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Millifluidic polyol synthesis of Ag nanowires and microplotter printing of transparent conductive films

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Abstract. Millifluidic polyol synthesis teflon tube (i.d. 1 mm) was studied and used to obtain silver nanowire dispersions. As a result of the experiments, the optimal concentrations of the reagents (silver nitrate $AgNO_3$, ethylene glycol and polyvinylpyrrolidone) were investigated and found to obtain homogeneous nanowires with high length-to-diameter ratios. As a result of the synthesis, Ag nanowires were obtained, which were used to form transparent conductive electrodes using microplotter printing. Transparent conductive electrodes with high transparency of more than 80% at a wavelength of 550 nm with a surface resistance of 52-229 Ohm/sq.

Keywords: Polyol synthesis, millifluidics, silver nanowires, microplotter printing, transparent electrode

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Миллифлюидный полиольный синтез серебряных нанопроволок и микроплоттерная печать прозрачных электродов на их основе

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Аннотация. Миллифлюидный полиольный синтез в тефлоновой трубке с внутренним диаметром 1 мм был изучен и использован для получения дисперсий серебряных нанопроволок. В результате экспериментов были исследованы и найдены оптимальные концентрации используемых реагентов (нитрат серебра $AgNO_3$, этиленгликоль и поливинилпирролидон) для получения однородных нанопроволок с высокими значениями отношения длины к диаметру). В результате синтеза были получены Ag нанопроволки, которые были использованы при формировании прозрачных проводящих электродов с помощью микроплоттерной печати. Были получены прозрачные проводящие электроды с высокой прозрачностью более 80% на длине волны 550 нм с поверхностным сопротивлением 229-52 Ом/кв.

Ключевые слова: Полиольный синтез, миллифлюидика, серебряные нанопроволки, микроплоттерная печать, прозрачный электрод

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Introduction

Transparent conductive electrodes (TCEs) are extensively utilized in electronic applications, including touch screens, solar panels, and optoelectronic devices. Currently, metal oxide films, particularly ITO, are the most commonly employed materials. However, these films are unsuitable for flexible or curved substrates due to their brittleness and limited mechanical flexibility [1–2]. Other drawbacks include their high refractive index and the expensive production processes associated with large-area metal oxide films. Consequently, TCEs made from carbon nanotubes, graphene, and metal nanowires are gaining popularity. A critical objective is to develop TCEs from elongated nano-objects that achieve a sheet resistance of less than 100 ohms per square while maintaining a transparency of at least 80% at a wavelength of 550 nm [3–6]. Among these materials, silver nanowires (AgNWs) are particularly advantageous due to their favorable optoelectronic properties [4, 5]. This study focuses on investigating TCEs based on AgNWs that are deposited using microplotter printing. Currently, several methods are employed to produce silver nanowires, including polyol synthesis, template methods, hydrothermal synthesis, wet chemical synthesis and ultraviolet irradiation methods. The polyol synthesis method is particularly noteworthy due to its advantages in both fundamental research and industrial applications. Benefits include a relatively straightforward reaction protocol that can be easily scaled, the elimination of templates, short synthesis times (often under an hour), and the high aspect ratios of the resulting elongated nanostructures. In this synthesis method, key components of the reaction system include polyols (such as ethylene glycol), which serve as reducing agents, polymers (specifically polyvinylpyrrolidone), which act as capping and growth-controlling agents for the formation of one-dimensional structures, and silver nitrate, which provides a source of metal cations. One of the known approaches to AgNW synthesis is synthesis in a thin capillary in a flow mode. The advantages of this approach are the possibility of implementing a continuous-action setup with subsequent scaling without changing the system parameters (increasing the number of channels), a lower synthesis temperature, and a reduction in synthesis time compared to the approaches to synthesis in a periodic mode presented in the literature [7, 8].

