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Marwa Alazzawi, Nabeel Abid Alsahib and Hilal Turkoglu Sasmazel

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Marwa Alazzawi[1], Nabeel Kadim Abid Alsahib[1*], Hilal Turkoglu Sasmazel[2]

[1] Al Nahrain University, Department of Biomedical Engineering, Al Jadriya Bridge, Baghdad, 64074, IRAQ; marwa.azzawi86@gmail.com (M.A.); n_k_alsahib@yahoo.com (N.K.A.A.)
[2] Atilim University, Department of Metallurgical and Materials Engineering, Incek, Golbasi, 06830, Ankara, TURKEY; hilal.sasmazel@atilim.edu.tr
* Correspondence to: N.K.A.A. e-mail: n_k_alsahib@yahoo.com

Abstract:

The nanofibrous scaffold that mimics the extracellular matrix in structure has gained immense popularity, especially in the tissue engineering field, in the last decade. Several techniques have been utilized for fabricating nanofibrous scaffolds. Electrospinning is one of the most popular techniques to generate the nanofibrous scaffold, owing to processability, a wide variety of polymers and materials used, and affordability. This research aims to fabricate a smooth and uniform nonfibrous structure from poly (vinyl alcohol) and glycine aqueous solution. The effect of aqueous solution concentration and PVA to Gly different ratios on electrospinnability was investigated qualitatively utilizing scanning electron microscopy. Three different concentrations have been investigated 6 (w/v) %, 8 (w/v) %, and 10 (w/v) %, each one of these concentrations have been electrospun in different PVA to Gly weight ratios 4:1, 4:2, 4:3, and 4:4. The nanofibrous structure was attained with 8 (w/v) % and 10 (w/v) % with average fiber diameter in the range of 232±66 nm to 591±186 nm. Therefore, the morphology of nanofibers was attributed to the effect of solution concentration, as well as was attributed to the electrospinning parameters including needle-to-collector distance, feeding rate, and applied voltage.

Keywords: PVA; Glycine; Electrospinning; Nanofibers

1. Introduction

Poly (Vinyl Alcohol) (PVA) is one of the most synthetic biodegradable polymers used in biomedical applications. Contrary to other biodegradable polymers, PVA is water-soluble and insoluble in organic solvents; and only poorly soluble in ethanol [1]. PVA is a biocompatible, nontoxic, noncarcinogenic, non-immunogenic and inert polymer; owing to its hydrophilicity and hydroxyl group content [2,3]. Glycine (Gly) is the simplest amino acid and one of the most important elements in the human body since it is involved in the formation of protein. Furthermore, Gly is involved in the antioxidative reaction, cholesterol transport, and lipid metabolism; and it has been used as a nutrient to improve immunity, cardiovascular disease, prevent tissue injury, wound healing, and inflammatory diseases [4]. Gly can be crystallized into three polymorphic phases which are (α, β, and γ). Besides biocompatibility, biodegradability, renewable nature, affordability, and processability, it has a high shear piezoelectric coefficient and excellent mechanical properties [5].

Tissue engineering is a multidisciplinary field that aims to use a combination of cells and scaffold to regenerate damaged tissue or organ. One of the methods that has been used to fabricate the scaffold, which provides a suitable environment for cells to grow, is electrospinning [6–8]. Electrospinning is a technique that uses the electrostatic force to generate a nanoscale/microscale fibrous scaffold with interconnected pores from polymer's solution or melt. The generated electrospun nanoscale fibrous scaffold mimics the natural extracellular matrix (ECM) in tissue. For instance, bone tissue is composed of interconnected pores with high porosity, in order to facilitate vascularization and cell migration during bone regeneration [9–11].

In recent years, electrospinning has become the most popular technique to generate a nanoscale scaffold, due to its processability for both laboratory research production and industrial production. Furthermore, different two-and three-dimensional nanofibrous structures can be produced, for example, aligned nanofibers, tubular nanofibers, and coaxial nanofibers [12]. In this technique, the polymer fiber is generated at the tip of a needle and dragged to the metallic collector by an electrical force. In this respect, to overcome the surface tension of the polymeric solution and generate a "Tylor cone", as shown in Figure 1, a distinct electrical field must be generated between the needle and the collector. During this process, the solvent evaporates before the polymer dry fiber accumulates at the collector. Different physical and chemical parameters, and ratios between solvent and solute have to be controlled in the electrospinning process [13]. Table 1 demonstrates different parameters that control the electrospinning process.

