Research Article

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Study on recrystallization process of nitroguanidine by directly adding cold water to control temperature

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Abstract: Nitroguanidine (NGu), as a kind of high-energy material, is widely used as explosive propellant and energy component of explosives and smokeless powder. However, NGu crystals prepared by crystallization process are hollow and long needles, and their bulk density and bombing performance are greatly limited due to the high energy density at the tip, large porosity, and poor fluidity. Surprisingly, the particle size and morphology of NGu can effectively be improved by the recrystallization process. In this article, the recrystallization process by directly adding cold water to control temperature is first proposed, aiming to improve the morphological characteristics and reduce the particle size of NGu. Through single factor experimental research, the influences of various operating parameters on the morphology and particle size of NGu during recrystallization process were studied in detail. The results showed that the smallest average particle size of NGu was 19.8 μm when the crude NGu concentration, cold water temperature, volume ratio of boiling to cold water, stirring speed, and polyvinyl alcohol concentration were 5 g/100 mL, 0°C, 1:1, 800 rpm, and 0.35 g/100 mL, respectively. Correspondingly, the morphology of NGu was short rod, which was helpful to improve the bulk density. This novel recrystallization process has great potential to improve the NGu morphological characteristics, providing a new idea for the preparation of military NGu with small particle size and high bulk density.

Keywords: direct cooling, cold water, recrystallization, nitroguanidine

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1 Introduction

Nitroguanidine (NGu) is an important organic chemical raw material, including medical raw materials, pesticide intermediates, insecticide intermediates, and the main components of explosive. As an energetic material [1], it is commonly used as explosive propellant and energy component of explosives and smokeless powder [2]. Compared to 2,4,6-trinitrotoluene, NGu has higher safety performance [3] due to the stabilization of mechanical and explosive stimulation [4]. At present, NGu is prepared by nitrating guanidine nitrate with sulfuric acid [5,6], and then, the water is added to crystallize. As a result, the obtained crude NGu crystal possesses the morphology of hollow and long needle [7]. Due to the problem of high energy density at the tip of the needle, large porosity, and poor fluidity, the bulk density and bombing performance of NGu [8–10] were severely limited. The efficient recrystallization process is expected to solve this problem and improve the military and civilian status of NGu [11,12]. Accordingly, the stress concentration phenomenon at the tip is reduced, and the mechanical properties and bulk density are simultaneously improved by reducing the particle size and improving the morphology of NGu.

The recrystallization process of crude NGu included water solvent method and organic solvent method. Using the water solvent method, the growth of NGu crystals was prevented by adding growth inhibitors (polyvinyl alcohol [PVA], sodium dodecyl benzene sulfonate, and so on) [13] to the water solvent. For the organic solvent method, anti-solvents were added to organic solvents to achieve a new partition balance and precipitate NGu crystals again [14]. The study of Zhang and Fang [15] showed that the particle size of NGu could effectively be reduced during recrystallization process by adding PVA growth inhibitors. Similarly, stirring speed and cooling rate had a crucial effect on reducing the particle size of NGu. Liu et al. [16] added a mixed growth inhibitor of methylcellulose and PVA to improve the crystal morphology of NGu during the recrystallization process. The results showed that when the concentration of methylcellulose, the concentration of PVA, the cooling rate, and the stirring speed were 1.5%, 1.5%, 0.4°C/min, and 800 rpm, respectively, the NGu crystal possessed spheroid morphology and the bulk density was greatly improved. The concentration of growth inhibitor should not be too high, and there were optimal values for cooling temperature and stirring speed. Li et al. [17] used N-methyl pyrrolidone (NMP) and acetone as solvent and anti-solvent to investigate the effects of operating parameters such as NGu/NMP concentration ratio, crystallization temperature, stirring speed, and stirring time on the particle size of NGu. As a result, the particle size of NGu could be controlled by changing the operating conditions. Among them, recrystallization temperature and stirring speed had great influence on particle size of NGu. Either way, the effect of recrystallization temperature on morphology and particle size of NGu was critical.

