



Statistical models assisted solvothermal synthesis of silver nanowires with controllable morphology

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ABSTRACT

Silver nanowires (AgNWs) are conductive materials used in various applications such as solar panels and electronic skin. The morphology of AgNWs, including length and diameter, significantly affects conductivity. Despite various synthesis methods, a comprehensive understanding of how synthesis factors affect morphology is still lacking. This study focuses on solvothermal synthesis and investigates the influence of different nucleants on morphology. Through statistical analyses, including multivariate control charts and analysis of variance (ANOVA), this work demonstrates the joint effects of nucleants on AgNWs synthesis, thus setting the basis for morphology control.

1. Introduction

The morphology of silver nanowires (AgNWs), including length, diameter, and aspect ratio, affects their performance in various applications such as solar panels and electronic skin [1]. Despite various synthesis approaches, achieving desired morphology, particularly a preferable aspect ratio, remains challenging. Polyol synthesis, although versatile, is sensitive to factors like stirring speed and chemical injection rate [2]. In contrast, solvothermal synthesis has gained attention due to its cost-effectiveness and simplicity. However, improving the aspect ratio of AgNWs in solvothermal synthesis remains underexplored [3].

Solvothermal synthesis involves mixing silver nitrate (AgNO_3), polyvinylpyrrolidone (PVP), ethylene glycol (EG), and nucleants, followed by heating in an autoclave to form AgNWs. Independent studies have explored factors like temperature and the PVP to AgNO_3 ratio [4], but achieving ideal aspect ratio is challenging. Additionally, current solvothermal method is slow (5–8 h) [4,5], raising concerns about cost efficiency and highlighting the need for faster AgNWs synthesis.

To demonstrate the individual and collective effects of different nucleants on AgNWs formation [6], this study investigates sodium chloride (NaCl), iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and sodium bromide (NaBr) for controlling morphology and expediting solvothermal synthesis. Furthermore, we develop statistical tools in

Matlab to digitally illustrate the roles of nucleants in AgNWs synthesis. Our findings set the basis for controlling solvothermal synthesis and producing AgNWs with tailorable morphology.

2. Experimental details

All chemicals used, including Ethylene glycol (EG, $\geq 99\%$), polyvinylpyrrolidone (PVP) with a molecular weight of 1.3×10^6 , silver nitrate (AgNO_3 , $> 99\%$), sodium bromide (NaBr , $\geq 99.99\%$), Ethanol ($\text{C}_2\text{H}_6\text{O}$, $\geq 99.9\%$), iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.99%), and sodium chloride (NaCl , $\geq 99\%$), were analytical grades and used in their as-received states from Sigma-Aldrich (Burlington, Massachusetts, USA).

In our modified solvothermal synthesis, we studied the effect of NaCl, $\text{Fe}(\text{NO}_3)_3$, and NaBr on morphology, using a three-level, three-factor experimental design. We adjusted nucleant concentrations as follows: 300, 600, and 900 μM for NaCl; 0.75 μM , 1.5 μM , and 2.5 μM for $\text{Fe}(\text{NO}_3)_3$; and 50, 100, and 200 μM for NaBr. Specifically, PVP (23.0 mmol) was dissolved in EG (70 mL) at 100°C under magnetic stirring (890 rpm). Concurrently, AgNO_3 (3.0 mmol) was dissolved in EG (10 mL) at room temperature, and nucleants with specific concentrations were dissolved in EG (20 mL) at 50°C , using magnetic stirring at 600 and 1200 rpm, respectively. EG solutions containing nucleants and