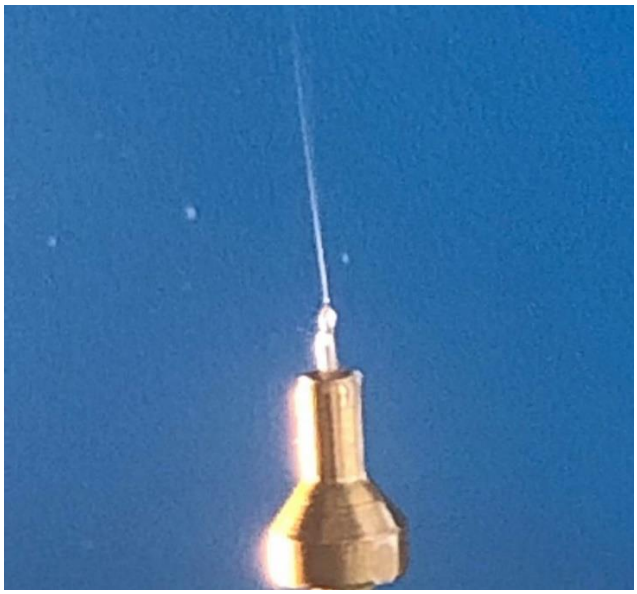

Figure 1. Tylor Cone.

Table 1. A list of electrospinning parameters that affect the final morphology of the polymer's fiber [13].

Solution Parameters	Process Parameters	Environmental Parameters
Viscosity	Voltage	Humidity
Concentration	Flow rate	Temperature
Conductivity	Shape of collector	Airflow
Dielectric constant	Needle gauge	
Surface tension	Distance	
Charge of jet	Angle	
Solvent type	Motion	
Polymer type		
Polymer molecular weight		
Polymer solubility		
Boiling point		

Although electrospinning of PVA with Glycine has been reported in the literature [14], the electrospinning parameters including polymer molecular weight, solution specific concentration, flow rate, and specific spinning voltage were not specified. Furthermore, the optimization process was not proved by scanning electron microscopy figures. Therefore, in this research, the PVA polymer was electrospun with Gly, and optimization of the processing parameters was performed to attain beadles nanofibrous structure.

2. Materials and Methods

2.1. Materials

Poly (vinyl alcohol) M_w 85,000-124,000, 99+% hydrolyzed was purchased from Sigma-Aldrich. Glycine ≥99% pure in the form of white powder was purchased from Sigma-Aldrich. Triton-X 100 was purchased from Merck (Germany). Pure water used in the solution preparation was attained in the laboratory with a water purification system using the reverse osmosis technique.

2.2. Electrospinning

The PVA/Gly solution was prepared in three different concentrations, which are 6 (wt/v)%, 8 (wt/v) %, and 10 (wt/v) % in 10 ml pure water. Each one of these concentrations was prepared in different PVA: Gly weight ratios, which are 4:1, 4:2, 4:3, and 4:4 as demonstrated in Table 2. The solution was completely dissolved utilizing a magnetic stirrer for two hours in 85-90^{o}C. Thereafter, a single jet commercial electrospinning apparatus (Inovenso NE200, Istanbul, Turkey) was utilized to fabricate the nanofibers. The fibers were collected onto a flat metallic collector covered with aluminum foil on top. In order to electrospin the PVA: Gly, the solution was fed through a 21-gauge needle (inner diameter =0.8mm), and the flow of the solution was controlled by an infusion pump.

Optimization of different concentrations and ratios of the electrospinning process was conducted under different process parameters until the one that generates electrospinning with continuity is chosen. For electrospinning process variables, the applied voltage from 10KV to 20KV (in a step of 2.5KV), a flow rate of 5µl/min, 10µl/min, and 15µl/min, and collector-to-needle distance of 7cm, 10cm, and 15cm, have been tried. Twelve samples were collected in the dissector before further use.

Table 2. Electrospun PVA and Gly different concentrations, ratios, and weights.

