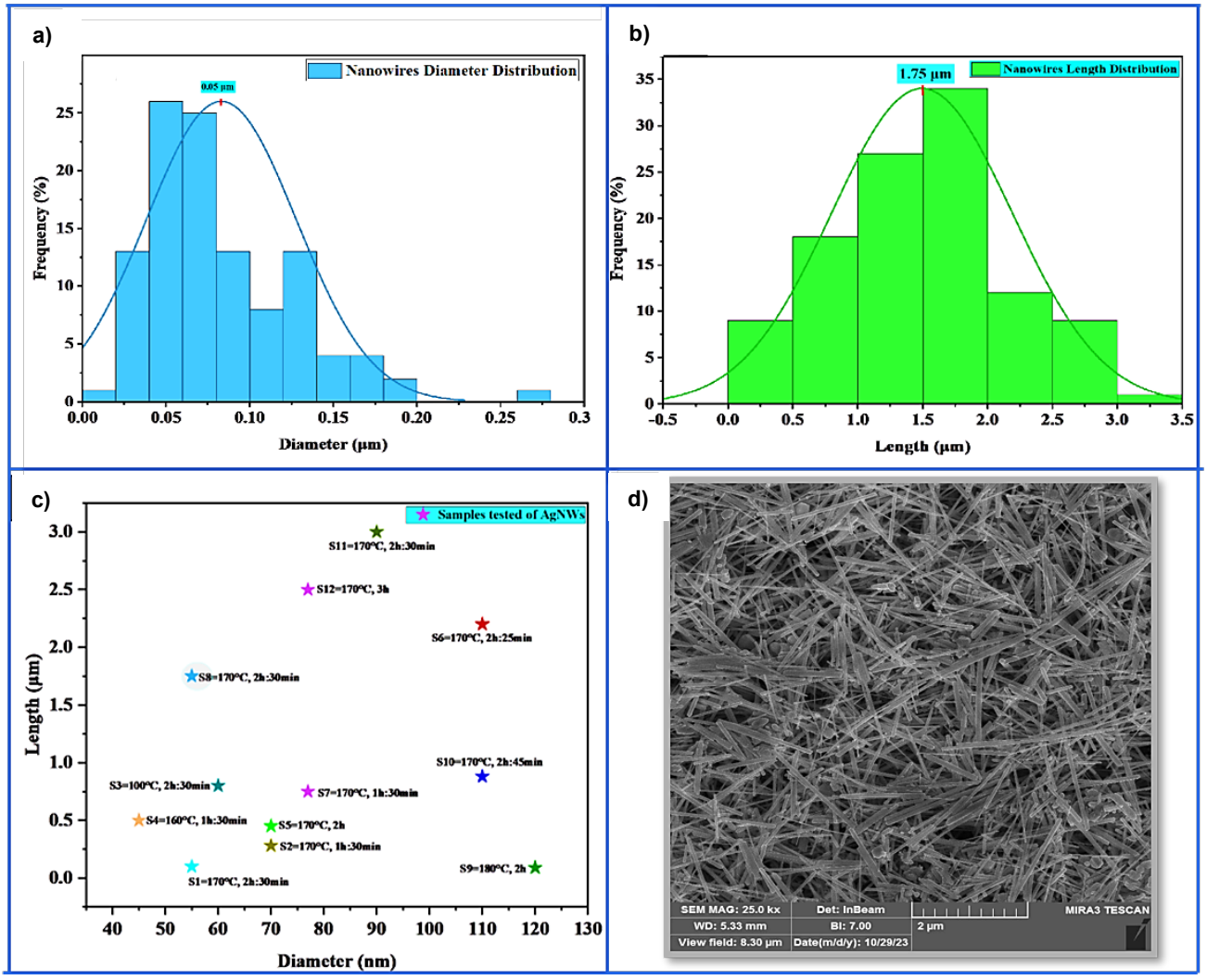

Fig. 19. a) Size distribution of silver nanowires and average diameter of 55 nm of nanowires, b) size distribution of silver nanowires and the average length of nanowires 1.75 micrometers, c) the effect of different conditions including time and temperature on the length and diameter of silver nanowires and tested samples, and d) FE-SEM image of silver nanowires with 2 µm magnification.

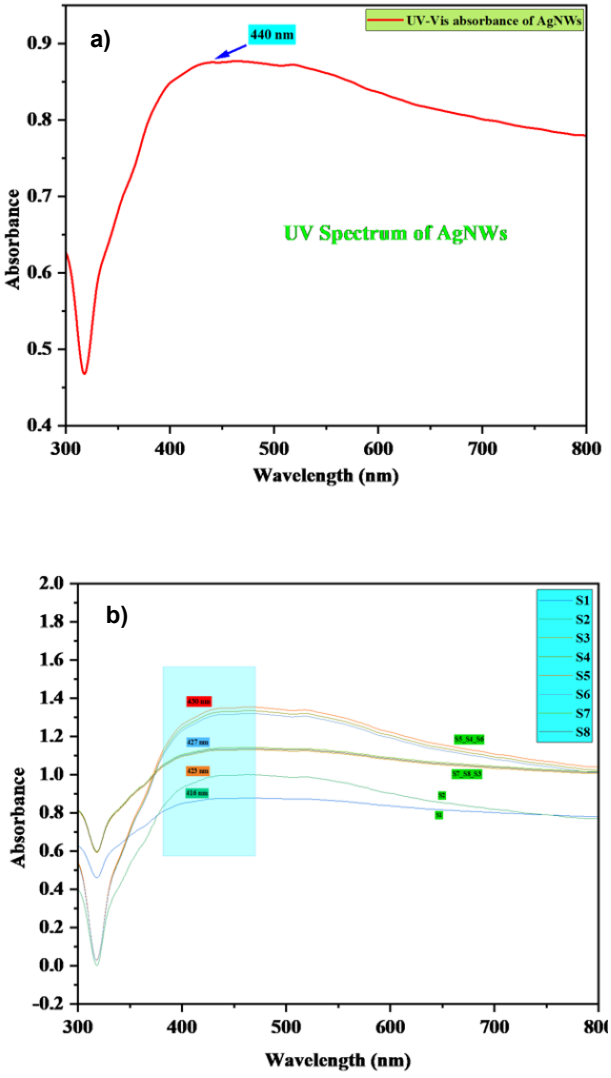

Fig. 20. Absorption spectrum (UV-Vis) of a) silver nanowires for S8 and b) for all samples in the wavelength range between 300 and 800 nm.