It is well known that crystal growth of NGu is dominated by surface diffusion and bulk diffusion, and operating factors, such as solvent, impurities, supersaturation, and temperature during recrystallization process, are very important for the nucleation and growth of NGu crystals [18,19]. Among them, the dispersion and arrangement of solvent and solute and the formation and degree of supersaturation would be affected by recrystallization temperature. When the temperature was low, the crystal nucleated in the two-dimensional direction because the crystal faces were flat; when the temperature was high, the crystal grew in the rough direction because the free energy of the rough crystal faces decreased to zero. Fortunately, recrystallization temperature was also a relatively easy condition to control in the recrystallization process [20]. Although the previous studies on the recrystallization process of NGu involved the dissolution of NGu in boiling water, the cooling rate was controlled by natural cooling or indirect cooling. This process has the characteristics of large energy loss, long cooling time, and high cost. It has not been reported that the recrystallization temperature is adjusted by direct cooling. If the recrystallization process of NGu is carried out by the means of direct cooling by adding cold water to control temperature, will it have a positive effect on improving the morphology and particle size of NGu under the premise of shortening the cooling time and reducing energy consumption?

Admittedly, the solvent degree of NGu in hot water is much higher than that in normal temperature water. At the same time, the temperature and supersaturation of nucleation ambient could also be changed by the addition of cold water at different temperatures. Under the premise of higher phase transformation driving force, namely, degree of supersaturation, the nucleation rate of NGu crystal is greater than the growth rate, and the nucleation of NGu crystals tends to be faster and smaller, which is expected to obtain NGu with small particle size [21]. Based on this analysis, a novel recrystallization process has been developed by directly adding cold water to control temperature in this study, aiming to reduce the particle size, improve the morphological characteristics, and increase the bulk density of military NGu.

2 Experimental part

2.1 Reagents

Crude NGu was purchased from Ningxia Dongwu Agrochemical Co., ltd. Its morphology and particle size are shown in Figure 1. The average particle size of NGu was 64.9 μm, and the particle size distribution of NGu was between 29 and 94 μm. PVA (Model: 0588) was supplied by Shanghai Chenqi Chemical Technology Co., ltd. Deionized water was produced by an ultra-pure water mechanism (Model: GWA-UN5F10).

2.2 Experiment

First, the three-port flask was connected to the electric stirring. The crude NGu aqueous solution with a certain concentration was added to the three-port flask after boiling for 0.2 h, and the cold water was put into the dropping funnel with different volume ratios. By controlling the dropping acceleration in the dropping funnel, each group of experiments was ensured to be added to the three-port flask within 0.5 min. After stirring and cooling to 40°C, the samples were filtered and then dried at 60°C for 10 h [22],

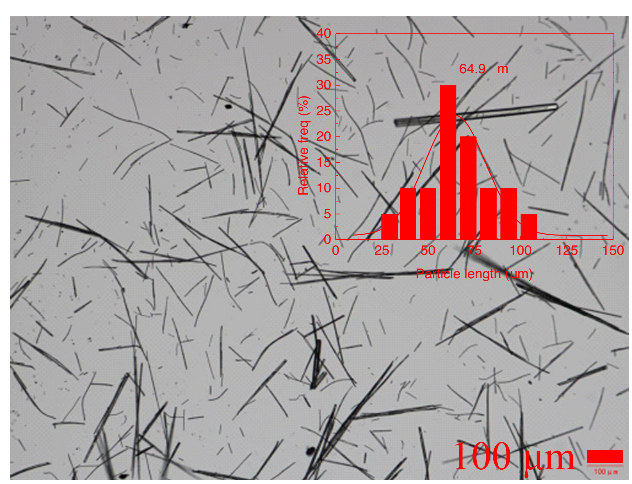

Figure 1: Morphology and particle size of crude NGu.

as shown in Figure 2. The collected samples were stored for subsequent testing.

In addition to recrystallization temperature, the growth rate of different crystal faces depends on the inherent properties of the system and recrystallization conditions, including solvent type, solute concentration, stirring operation, and additive type [18]. Among them, the supersaturation (the driving force of recrystallization process) is affected by the concentration of NGu in the recrystallization process. In the process of crystal nucleation growth, the state of solution flow is changed by stirring operation, and secondary nucleation is promoted by the solution disturbance. Crystal growth inhibitors can selectively interact with specific growth crystal faces, and the products with controllable morphology and particle size can be prepared under the regulation of crystal growth inhibitors. Therefore, the subsequent experiments mainly investigated the effects of the crude NGu concentration, the cold water temperature, stirring speed, and PVA concentration on the particle size and morphology of NGu.