Concentration (w/v) %	(PVA: Gly) Weight ratio	PVA (g)	Gly (g)
6%	4:1	0.48	0.12
	4:2	0.4	0.2
	4:3	0.34	0.26
	4:4	0.3	0.3
8%	4:1	0.64	0.16
	4:2	0.53	0.27
	4:3	0.46	0.34
	4:4	0.4	0.4
10%	4:1	0.8	0.2
	4:2	0.67	0.33
	4:3	0.57	0.43
	4:4	0.5	0.5

2.3. Characterization

The morphology of electrospun fibers was characterized using Image Scanning Electron Microscopy (Zeiss EVO 15LS, Germany). The average fiber diameter, average pore size and porosity values were calculated using ImageJ Launcher software program, USA.

3. Results and Discussion

The common solvent that has been widely utilized in the literature to electrospin PVA is pure water [15,16]. Therefore, in this study pure water is used to make PVA: Gly solution. However, the water's high surface tension prevented the formation of electrospinning fibers. In order to control the formation of beads and spraying instead of fiber formation, a surfactant was needed. The surfactant has been introduced in the polymer's solution to decrease the surface tension and stabilize the electrospinning jet, and consequently overcome the beaded nanofibers problem [17]. In this respect, 0.5 ml of Triton X-100 has been added to the PVA: Gly aqueous solution [18].

We initially present the results of electrospinning 6 (wt/v) % concentration of PVA: Gly in four different ratios, with the needle feeding rate 10 µl/min, needle-to-collector distance 10 cm, and 10 kV voltage. As shown in Figure 2, that at 6 (w/v) % concentration the fibers produced contained beads for all different ratios. Based on literature studies, the solution concentration affects on solution viscosity, and therefore the formation of uniform fibers because the critical chain entanglement is attained [19]. Therefore, the solution concentration 6 (w/v) % is not enough for electrospinning of PVA with Glycine.

At 8 w/v % concentration, the feeding rate and needle-to-collector distance were the same only the applied voltage was 11.5 kV. The bead formation was decreased significantly as shown in Figure 3. In the 4 :1 PVA to Glycine weight ratio, the fibers were bead-less, although some melt-down exists. According to Akduman and Kumbasar [20], the formation of melt-down is due to the insufficient needle-to collector distance, which causes incomplete solvent evaporation.

Moreover, they showed that the raised feeding rate may cause a melt-down electrospun fibers. Therefore, in order to reduce formation of membrane-like surface instead of nanofibers either the needle-to-collector distance increased, or the feeding rate is decreased. The resulted average fiber diameter of the 4:1 PVA to Glycine weight ratio was found 346±125 nm as shown in Figure 4. Furthermore, the average pore size and porosity were calculated using ImageJ software and found to be 3.52±1.23 µm and 55%, respectively.

For the same concentration 8 (w/v) %, the electrospun fibers of PVA to Glycine weight ratios 4:2, 4:3, and 4:4 produced beaded fibers. In this regard, the formation of smooth fibers with no beads is determined by a balance between surface tension and viscoelastic force. The viscosity of the polymer's solution increases with increasing concentration [21]. In this study, the aqueous solution contains PVA and Glycine but the bead formation is mainly affected by the concentration of PVA in the solution. As shown in Table 2 that the PVA amount is less in 4:2, 4:3, 4:4 weight ratios, due to this the beads on string have formed in these ratios.