Materials and Methods

In this study, silver nanowires (AgNW) were synthesized using the polyol method. The schematic representation of the synthesis process is illustrated in Fig. 1. An electric syringe pump (SPLab02, UNIX Instruments) was used to inject the solutions into the millifluidic reactor, which pumped the solutions into the reactor at a given flow rate. As in the case of synthesis in a periodic mode, a polyol process was carried out in a millifluidic reactor, i.e., the reduction of silver by means of aldehydes obtained by thermal decomposition of polyhydric alcohols. The setup in Fig. 1 was a teflon tube with an internal diameter of 1 mm., the tube was immersed in an oil bath, the solution was supplied and the flow rate was controlled by a syringe pump, the temperature was controlled by a thermocouple, and a product receiver was placed at the outlet of the heating zone and cooled with cold water.

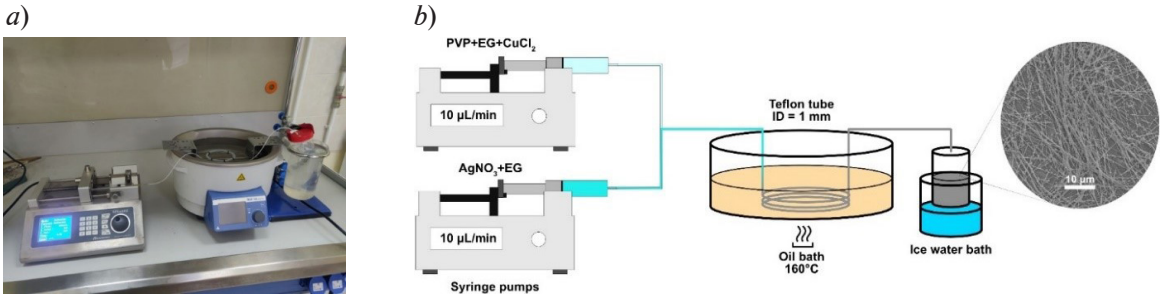

Fig. 1. Photo of experimental setup (*a*) and schematic illustration of AgNWs synthesis process (*b*)

It is known that the shape and size of Ag nanoparticles depend on such synthesis parameters as: temperature, reagent concentration and their molar ratios. Anisotropic growth of AgNWs is supported by a surfactant that covers certain faces of the growing crystal, leaving other faces free, thereby ensuring growth in one direction. In this regard, the influence of the molar ratio of surfactant to Ag becomes obvious. In the course of the work, polyvinylpyrrolidone (PVP) was used as such a surfactant. The literature reports on optimal PVP/Ag molar ratios. Some sources [9] claim that the optimal PVP/Ag molar ratio is 6/1, other sources [10] that it is 3/1, and the synthesis is also carried out at a molar ratio of 1.5 [11]. It follows that due to the complexity of the physicochemical processes occurring during the synthesis, the optimal values of the concentration parameters can vary depending on the system parameters. However, the PVP/Ag molar ratio is the most important factor influencing the morphology and size of the resulting Ag nanoparticles. Reagent solutions containing $CuCl_2$, polyvinylpyrrolidone (PVP), and $AgNO_3$ were prepared using ethylene glycol (EG) as the solvent. In the synthesis process, 40 μL of $CuCl_2$ was added to each solution of PVP and $AgNO_3$, which had concentrations of 20 mg/ml and 10 mg/ml in EG, respectively. Subsequently, 5 mL of the $AgNO_3$ solution and 5 mL of the PVP solution were injected into an oil bath through a syringe pump, utilizing a Teflon tube with a 1.0 mm inner diameter at a flow rate of 10 μL/min. The Teflon tube was coiled and immersed in an oil bath maintained at a temperature of 160°C. The duration of the reaction was controlled by adjusting the flow rate.

Ag nanowires based films were fabricated on quartz glass substrates with the use of SonoPlot GIX Microplotter II (SonoPlot, Middleton, USA). Ag NWs based inks were loaded into glass capillary with a tip inner diameter of about 340 μm, which was used for films deposition. Ag NWs based films with the size of 12×12 mm and various number of layers were printed by moving the dispenser at a speed of 10 mm/s. After printing, all the films were dried at a temperature of 100 °C for 1 hour in an air atmosphere.