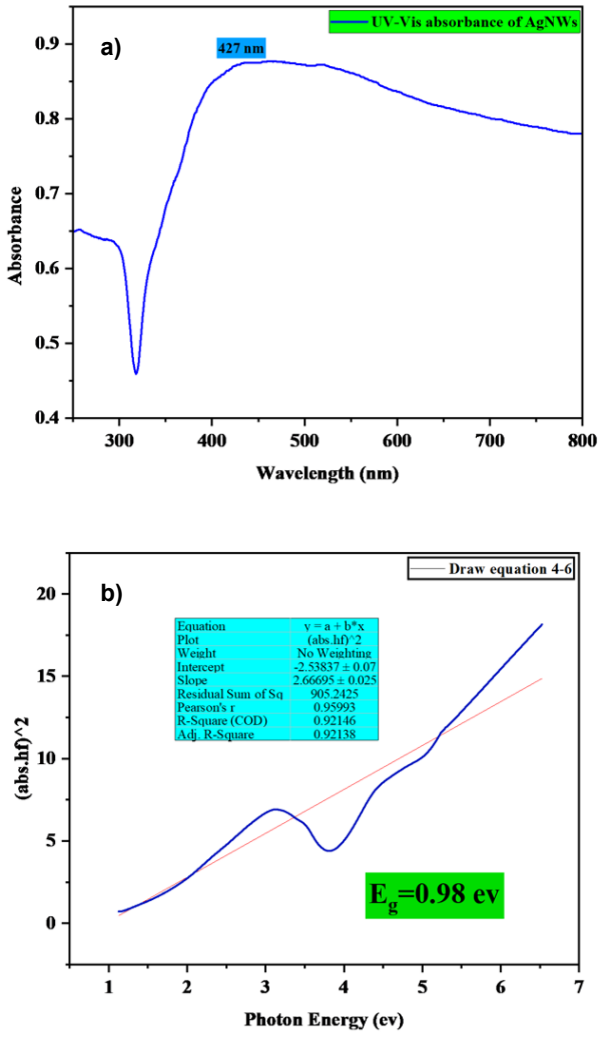

Fig. 21. a) Absorption spectrum of silver nanowires dispersed in ethanol in the range of 200 to 800 nm and b) drawing the equation of the line and obtaining the band gap energy.

addition, transparency and conductivity have a reciprocal relationship with each other. Longer nanowires have more free electrons and a longer mean free path for electron transport, resulting in higher electrical conductivity. This is because the electrons in the longer nanowires have a greater chance to collide with other electrons and transfer energy, which facilitates the electrical current.

On the other hand, a balance and an optimal sample should be found between transparency and conductivity. Because larger-diameter nanowires have a larger cross-sectional area that allows more electrons to flow through them. However, thicker nanowires have a lower surface-to-volume ratio, which can lead to increased electron scattering and reduced electrical conductivity. Now we can conclude that nanowires with larger diameters have lower electrical resistance, which indicates higher electrical conductivity due to larger cross-sectional area.

So, with these interpretations, the sample (S8) which has an average diameter of 55 nm and an average length of 1.75 micrometers has a conductivity of 2.8 and also a transparency of 77%, which is an optimal and balanced sample. Because this sample has longer nanowires with a smaller diameter, they scatter more light and, as a result, have better transparency. This is because longer and smaller diameter nanowires have a larger surface area, which increases the likelihood of light interacting with the nanowires and scattering. So overall, shorter (less length) and thinner (smaller diameter) nanowires are more transparent due to reduced light scattering. On the other hand, longer (more length) and thicker (more diameter) nanowires have less transparency due to increased light scattering from the larger surface and volume. As a result, nanowires should be obtained and their diameter should be adjusted, which have properties between these two conditions, and the sample S8 with longer nanowires (longer length) and smaller diameter is the best condition between these conditions, and it has full conductivity and transparency. An ideal has been achieved.