2.3 Characterization

The morphology and particle size of NGu were measured by optical microscope (Model: MF43-N). Before use, the light path and focal length of the optical microscope must be adjusted until the field of view is clear under the premise of keeping clean.

3 Results and discussion

3.1 Influence of cold water temperature on the particle size of NGu

As shown in Figure 3, it can be significantly found that when the cold water with a temperature of 16 and 0°C was added to the boiling water with crude NGu concentration of 4, 5, and 6 g/100 mL, respectively, the particle size of NGu obtained by recrystallization process at 0°C was smaller than at 16°C. Obviously, the particle size distribution of NGu between 25 and 65 μm at 0°C was significantly narrower than that 35–74 μm at 16°C when the crude concentration of NGu was 5 g/100 mL, as shown in Figure 3c and d. At 0°C, the average particle sizes of NGu were 49.8, 38.9, and 60.8 μm, respectively, when the crude NGu concentrations were 4, 5, and 6 g/100 mL, as shown in Figure 3b, d, and f. Apparently, the lower the temperature of cold water added, the lower the temperature of the whole recrystallization system would become at the same time. As a result, the higher supersaturation was conducive to the formation of a large number of crystal nuclei, and the particle size of NGu obtained from recrystallization process was smaller. On the other hand, whether the cold water with a temperature of 16°C or 0°C was used as a non-solvent, the particle size of NGu was lower when the crude NGu concentration was controlled at 5 g/100 mL than that at 4 and 6 g/100 mL. Similarly, the particle size distribution of NGu between 25 and 65 μm at the crude NGu concentration of 5 g/100 mL was narrower than that between 19 and 126 μm at 4 g/100 mL and 28 and 101 μm at 6 g/100 mL. Indicatively, the crude NGu concentration was important in recrystallization process [18]. In other words, explosive nucleation environment could not be formed when the crude NGu concentration was too low, and excessive supersaturation would be obtained when the crude NGu concentration was too high. Obviously, it was possible to obtain NGu crystals with large particle size due to the great increase of the crystal nucleation and crystal growth rate at the high crude NGu concentration. It was necessary to ensure that the crude NGu concentration was in a suitable range to obtain NGu with small particle size.

3.2 Influence of volume ratio of boiling to cold water on particle size of NGu

When the volume ratio of boiling to cold water decreased, the particle size of NGu decreased obviously and then increased slightly, as shown in Figure 4. With the increase in the volume ratio, the maximum uniformity of concentration and

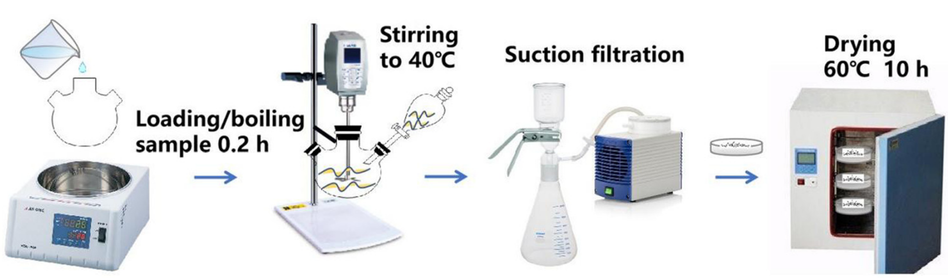

Figure 2: Schematic diagram of the recrystallization process of crude NGu.