Conductivity of transparent films based on a sparse grid of extended nanostructured objects with a transmission coefficient >50% (at 550 nm) can be described using a percolation theory [12]. The correlation between the transmission coefficient T and the sheet resistance R_s can be expressed as:

$$T = \left[1 + \frac{1}{\Pi}\left(\frac{Z_0}{R_s}\right)^{\frac{1}{n+1}}\right]^{-2}, \quad (1)$$

where Z_0 is the impedance of the free space (377 Ohm), n is the percolation exponent, and Π is the percolative figure of merit [12]:

$$\Pi = 2\left[\frac{\sigma_{dc,B}/\sigma_{op}}{\left(Z_0 t_{\min}\sigma_{op}\right)^n}\right]^{1/(n+1)}, \quad (2)$$

where $\sigma_{dc,B}$ is the bulk dc conductivity of the film, t_{min} is the thickness below which the dc conductivity becomes thickness dependent, σ_{op} is the optical conductivity related to the absorption coefficient α as $\sigma_{op} \approx \alpha/Z_0$.

Results and Discussion

The microstructural characteristics of the synthesized silver nanowires (AgNWs) were examined using electron microscopy. To perform the scanning electron microscopy (SEM) analysis, an AgNWs film was prepared by applying a suspension of the metallic structures in isopropyl alcohol onto a glass substrate using the drop casting method. After application, the film was dried at a temperature of 80 °C to ensure proper adhesion and removal of the solvent, allowing for detailed examination of the nanowire morphology and structure. In Fig. 2, images of the SEM of AgNWs obtained at different molar ratios are presented. As seen in Fig. 2, *a*, at a PVP/Ag molar ratio of 0.4, the product primarily consists of thick rods with a wide distribution in diameter and length, along with large spherical particles, indicating an insufficient amount of PVP. With an increase in the amount of PVP to a PVP/Ag molar ratio of 1.25, the main product consists of AgNWs (see Fig. 2, *b*). The obtained AgNWs have lengths ranging from 20 to 60 μm and diameters of 80–100 nm. Notably, as the molar ratio increases to 2.5, AgNWs are still predominantly formed; however, a slight increase in wire diameter (over 100 nm) is observed with the increasing PVP/Ag molar ratio, along with a larger amount of polymer in the resulting suspension, which needs to be removed to ensure good conductivity of the subsequently obtained films. An increase in the molar ratio to 3, as seen in Fig. 3, *c*, leads to the appearance of relatively large Ag nanoparticles. Further increasing the PVP/Ag molar ratio to 6 results in an even higher number of large Ag nanoparticles (see Fig. 2, *d*), indicating that a large amount of PVP relative to Ag results in complete coverage of all particle facets, leading to isotropic growth.