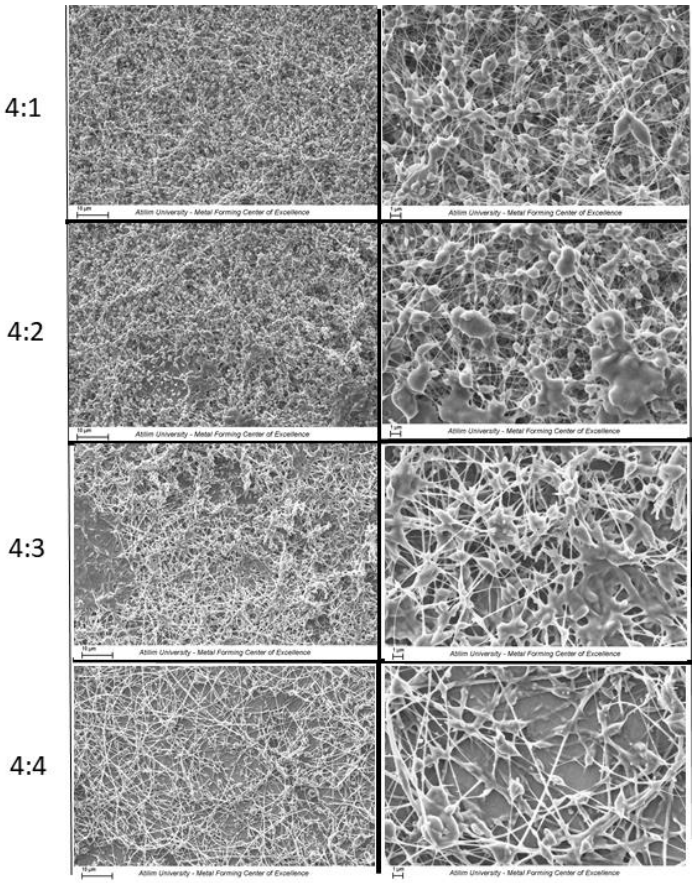

Figure 2. The SEM images of 6 (w/v) % concentration of PVA and Glycine electrospun mats in different PVA: Gly weight ratios (4:1, 4:2, 4:3, and 4:4), different marker bars are shown for each ratio (10 µm-left, 1µm right).

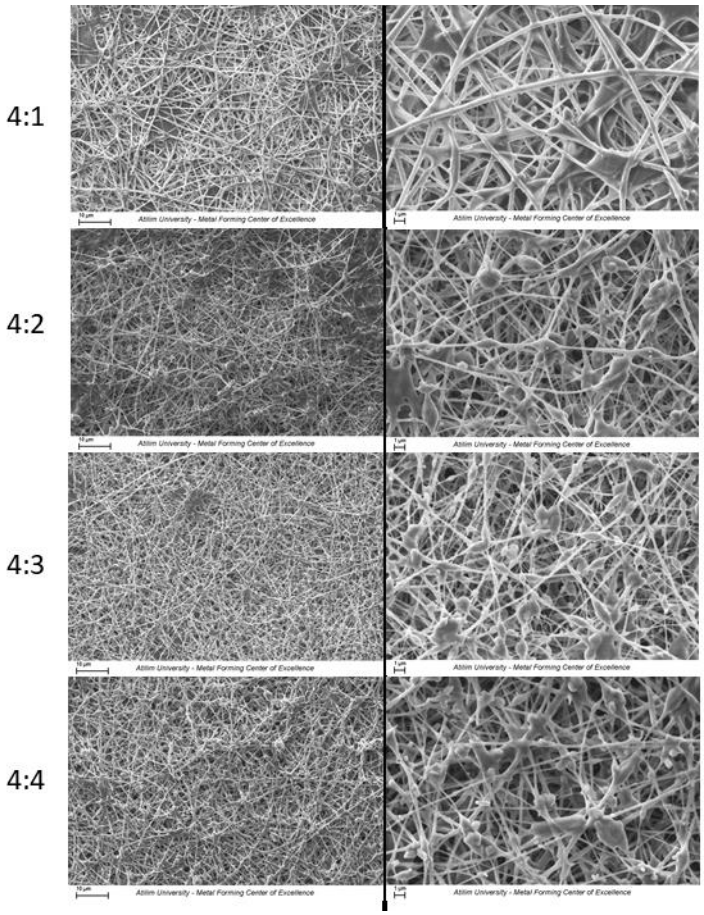

Figure 3. The SEM images of 8 (w/v) % concentration of PVA and Glycine electrospun mats in different PVA: Gly weight ratios (4:1, 4:2, 4:3, and 4:4), different marker bars are shown for each ratio (10 µm-left, 1µm right).