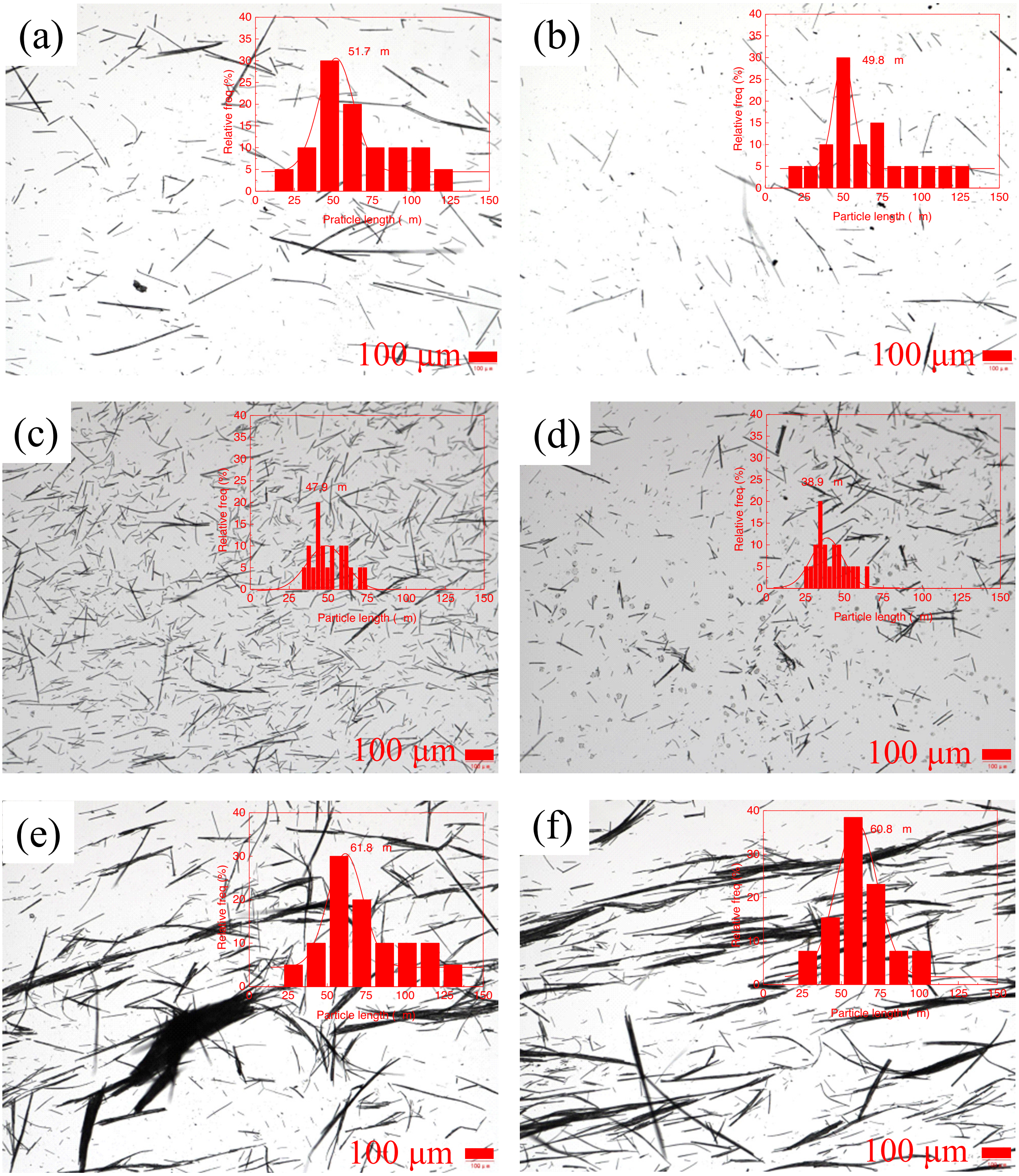

Figure 3: Morphology and particle size of NGu when the crude NGu concentration were 4 g/100 mL: (a) 16°C and (b) 0°C; 5 g/100 mL: (c) 16°C and (d) 0°C; 6 g/100 mL: (e) 16°C and (f) 0°C (stirring speed of 800 rpm and volume ratio of boiling to cold water of 1:1).

temperature was conducive to the increase of the supersaturation degree of the recrystallization zone, and the particle size of NGu decreased with the increase in nucleation rate. When the volume ratio was 1:1, the average particle size of NGu was 38.9 µm. However, it increased when the volume ratio was 1:2. Simultaneously, the particle size distribution of NGu widened from 25 to 65 µm at the volume ratio of 1:1 to 17 to 87 µm at the volume ratio of 1:2. The supersaturation degree of the entire recrystallization system reduced as the volume ratio continued to increase, and explosive nucleation environment could not be achieved. When the volume ratio was 1:2, the average particle size of NGu was 39.5 μm because the crystal growth rate was faster than the nucleation rate, as shown in Figure 4c. The aforementioned experiments showed that controlling the volume ratio of the boiling to cold water was crucial to regulating supersaturation in the recrystallization process, directly affecting the particle size of NGu [19].