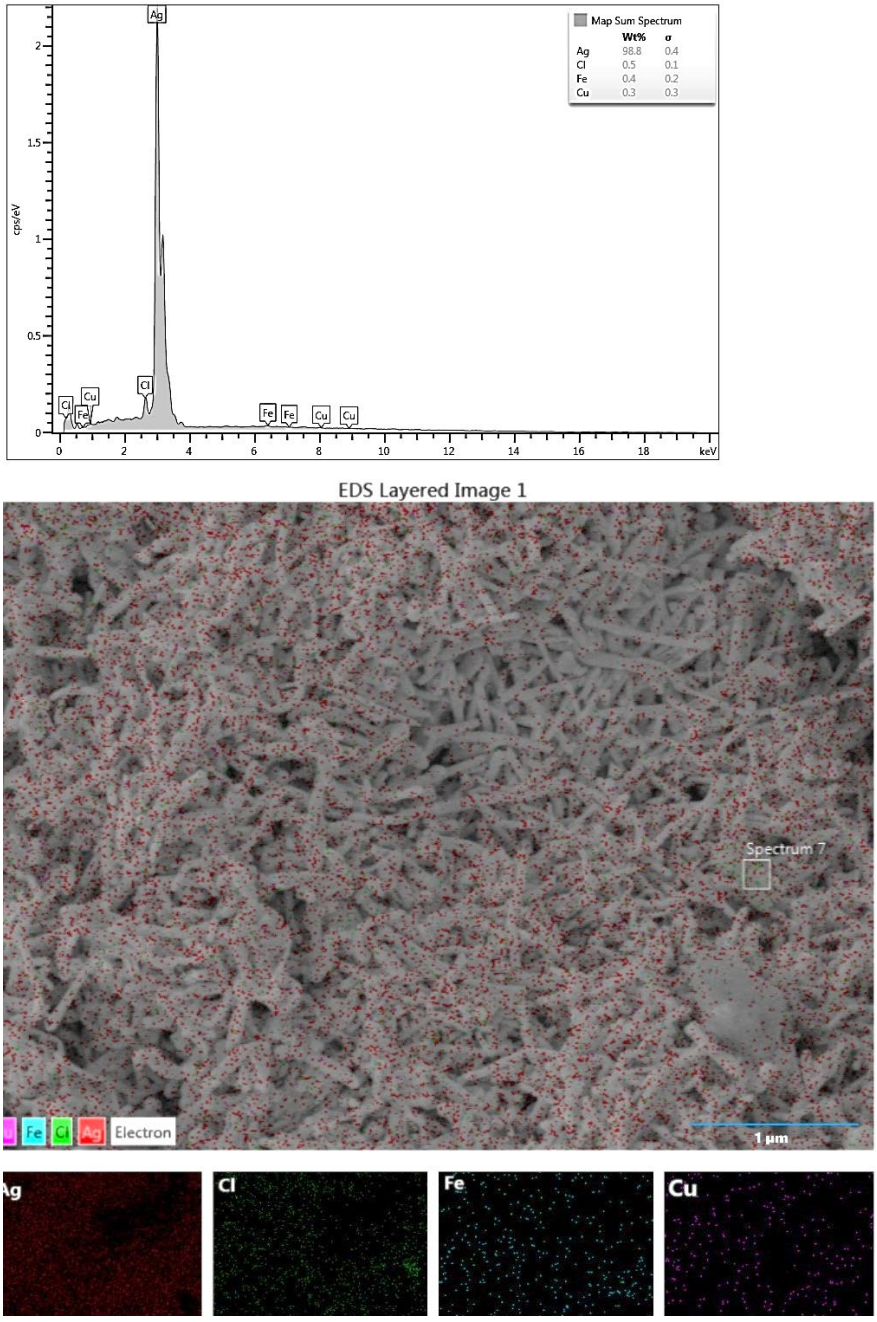

Fig. 22. EDS patterns related to silver nanowires sample added with iron chloride and elemental distribution images of Ag, Cl, Fe and Cu forming silver nanowires.

3.10. UV-vis analysis

The unique optical properties of AgNWs arise from their localized surface plasmon resonance (LSPR), which is a collective oscillation of conduction electrons in nanowires. Larger AgNWs have longer wavelengths and thinner AgNWs have broader peaks. In addition to the absorption peak (peak), the UV spectrum of silver nanowires also shows a depression. The depression is caused by the scattering of light by the nanowires. Fig. 20a shows the UV-vis spectrum of the produced silver nanowire sample in ethanol. By comparing this spectrum with the cases reported by other researchers of synthesized silver nanowires, there is a good agreement between the main peak at 440 nm and the absorption at 328 nm of this spectrum with the spectra in global reports.

As can be seen in the uv diagram shown in Fig. 20b, for all the eight main tested samples, a common and main peak can be seen, which is respectively for samples S5, S4, and S6 at a wavelength of 430 nm and one A shift can be seen at 328 nm. Also, for samples S7, S8, and S3, a common peak was seen at 427 nm, correspondingly, for samples S1, and S2, a main peak at 423 and 416 nm and a depression at 320 and

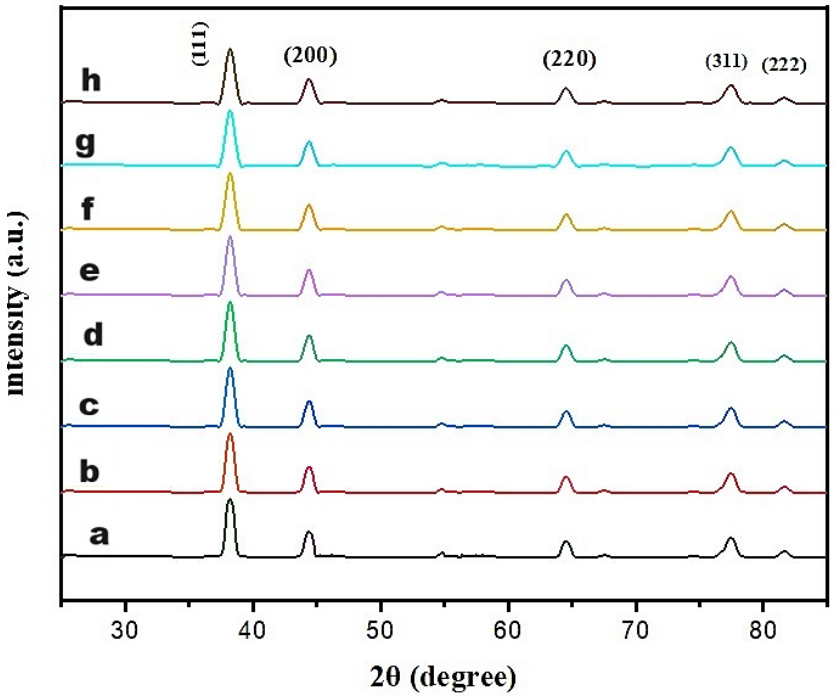

Fig. 23. X-ray diffraction pattern of silver nanowires.