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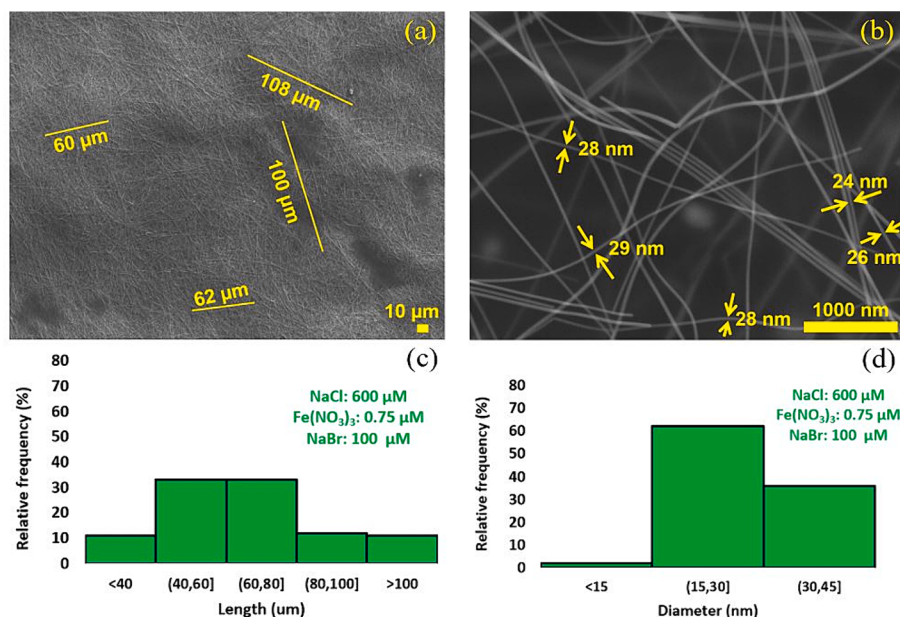


Fig. 1. (a) and (b) are two typical SEM images used to demonstrate the length and diameter of AgNWs, (c) and (d) show the distributions of the length and diameter of synthesized AgNWs.

Table 1

Exploratory experimental conditions for AgNWs synthesis to gain insights into the effect of nucleants on morphology.

NaCl (μM)	Fe(NO ₃) ₃ (μM)	NaBr (μM)	Length (μm)	Diameter (nm)	Aspect ratio
600	0	0	50	70	700
600	0.75	0	75	44	1700
600	0.75	100	68	29	2400

AgNO₃ were individually introduced into the EG solution containing PVP, followed by three minutes of stirring at room temperature. The resulting mixture was then transferred into a vacuum oven preheated to 150 °C for a 90-minute reaction without stirring. The resulting AgNWs solution was centrifuged, and the harvested AgNWs were dispersed in ethanol (20 mL) for analysis. The morphology of AgNWs was characterized using a scanning electron microscope (SEM) (JEOL JSM-7900FLV, Tokyo, Japan). A drop of AgNWs dispersed in ethanol was spread onto a carbon coated SEM holder and dried in an oven at 100 °C for 10 min. We used ImageJ to quantify length and diameter for aspect ratio calculation: 75 AgNWs per synthesis were identified from SEM images to calculate average length and 50 AgNWs were used for average diameter estimation.

3. Results and discussion

3.1. Morphological properties of AgNWs

Fig. 1 shows AgNWs' morphology of solvothermal synthesis at NaCl, Fe(NO₃)₃, and NaBr concentrations of 600, 0.75, and 100 μM, respectively. Fig. 1 (a) and (b) highlight length and diameter, thus confirming the successful synthesis of high purity materials with limited presence of other silver nanostructures. Further analysis in (c) and (d) shows that over 70 % of AgNWs exceed 40 μm in length, surpassing recent polyol method results [3,7]. Additionally, approximately 65 % of AgNWs exhibit diameters between 15 and 30 nm. In consistence with literature [6,8,9], nucleants serve as catalysts to facilitate AgNWs growth and subsequently absent in final products.

Table 1 shows exemplary results of the three-level, three-factor

experimental design, illustrating the effect of nucleants and concentrations on morphology. The absence of NaCl, Fe(NO₃)₃, and NaBr resulted in nanoparticles, thus results are not given. Independently using 600 μM NaCl resulted in an average length and diameter of 50 μm and 70 nm, respectively, yielding an aspect ratio of approximately 700. The introduction of Fe(NO₃)₃ proved crucial, achieving an aspect ratio of approximately 1700. NaBr, as the third nucleating agent at 100 μM, substantially increased the aspect ratio by decreasing average diameter to 29 nm. Although there was a slight reduction in the average length to 68 μm, the aspect ratio reached about 2400, which was 1.5 times greater than that of AgNWs synthesized exclusively with NaCl and Fe(NO₃)₃.