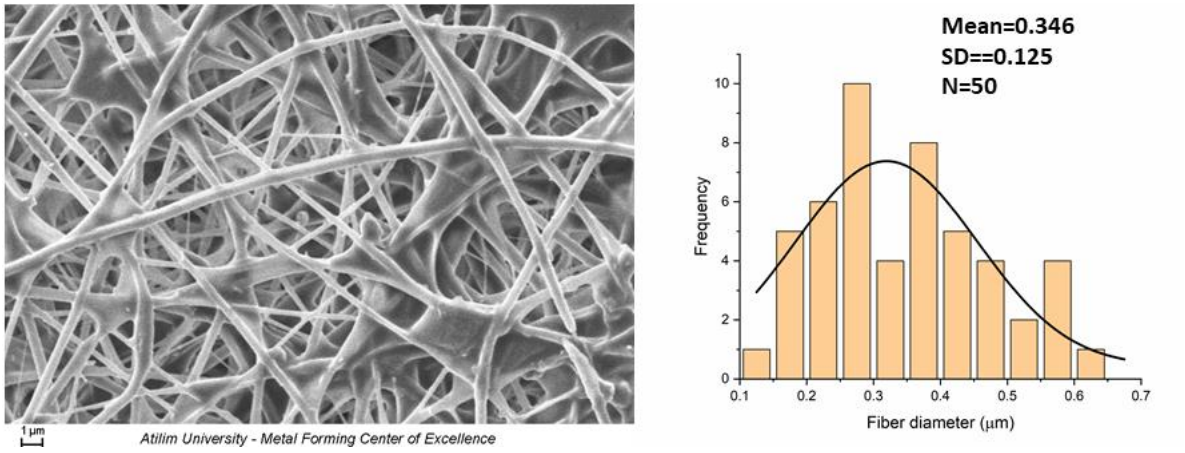

Figure 4. The SEM image of 8 (w/v) % concentration of PVA:Gly in 4:1weight ratio (marker bar=1 µm)(Left), frequency distribution and average diameter histogram of the electrospun mat (Right).

As the concentration of PVA and Glycine aqueous solution increased, absence of beads was observed. In 10 (w/v) % concentration, the electrospinning parameters (collector to needle distance and feeding rate) were the same, but the applied voltage was 12.5 kV. No beads formation was observed and smooth and uniform fibers were obtained as indicated in Figures 5 and 6. For instance, the average fiber diameter in 4:1 PVA to Glycine weight ratio was 591±186 nm and the porosity and average pore size were 65% and 30±11.18µm, respectively. Whereas, fibers in 4:2 weight ratio were highly uniform with 232±66 nm average diameter, 53% porosity, and 2.688±1.74µm average pore size.

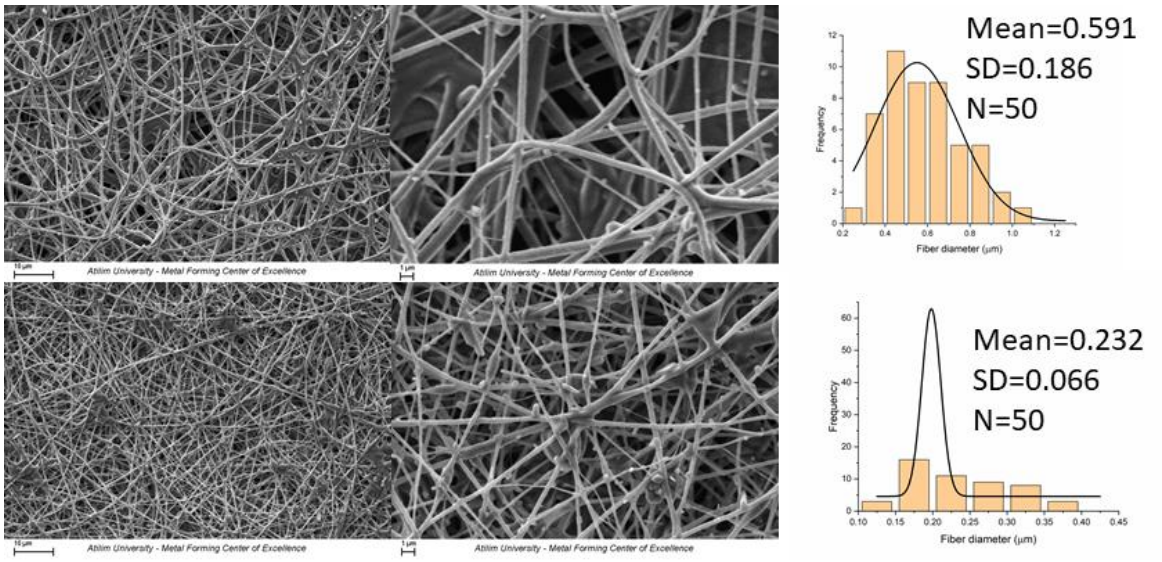

Figure 5. The SEM image of 10 (w/v) % concentration of PVA:Gly (marker bar=1 µm and 10µm), and frequency distribution and average diameter histogram of the electrospun mat for 4:1 PVA to Glycine weight ratio (up) and 4:2 PVA to Glycine weight ratio (down)