3.3 Influence of stirring speed on particle size of NGu

With the increase in stirring speed, the particle size of NGu decreased first and then increased, as shown in Figure 5. When the stirring speed was 800 rpm, the average particle size of NGu was 38.9 μm. A highly dispersed and strongly mixed nucleation solution was provided by higher stirring speed, and uniform supersaturation was conducive to the nucleation and growth of NGu crystals. Under the condition of low stirring speed, the existence of non-uniform concentration region led to the formation of NGu with larger particle size [5]. As a result, NGu with larger particle size was formed under the condition of the same concentration. This stimulation effect gradually weakened as the stirring speed continued to increase, and the particle size increased and the particle size distribution widened due to the strong turbulence and fast growth rate of crystal nuclei, as shown in Figure 5c. It could be seen that the most suitable operating condition was at 800 rpm.

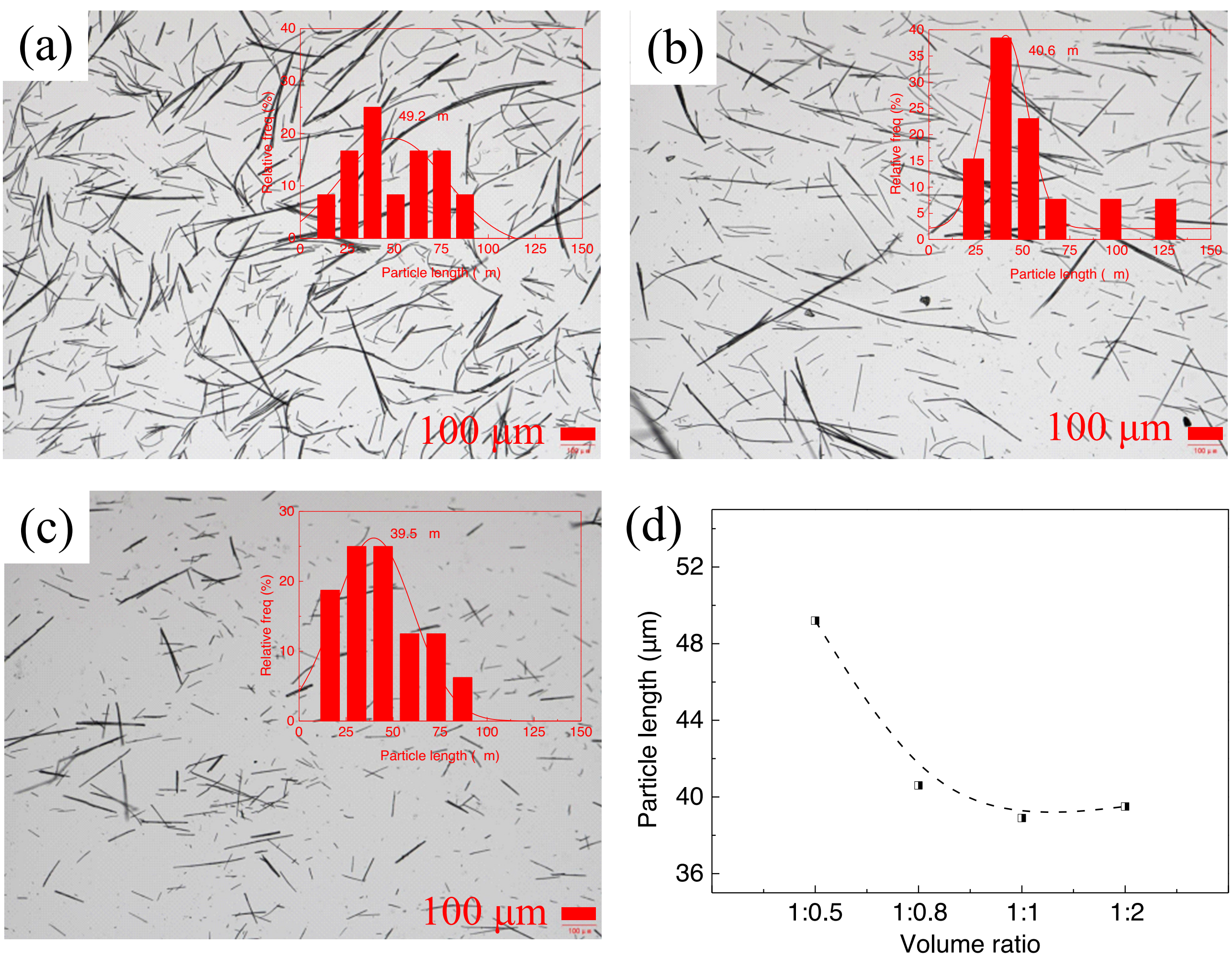

Figure 4: Morphology and particle size of NGu when the volume ratio of boiling to cold water: (a) 1:0.5, (b) 1:0.8, (c) 1:2, and (d) distribution figure (cold water temperature of 0°C, crude NGu concentration of 5 g/100 mL, and stirring speed of 800 rpm).