325 nm were observed. Also, peak 6 of the first sample is wider than the second one. Also, Table 3 shows all the parameters that are designed in these 8 final tests using Design Expert software (v. 12).

3.11. Bandgap calculation of silver nanowires

For bulk silver, the valence band and conduction band are very close in energy. This means that the electrons in the valence band can easily move to the conduction band, resulting in high electrical conductivity. Quantum effects occur when electrons are confined in a small space such as a silver nanowire. As a result, valence band electrons must absorb enough energy to overcome the band gap and move to the conduction band to conduct electricity. Now, if the band gap is too large, fewer electrons can carry out this transfer, resulting in less electrical conductivity. So it can be concluded that the gap band of silver nanowires can be adjusted by controlling their size and shape. This issue can be done by using changes in the method of synthesis or its growth. By adjusting the band gap, the electrical conductivity of silver nanowires can be optimized for specific applications, including conductivity and transparency.

In this research, Tauc theory was used to calculate the bandgap of silver nanowires [26]. Tauc's idea is that the energy-dependent absorption coefficient can be expressed by the following relation:

$$(a.h\nu)^{\frac{1}{\gamma}} = B(h\nu - E_g) \quad (8)$$

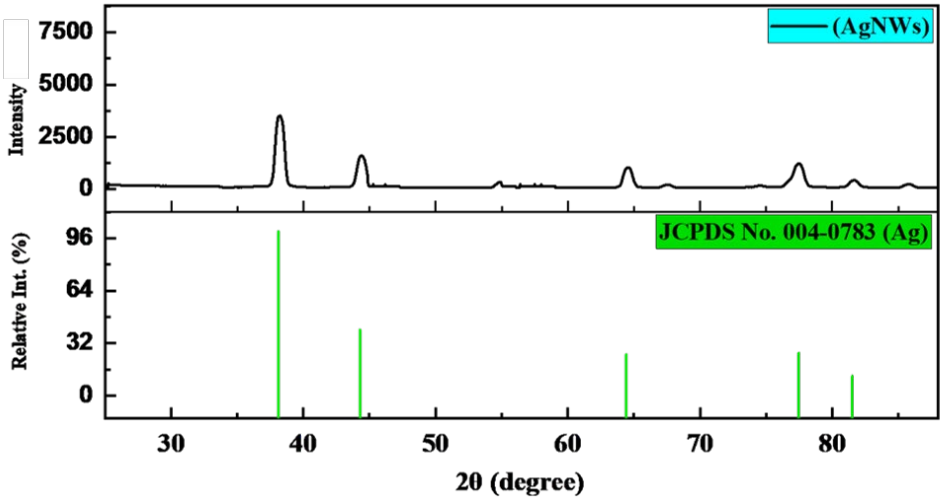

Fig. 24. X-ray diffraction pattern of silver nanowires and their compatibility with Ag and AgCl phase.

Table 3. A summary of the synthesis variables of silver nanowires during the modified polyalcohol process.

	PVP (Mw:40.000)							
Sample code	S1	S2	S3	S4	S5	S6	S7	S8
PVP	0.07 g	0.229 g	0.065 g	0.70 g	0.49 g	0.70 g	0.75 g	0.8 g
EG	30 ml	30 ml	30 ml	30 ml	30 ml	30 ml	30 ml	30 ml
$CuCl_2$	114 mM	98 mM	95 mM	90 mM	80 mM	110 mM	134 mM	77 mM
$AgNO_3$	0.0450 g	0.101 g	0.0450 g	2.64 g	1.19 g	1.95 g	1.8 g	1 g
Molar ration	1/8	7/5	1/75	1/2	1/7	1/5	1/5	1/5
Temperature	170 °C	170 °C	100 °C	160 °C	170 °C	170 °C	170 °C	170 °C
Reaction time	2.5 h	1.5 h	2.5 h	2.5 h	2 h	2 h & 25 min	1.5 h	2.5 h
Mixing rate	750 rpm	750 rpm	750 rpm	750 rpm	750 rpm	750 rpm	750 rpm	750 rpm

This is the equation of a line:

$$(a.h\upsilon)^{\frac{1}{\gamma}} = y, \quad h\upsilon = x \tag{9}$$

$$y = B(x - E_g) \tag{10}$$

where Eq. 10 intersects the line of the x graph will be equal to the bandgap energy:

$$y = 0, \quad B(x - E_g) = 0, \quad x = E_g \tag{11}$$

But in the above equations, a is the absorption coefficient, γ is the power constant of Tauke's equation, υ is the radiation frequency, h is Planck's constant, and E_g is the bandgap energy. According to the graph to find the gap band, a line with a positive slope should be drawn to the curved part of the graph. The point where this line intersects the horizontal axis will be equal to the bandgap energy. Now, according to the calculations of the above equations and drawing the absorption diagram in Fig. 21a.

Now we have to calculate the equation of line 4 and draw it, which can be seen in Fig. 21b. Finally, by fitting the obtained equation and dividing the Intercept by Slope, the bandgap energy is obtained and is equal to E_g =0.98 eV.

The bandgap energy of 0.98 for silver nanowires indicates a relatively small difference in energy between the valence band and the conduction band. This small difference in energy allows electrons to easily move from the valence band to the conduction band, resulting in high electrical conductivity. However, this small band gap also means that silver nanowires can absorb light in the visible spectrum, which can affect their transparency.