Moreover, an average diameter of 414±156nm and 270±78nm were obtained from electrospinning PVA and Glycine in 10 (w/v) % of 4:3 and 4:4 PVA to Glycine weight ratio, respectively. According to Figure 6, no beads can be observed only melt-down in 4:3 PVA to Glycine weight ratio was observed, owing to the insignificant needle to collector ratio or insignificant feeding rate which cause incomplete solvent evaporation [20]. The porosity and average pore size of 4:3 and 4:4 weight ratios, were 42%, 5.942±3.9µm, and 65%,4.418±1.94µm, respectively. In 10 (w/v) % concentration of PVA and Glycine electrospinning a very small average fiber diameter of approximately 200nm was attained, and smooth and uniform fibers can be fabricated.

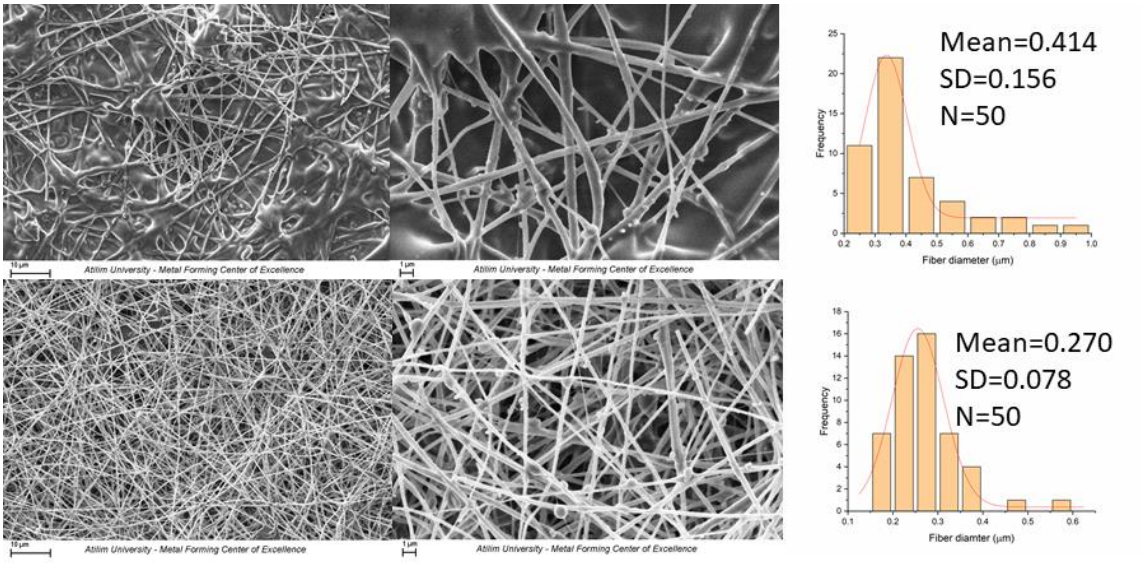

Figure 6. The SEM image of 10 (w/v) % concentration of PVA:Gly (marker bar=1 µm and 10µm), and frequency distribution and average diameter histogram of the electrospun mats for 4:3 PVA to Glycine weight ratio (up) and 4:4 PVA to Glycine weight ratio (down)

4. Conclusion

The nanofibrous electrospun structure with a high surface-to-volume ratio is ideal for biomedical applications including scaffolds and drug delivery. Even though the effect of solution parameters including viscosity, and surface parameters including needle-to-collector distance, applied voltage, and feeding rate have been studied deeply, several basic mechanisms that control nanofibrous formation are not completely understood.

In this study, the formation of PVA and Glycine aqueous solution electrospun nanofibrous structure was achieved with concentration of 10 (w/v) %. Among lower concentrations, only 8 (w/v) % concentration with 4:1 PVA to Glycine weight ration nanofibers could be attained. The average nanofibers diameter that could be fabricated was in the range of 232±66 nm to591±186 nm.

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