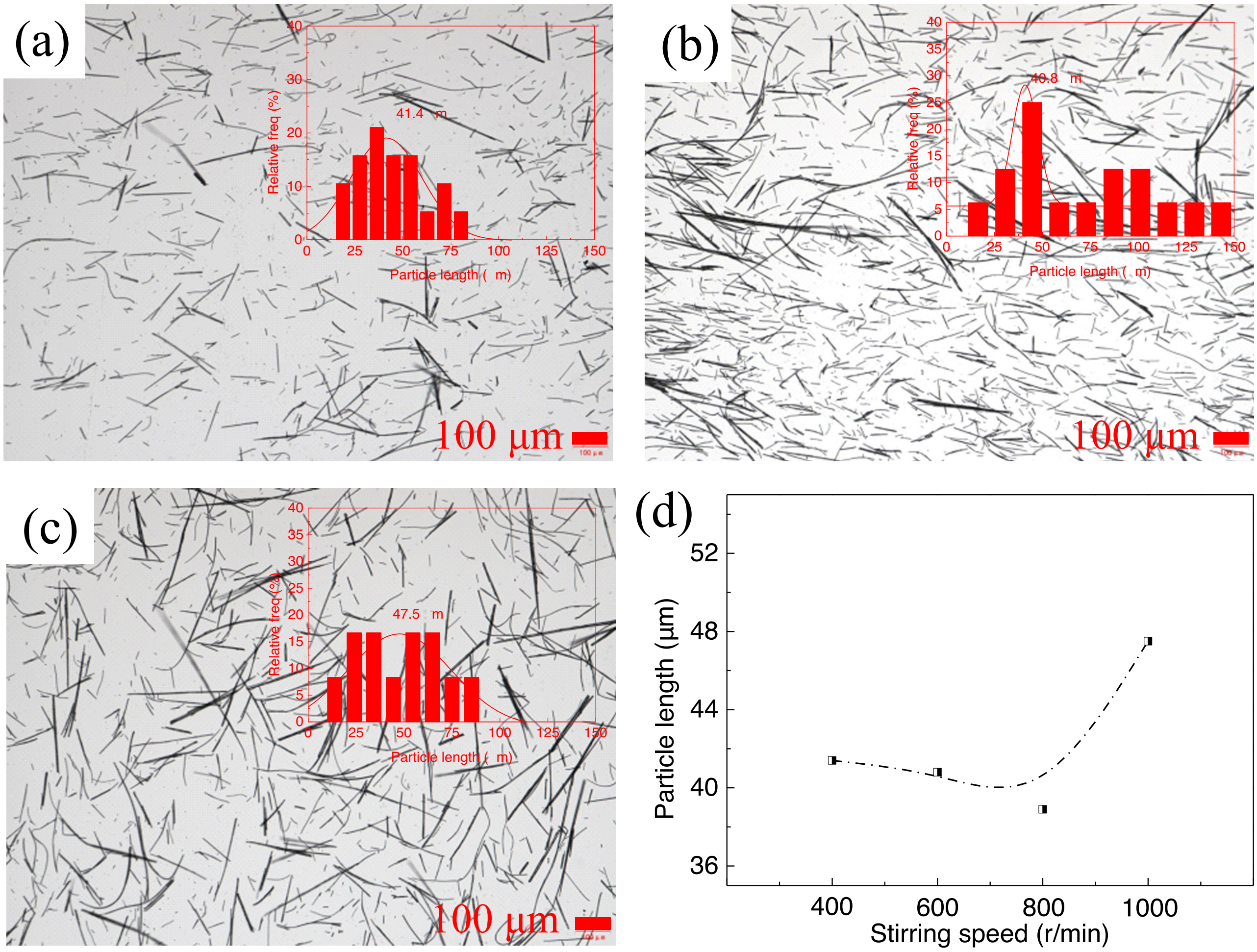

Figure 5: Morphology and particle size of NGu when the stirring speed was (a) 400 rpm, (b) 600 rpm, (c) 1,000 rpm, and (d) distribution figure (cold water temperature of 0°C, crude NGu concentration of 5 g/100 mL, and volume ratio of boiling to cold water of 1:1).