3.2. Statistical analysis

Multivariable control charts, as shown in Fig. 2, illustrate the varied impact of nucleants and concentrations on morphology and indicate interactions among nucleants. For example, in Fig. 2, (a-1) for 50 μM NaBr, the longest AgNWs were produced from 600 μM NaCl and 0.75 μM Fe(NO₃)₃. Additionally, the red dotted lines represent the mean values of morphology for different experimental conditions. Notably, increasing NaBr from 50 to 100 μM in Fig. 2 elevated average length, decreased diameter, and significantly increased aspect ratio. However, with 200 μM NaBr, there was a decrease in length, leading to a reduction in aspect ratio.

Data were analyzed by ANOVA to quantify interactions and assess statistical significance, as summarized in Table 2. Significant differences were found in both the *F*-statistic and *P*-value. For example, when NaCl served as the nucleant, the *P*-value for AgNWs length (0.0022) indicates dominant role in controlling morphology, given that the *P*-value is less than 0.05. Similarly, NaBr significantly affects diameter as reflected in the *P*-value (0.0043).

Comparing the results of Fig. 2 and Table 2, selective synthesis of AgNWs with preferable morphology is achieved by selecting nucleants and concentrations. In this work, optimal concentrations were identified as 600 μM NaCl, 0.75 μM Fe(NO₃)₃, and 100 μM NaBr for solvothermal synthesis. Further refinement of AgNWs is feasible through manipulation of the statistical analysis findings. For example, as in Fig. 2 (a-1), (a-2), (b-1), and (b-2), adjusting NaCl and NaBr concentrations from 300 to 600 μM and 50 to 100 μM, respectively, can result in longer and thinner AgNWs, offering a tunable approach based on the observed trends.