The bandgap energy of silver nanowires is influenced by several factors including their size and shape. Smaller nanowires (smaller diameter) have a larger bandgap energy (greater than one) due to quantum effects, which can decrease their electrical conductivity but also increase their transparency. Larger nanowires (larger diameter) have smaller bandgap energy (less than 0.1), which can increase their

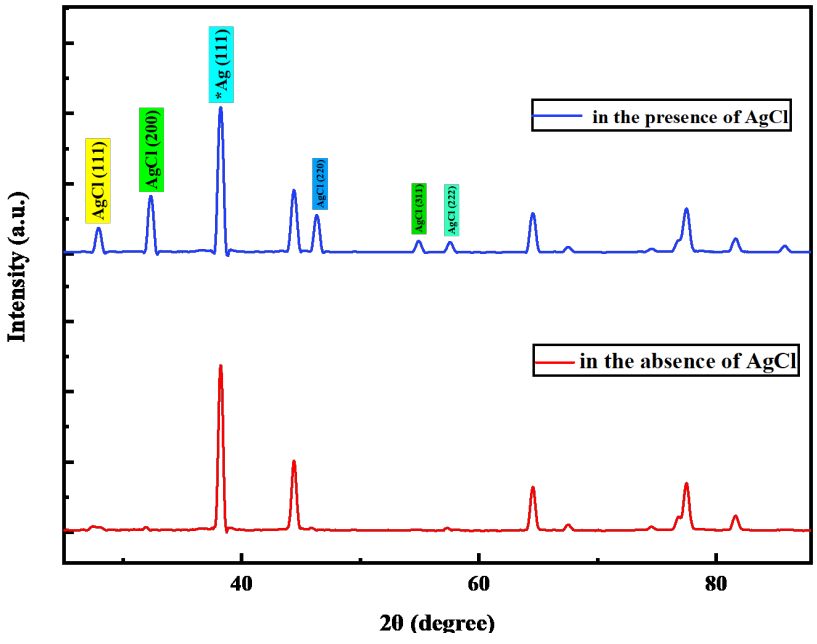

Fig. 25. X-ray diffraction pattern in the presence and absence of silver chloride nanoparticles in the synthesis of silver nanowires.

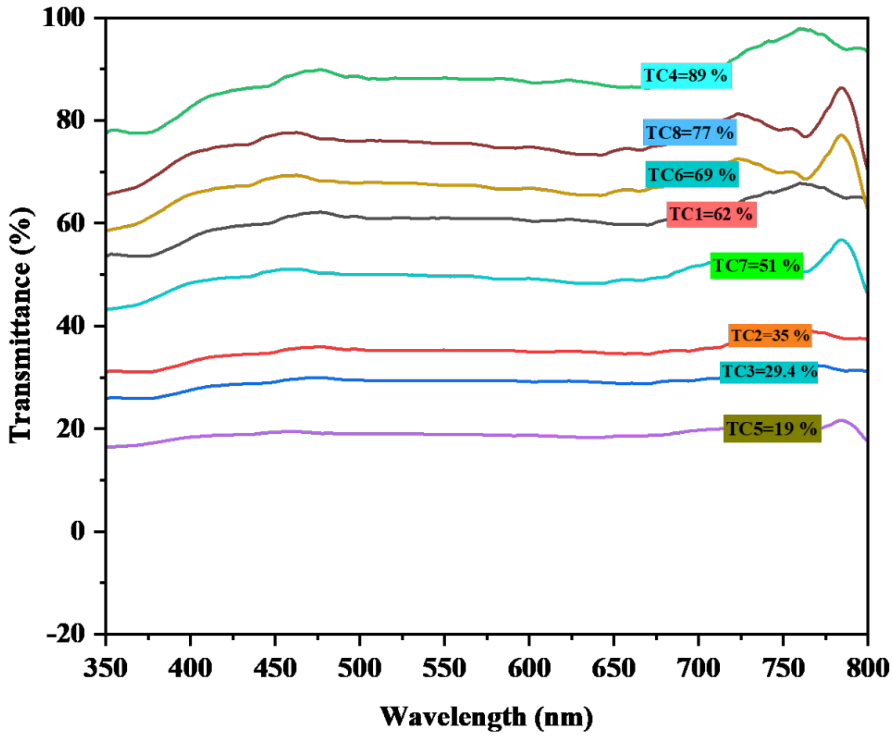

Fig. 26. The percentage of spectrum transmittance of all samples coated with silver nanowires (TC1 to TC8).

electrical conductivity but decrease their transparency. Finally, this bandgap energy indicates the balance between electrical conductivity and transparency of nanowires. EDS and XRD analysis

Another one has been used by using $FeCl_3$ additive as a metal salt for oxygen scavenging and electrostatic stabilization of Ag ions. In the sample, the morphology and size of AgNWs were adjusted by adding iron chloride ($FeCl_3$) as a mediator and nucleating agent and PVP as a coating agent for the synthesis of AgNWs, and the EDS patterns and the corresponding elemental distribution diagram can be seen in Fig. 22.

Fig. 23 shows the X-ray diffraction pattern. The diffraction angles of the peaks correspond well with the standard card number (004_0783) and confirm the correctness of the formation of the cubic structure of the surface center of silver. In Fig. 23 below, the XRD spectrum confirms the formation of a "silver single phase". According to the X-ray diffraction pattern in the prepared sample, the peaks according to the standard peaks, respectively, from small to large angles corresponding to planes (111), (200), (220), (311), and (222) corresponding to angles of 38.11 °, 44.29 °, 64.43 °, 77.39 °, and 84.45 ° and have a faceted center rhombic structure (FCC). Using Scherer's relation, the crystal lattice constant for the optimal sample was calculated as 4.083 ± 0.004 angstroms, which is consistent with the value of 4.086 angstroms in the mentioned standard card. Also, the angles between the grid, considering that in the FCC structure, all angles are equal, so we have: α=B=y=90 °.