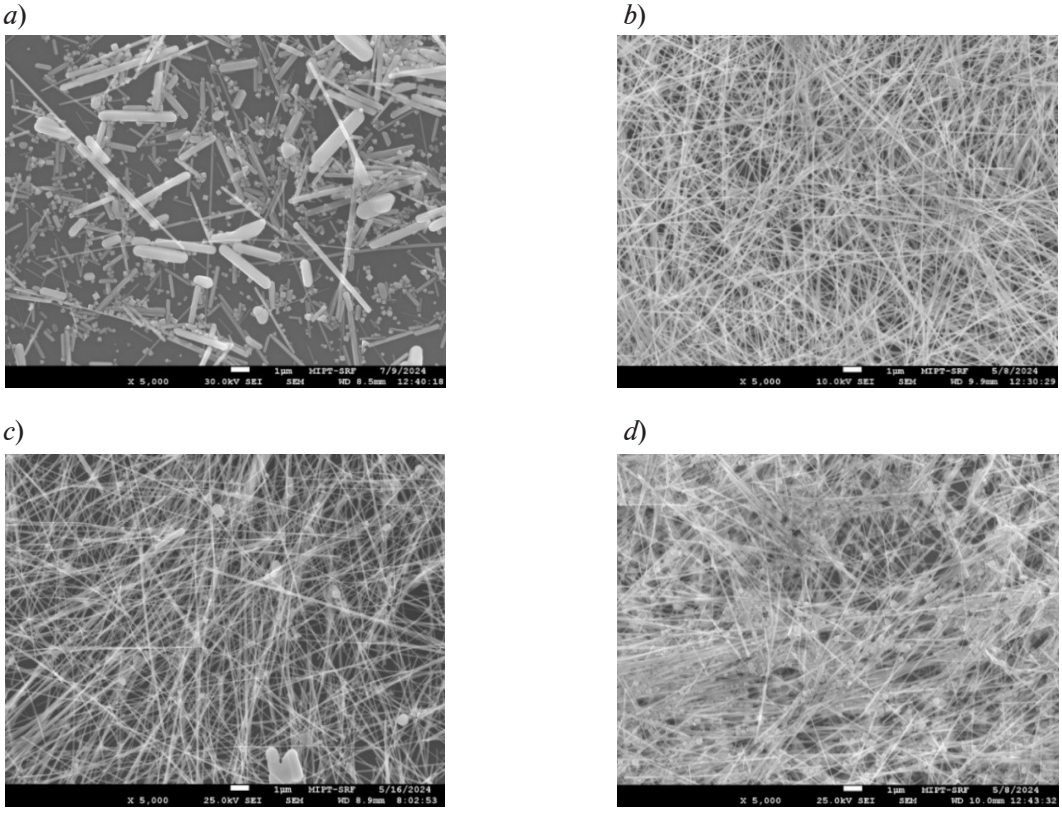

Fig. 2. SEM images of AgNWs obtained at PVP/Ag molar ratios of 0.4 (*a*), 1.24 (*b*), 3 (*c*) and 6 (*d*)

The sheet resistance of films was measured using digital multimeter APPA 505 (MGL APPA Corporation, Taipei). The transmission specrta in the range of 400–2500 nm was measured using spectrophotometer Jasco V-770 (Jasco, Easton). Fig. 3 demonstrates transmission spectra of the films (Fig. 3, *a*) and fitted dependence (according formula 1) of the film transmittance on the sheet resistance (Fig. 3, *b*), with fitting parameters on the insert.

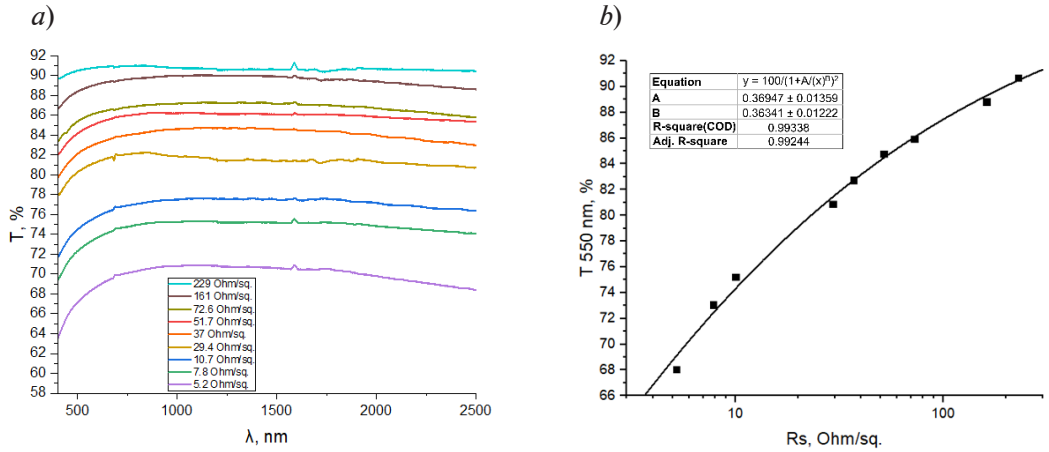

Fig. 3. Transmission spectra of dried printed films based on synthesized Ag nanowires (*a*); transmittance versus sheet resistance for printed films based on silver nanowires at a wavelength of 550 nm (*b*)

Conclusion

A study was carried out on the formation of silver nanostructures with different PVP/Ag molar ratios. It was found that PVP/Ag optimal molar ratio is 1.25, in that case the main product consists of AgNWs with lengths ranging from 20 to 60 μm and diameters of 80–100 nm. Obtained transmittance versus sheet resistance dependences of printed layers based on AgNWs are in good agreement with the theory known from the literature [7]. In addition, films with a high transparency of more than 80% were obtained at a wavelength of 550 nm with a sheet resistance of 52–229 ohms/sq. These microplotter printed films are suitable for creating transparent conductive electrodes in optoelectronic devices.

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