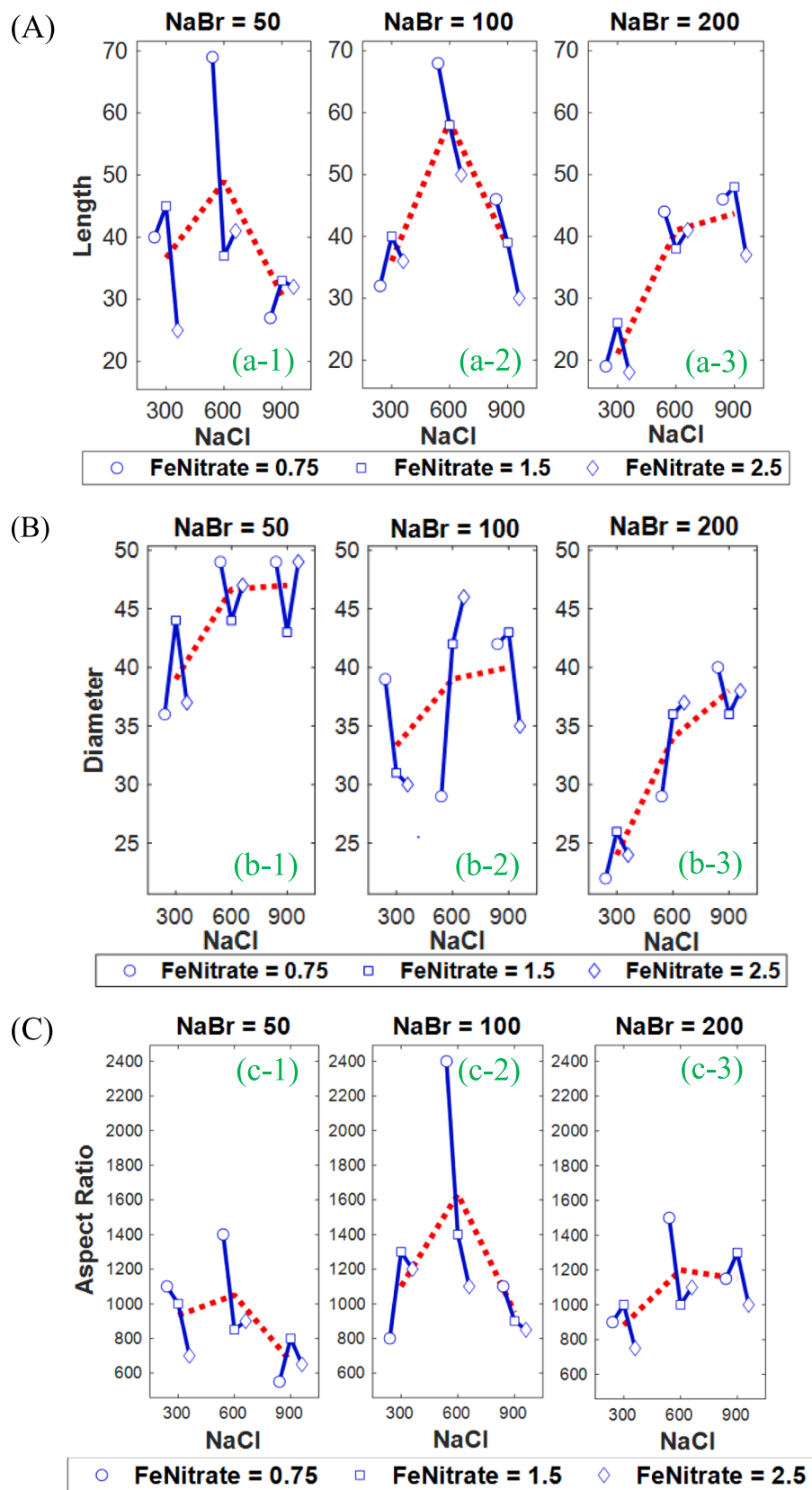


Fig. 2. Multivariate control charts for the length, diameter, and diameter of AgNWs.

Table 2
Three-ways Analysis of Variance (ANOVA).

Source	Length					Diameter					Aspect ratio				
	SSE	df	MS	F	P-value	SSE	df	MS	F	P-value	SSE	df	MS	F	P-value
A	1560.67	2	780.333	14.42	0.0022	464.89	2	232.444	7.99	0.0124	734629.6	2	367314.8	6.24	0.0233
B	378	2	189	3.49	0.0812	6.22	2	3.111	0.11	0.8998	390185.2	2	195092.6	3.32	0.0894
C	379.56	2	189.778	3.51	0.0806	674.89	2	337.444	11.6	0.0043	536851.9	2	268425.9	4.56	0.0476
A & B	412.67	4	103.167	1.91	0.2028	119.56	4	29.889	1.03	0.4489	736181.5	4	184120.4	3.13	0.0795
A & C	817.11	4	204.278	3.78	0.0520	47.56	4	11.889	0.41	0.7979	444814.8	4	111203.7	1.89	0.2057
B & C	69.78	4	17.444	0.32	0.8554	14.89	4	3.722	0.13	0.9680	24259.3	4	6064.8	0.1	0.9783
Error	432.89	8	54.111			232.67	8	29.083			470740.7	8	58842.6		
Total	4050.67	26				1560.67	26				3,337,963	26			

Note: A, B, and C in Table 2 represent three nucleants NaCl, Fe(NO₃)₃, and NaBr, respectively. SSE represents the Type III sum of squares, df denotes the degree of freedom, MS is the Mean Square, F means the F-statistic, and P-value quantifies the significance of individual nucleants on the length, diameter, and aspect ratio of AgNWs.

4. Conclusions

We used a modified solvothermal method to control AgNWs morphology, studying three nucleants and their impacts on synthesis. Ultimately, NaCl and NaBr played vital roles in length and diameter control, yielding aspect ratios around 2400 and shortening reaction time to 90 min. Our statistical analysis offers insights for researchers to form AgNWs with controlled morphology. Future work will explore adjusting AgNWs aspect ratios for enhanced functionality in sensing applications like electronic skin.

CRediT authorship contribution statement

Aryan Najjari: Investigation, Writing – original draft, Validation.
Dongping Du: Formal Analysis, Data curation, Writing – original draft.
Mary Namisnak: Investigation. **Esperanza Vazquez:** Validation.
Massimo McCormick: Investigation. **Yuncheng Du:** Conceptualization, Methodology, Project administration, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Yuncheng Du reports financial support was provided by National Science Foundation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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