Also, in the diffraction pattern of the silver nanowire produced and compared with the corresponding standard card shown in Fig. 24, it can be seen that the intensity of the peak corresponding to the (111) plane is significantly higher compared to other peaks, which confirms the preferential growth. The nanowires produced are in these directions. In the synthesis of silver nanowires, PVP was used as a stabilizer. The main reason for the preferential growth of nanowires along the (111) direction is that the chemical bond between the (100) planes and PVP is stronger compared to the (111) planes and PVP, and because of this, the (111) plane remains more active and causes nanoparticles to be deposited. Silver is regenerated on this plate and nanowires grow in this direction.

Adding chlorine ions in the reaction helps to stabilize Ag^+ by forming AgCl nanocrystals whose solubility is lower than that of $AgNO_3$ in solution. Hence, Ag grains are formed at a very slow rate, and as a result of low solubility, Ag ions are also released in the solution at a slower rate. As a result of these cases, it reduces the speed of the reaction, which causes the anisotropic growth of nanowires in a certain direction. As can be seen in Fig. 25, in the absence of silver chloride, a very small number of silver nanowires are formed with irregular growth, as well as five main peaks. It is not seen and this state can be due to the presence of silver chloride and their preferential growth in these directions. But when silver chloride is added to the reaction solution, in the original X-ray diffraction pattern in the presence of AgCl, (111), (200), (220), (311), and (222) plates are formed respectively. Finally, this issue causes the preferential growth of silver nanowires in the (111) direction.

3.12. Transparency of the produced silver nanowire thin layer and its sintering

After performing the XRD test, the coated samples were subjected to the transmission spectrum test to determine the percentage of transmission. It can be seen that in Fig. 26, the TC4 sample with the lowest coating density has the highest transmission rate compared to the other tested samples, which is caused by the large distance of the nanowires from each other, and therefore the light scattering and reflection decreases.

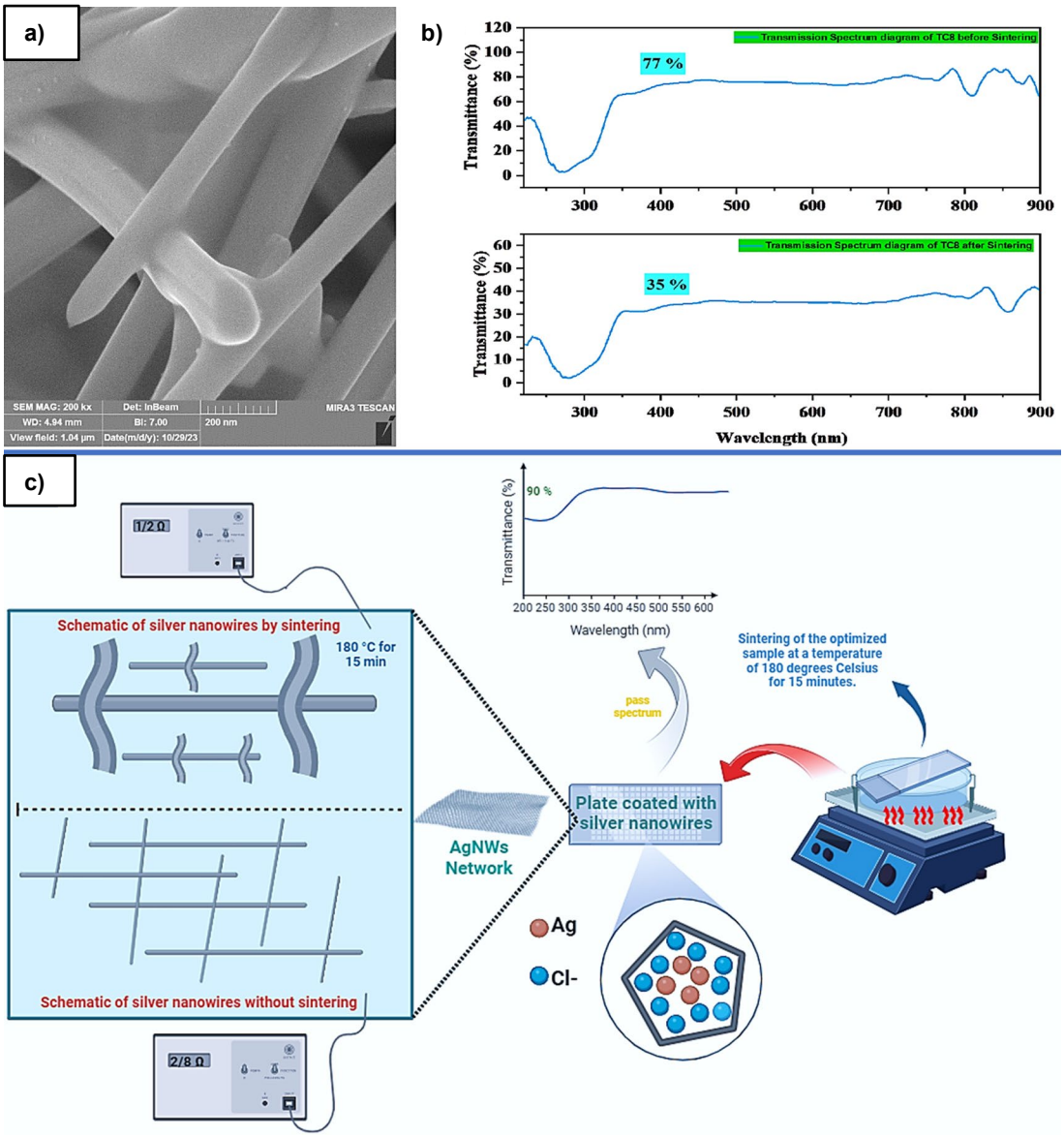

Fig. 27. a) FE-SEM image of silver nanowires after sintering at 180 °C, b) transmittance spectrum diagram of TC8 before (77%) and after (35%) sintering, and c) schematic method of sintering coated silver nanowires and its investigation.