3.4 Influence of PVA concentration on morphology of NGu

The aforementioned studies showed that the particle size of NGu could be effectively reduced by recrystallization process, especially in terms of reducing the particle length, but the change of particle width was not obvious. Unfortunately, the bulk density of NGu in practical applications would be affected by the particle width. Therefore, the effect of PVA concentration on the particle size of NGu during recrystallization process was studied by adding PVA in boiling water as a crystal growth regulator. As shown in Figure 6, the particle length of NGu obtained by recrystallization process gradually decreased and the particle width of NGu gradually increased with the increase of PVA concentration. Expectantly, the overall morphology changed from long needle shape to long rod shape and finally to short rod shape and block shape [20]. The parts of the NGu crystal that grow faster were effectively inhibited by the addition of PVA [4]. When the PVA concentration reached a certain range, the growth rate of all crystal faces on the NGu crystal gradually tended to be the same level, and the crystal morphology gradually transited to blocky or even spherical. However, the particle size of NGu increased due to the increase of solution viscosity and the decrease of nucleation rate when the PVA concentration was 0.4 g/100 mL. In the experimental range, the most suitable operating condition was at 0.35 g/100 mL. The average particle size of NGu was 19.8 µm, and the particle size distribution of NGu was between 8 and 43 µm. This result was further compared to other recrystallization methods, as shown in Table 1. Obviously, the particle size distribution of NGu prepared in this study was narrower than most other recrystallization methods. Visibly, this morphology and particle size of the decrease of particle length and the increase of particle width of NGu were conducive to the