Finally, this research investigated the effect of sintering on the thin film based on silver nanowires. Sintering is an important step in the fabrication of thin films based on silver nanowires (AgNWs) because it increases their electrical conductivity and transparency. During this process, the AgNWs melt at their junctions, creating a network of interconnected nanowires that can efficiently transport electrons. Fig. 27 shows the silver nanowires that were first coated on the glass and then subjected to the sintering process.

As shown in Fig. 27, the samples were heated at 180 °C for 15 minutes. This heat during sintering increases the kinetic energy of the silver atoms, allowing them to overcome their interatomic forces and spread across the interface of the nanowires. This diffusion process leads to the formation of strong interparticle bonds, effectively welding the nanowires together, as illustrated in Fig. 27a.

The effect of annealing on transparency can be seen in the diagram of Fig. 27b. As a result, during the sintering, the increase in the diameter of the nanowires is inevitable, and therefore the length of the nanowires has increased along with their diameter, finally, the transparency of the thin layer has increased and the conductivity has increased.

3.13. Investigating the efficiency of EMI protection

To calculate the EMI shielding efficiency in terms of dB theoretically [27], we use the following relationships for each sample according to the Table 4 where the electrical resistance of each covered sample is obtained. First, by using Eq. 12, r_f (surface depth of electromagnetic wave input in m) was calculated, which can be seen in Eq. 13. Now, for example, for sample one (TC1), having the mentioned values and placing them in the following relation, we have:

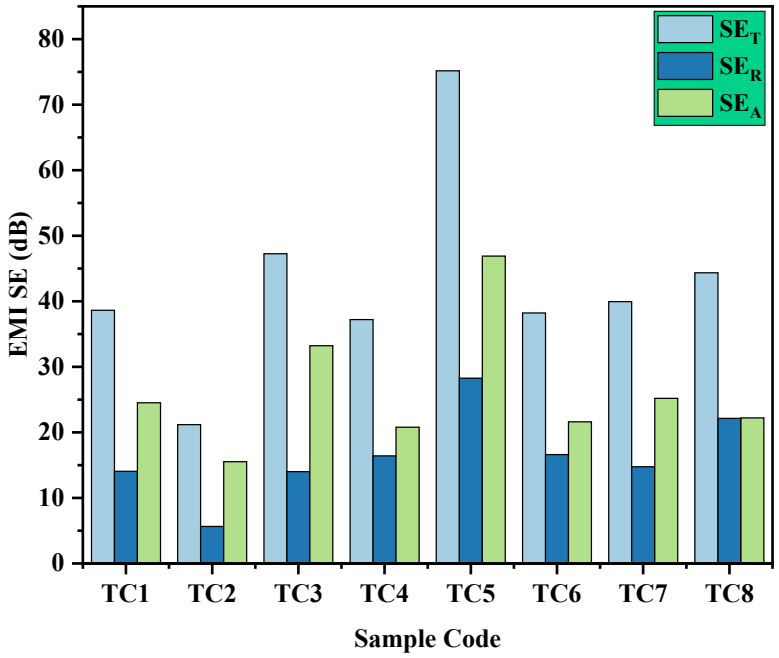

Fig. 28. Relative distribution of EMI shielding efficiency in dB for samples coated with silver nanowires.