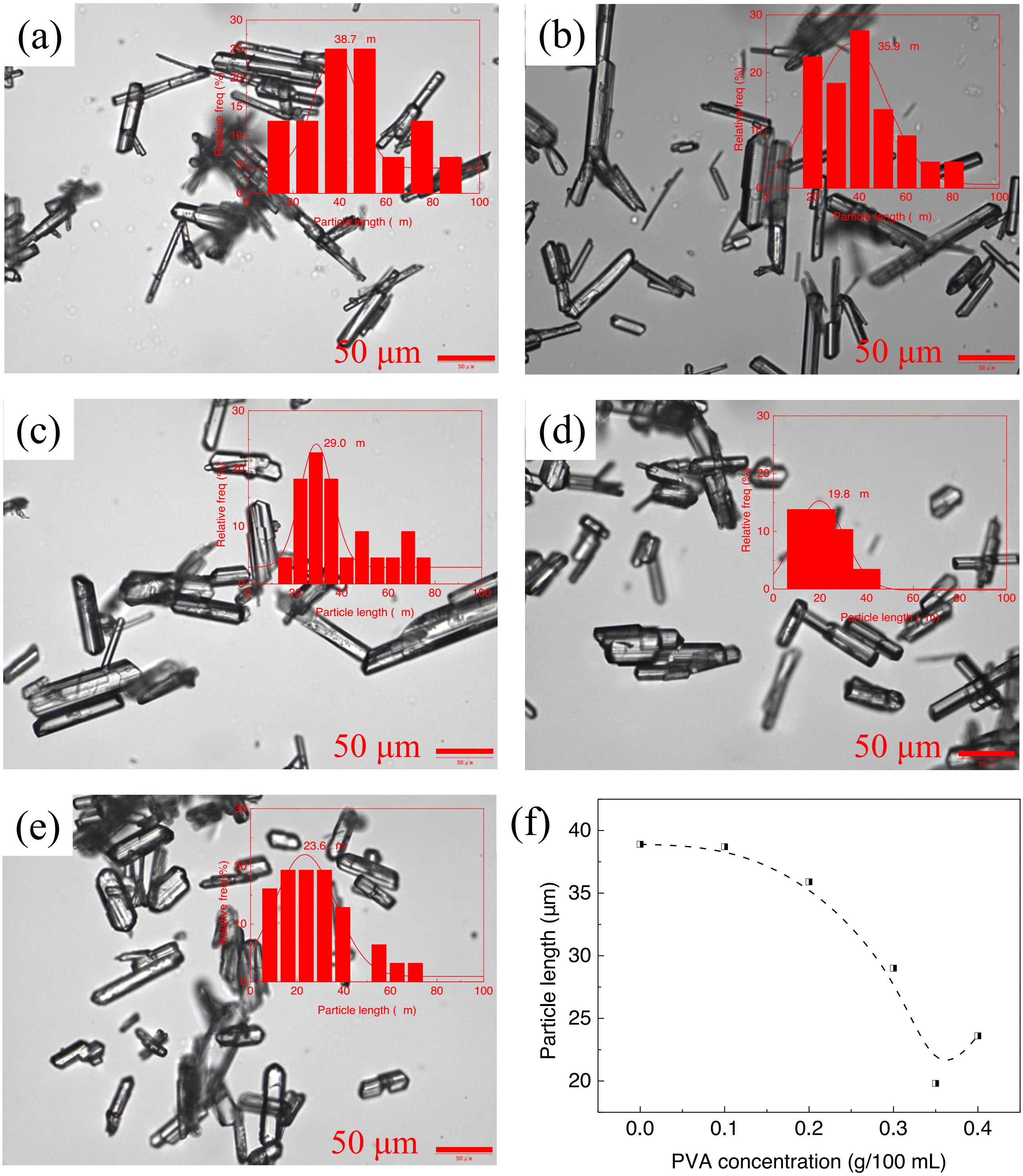

Figure 6: Morphology and particle size of NGu when PVA concentrations were (a) 0.1 g/100 mL, (b) 0.2 g/100 mL, (c) 0.3 g/100 mL, (d) 0.35 g/100 mL, (e) 0.4 g/100 mL, and (f) distribution figure (cold water temperature of 0°C, crude NGu concentration of 5 g/100 mL, volume ratio of boiling to cold water of 1:1, and stirring speed of 800 rpm).

Table 1: Comparison of particle sizes of NGu prepared by different recrystallization methods

Recrystallization method	Solvent	Particle size of NGu		Ref.
		Before recrystallization	After recrystallization	
Water solvent method	PVA	>300 μm (80%)	<300 μm (96.8%)	[15]
Water solvent method	NMP		100–200 μm	[17]
Water solvent method	PVA		178–250 μm	[23]
Organic solvent method	N,N-dimethylformamide/ ethyl alcohol	More than 20 μm	Around 20 μm	
Mechanical ball milling method		Around 20 μm	200–500 nm	
Water solvent method	NMP		50–200 μm	[24]
	N,N-dimethylformamide	50–200 μm	70–100 μm	
Organic solvent method			49–62 nm	[25]
Electrostatic spraying			318 nm	
Water solvent method and process intensification		More than 18 μm	2–6 μm	[5]
Water solvent method	PVA	29–94 μm	8–43 μm	This work

formation of higher bulk density, enthusiastically servicing for practical application on special occasions.

4 Conclusion and prospect

In this study, a novel recrystallization process by directly adding cold water to control temperature was developed first to reduce the particle size of NGu. The influences of various operating parameters, including the crude NGu concentration, cold water temperature, volume ratio, stirring speed, and PVA concentration, on the morphology and particle size of NGu during recrystallization process were studied in detail. The degree of supersaturation in the recrystallization environment would be affected by the crude NGu concentration and volume ratio. The cold water temperature and stirring speed had the great influence on the cooling rate, and the PVA concentration should not be too high. In the experimental range, the most suitable operating conditions were the crude NGu concentration, cold water temperature, volume ratio, stirring speed, and PVA concentration of 5 g/100 mL, 0°C, 1:1, 800 rpm, and 0.35 g/100 mL, respectively. Correspondingly, the average particle size of NGu was 19.8 μm, the particle size distribution of NGu was between 8 and 43 μm, and the morphology was short rod, which was conducive to the improvement of its bulk density compared with crude NGu. This novel recrystallization process has great potential to improve the NGu morphological characteristics, providing a new idea for the preparation of NGu with small particle size and high bulk density. Simultaneously, this technology has wide application prospects and significant advantages in cost saving and process optimization, and it is expected to produce military NGu with high bulk density and bombing performance in large quantities after the technology is mature. The popularization of this technology still needs solid theoretical basic research, including the transformation and formation process of NGu crystal at different recrystallization temperatures, the effect of nucleation environment on particle size distribution, and the influence of process intensification technology and control methods on the transformation of crystal morphology.

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Ethical approval: The conducted research is not related to either human or animal use.

Data availability statement: The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request.

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