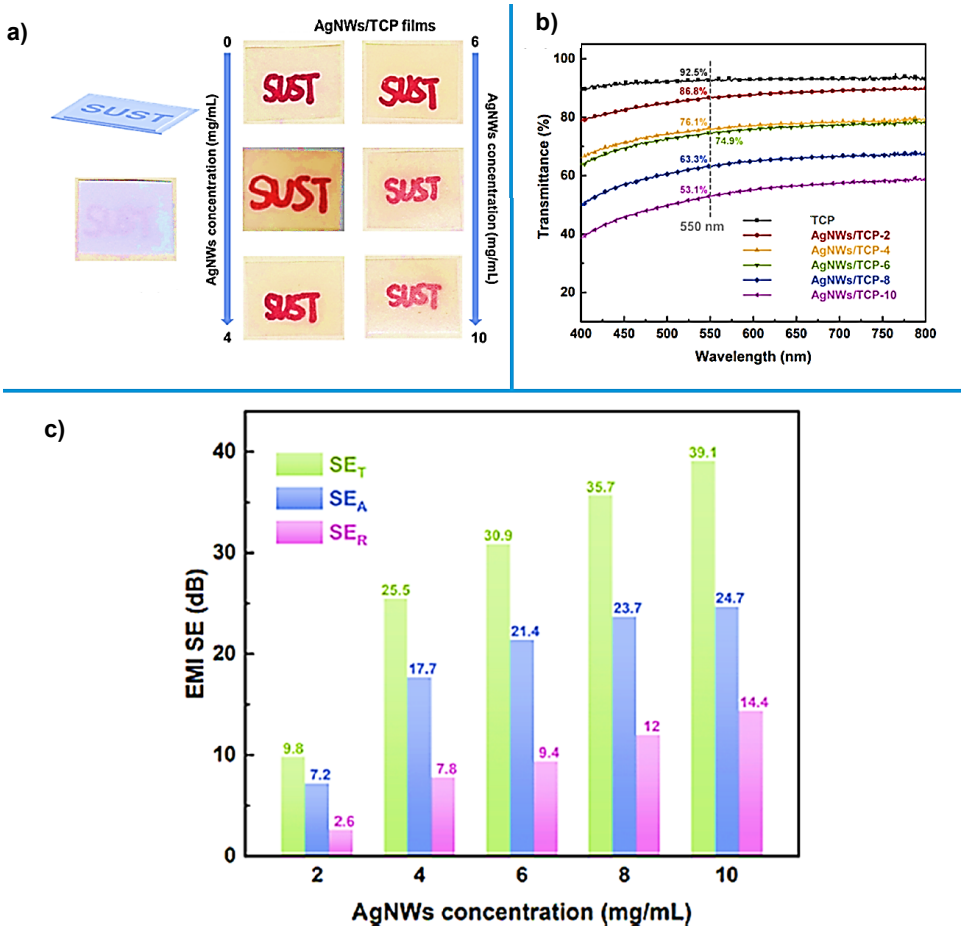

Fig. 29. a) Coated glass samples, b) Transparency of light transmission spectrum of six samples coated with silver nanowires, and (c) protective efficiency of samples coated with AgNWs in dB with different concentrations. With Permission from Elsevier B. V. [17].

$$r_f = 0.63 \times \sqrt{\frac{1}{(1 \times 0.0950 \times 10^9)}} = 6.4 \times 10^{-5}\,\text{m} \quad (12)$$

Then, according to Eq. 13, we will place the obtained r_f and we will have:

$$SE = 20 \times \log(1 - \frac{r_f}{r_0}) = -0.01173 \quad (13)$$

In the above equation, r_0 is the wavelength of the free space and its value is equal to (0.0477 m).

$$SE_T = SE_A + SE_R \quad (14)$$

$$SE_T = 10 \times \log(\frac{1}{SE^2}) \quad (15)$$

$$SE(\%) = 100 - (\frac{1}{SE_T}) \times 100 \quad (16)$$

$$SE_T = 10 \times \log\left(\frac{1}{(-0.01173)^2}\right) = 38.63\ \text{dB} \quad (17)$$

So it can be concluded that the sample TC1 repels about 39 dB of incoming electromagnetic waves and by increasing its conductivity and changing its resistance, its EMI shielding percentage can also be changed and optimized. For this purpose, in Table 4, SE in dB of all samples is calculated and placed according to the method described for the TC1 sample. As can be seen, sample five, which is TC5, has the lowest electrical resistance and at the same time has the highest conductivity among the samples, which can be seen to have the highest EMI shielding efficiency of 75 dB. Therefore, it can be seen that the high conductivity of AgNWs plays a significant role in protecting EM waves, but they may have less transparency. As can be seen in Fig. 28, for all the samples, the absorption shielding efficiency of the sample is shown as SE_A and the electromagnetic wave that hit the sample is shown as SE_R. In general, to calculate SE_T, Eq. 17 is used, for SE_A, Eq. 18, and for SE_R, Eq. 19 is used.

$$SE_A = 10 \times \log(\frac{1 - SE_T^2}{SE^2}) \quad (18)$$

$$SE_R = 10 \times \log(\frac{1}{1 - SE_T^2}) \quad (19)$$

Table 4. EMI shielding efficiency of coated samples based on silver nanowires

Sample	Resistance, Ω	Conductivity, s/m	SE, dB
1	10.52	0.0950	38.63
2	3.73	0.26	21.18
3	0.95	1.052	47.25
4	22	0.045	37.21
5	0.45	2.22	75.17
6	12.22	0.0818	38.23
7	7.70	0.129	39.95
8	2.8	0.357	44.35

During research on the synthesis of silver nanowires and their coating on the glass substrate, Meng and his colleagues [20] achieved a transparency of 92% and a protective efficiency of 40 dB in the best case. First, they synthesized silver nanowires by the polyol method, and using the spray coating method, they achieved transmission transparency of 53% for the mentioned samples. In addition, their optimized sample achieved an electrical resistivity of 6.4 Ω/sq^{-1}, and the interconnected AgNW network after sintering effectively enables electron transport and effectively reduces the electrical resistance [20].

It can be seen in Fig. 29b the transparency of the light transmission of six samples coated with silver nanowires. Also, in Fig. 29a, you can see a sample of coated glass. They also used the electrical resistance of the sample to obtain the EMI shielding efficiency by using the above relationships, and its efficiency can be seen in Fig. 29.

4. Conclusions

AgNWs are a potential material for transparent conductive coatings, with substantial advantages over conventional materials such as indium tin oxide. The findings of this study show that silver nanowires manufactured via the polyol approach, when adjusted for length and homogeneity can attain equivalent or even superior characteristics to ITO. These AgNW coatings remained highly transparent while also providing outstanding electrical conductivity. The sintering procedure improved conductivity by minimizing energy loss at the nanowire connections. The findings show that AgNWs have the potential to be a viable alternative to ITO in a variety of transparent electronic applications.

CRediT authorship contribution statement

Ali Borchloo: Conceptualization, Formal analysis, Investigation, Methodology, Resources, Software, Supervision, Visualization, Writing original draft, Writing – review & editing.

Reza Shoja-Razavi: Data curation, Funding acquisition, Project administration, Validation, Visualization, Writing – review & editing.

Hamed Naderi-Samani: Data curation, Funding acquisition, Project administration, Validation, Visualization, Writing – review & editing.

Data availability

The authors are unable or have chosen not to specify which data has been used.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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