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Comparison of particle size and standard deviation of TiO_2 particles prepared by batch, semi-batch and continuous reaction method

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Abstract

A new preparation method for TiO_2 nanoparticles was introduced, which consisted of a small reactor for controlling the hydrolysis rate and continuous aging tube for reducing the size and standard deviation of TiO_2 particles. In this process, TiO_2 nanoparticles were synthesized from the hydrolysis and condensation of TEOT without HPC dispersant. The particles prepared by using a continuous reaction method without dispersant had a smaller mean particle size and a smaller standard deviation than those obtained from batch or semi-batch processes using dispersant. In this work, it was also found that the size of TiO_2 particles decreased by applying intermittent flow to the aging tube. By using the above conditions, mean diameters as small as 30 nm were obtained. © 2002 Published by Elsevier Science Ltd.

Keywords: Continuous reaction method; Powders-chemical preparation; Reactor system; TiO_2

1. Introduction

Particles, such as Al_2O_3, SiO_2,[1, 2] Ta_2O_5, TiO_2,[3–5] SiC, ZrO_2, and $BaTiO_3$ are prepared by the hydrolysis of metal alkoxides in a dilute alcohol solution and the thermal hydrolysis of the metal salts in an aqueous solution. Of these particles, TiO_2 has been studied extensively because of its wide applications in pigments, photocatalysts, fillers, coatings, and photoconductors.[6, 7] TiO_2 is obtained either from its minerals or from a solution of titanium salts or alkoxides.[8, 9] In recent years, significant research has been focused on TiO_2 nanoparticles. Spherical nanoparticles with a narrow size distribution, desirable for producing advanced ceramics with enhanced reliability, have been prepared by chemical methods.

In general, the synthesis of particles has been developed by a batch or semi-batch process. In addition, Kim et al.[10] have already prepared TiO_2 nanoparticles by hydrolysis of TEOT (tetraethylorthotitanate) in a semi-batch/batch two stages mixed process. However, on an industrial scale, the batch and semi-batch process are not suitable; a continuous process is required for mass production. The stirred tank reactors used in industrial processes usually tend to produce powders with a wide particle size distribution because of the wide distribution of residence times in reactors. Therefore, the residence time of particles in a stirred tank reactor must be constant for the continuous precipitation of monodispersed particles.

To produce monodispersed nanoparticles at high efficiency, it is necessary to develop a continuous synthesis system. Jean et al.[11] have proposed a continuous method using packed bed or static mixer reactors. In their method, the aging of fine particles is performed in a batch tank reactor. As pointed out by Ring et al.,[12] however, the production of ceramic powders by a batch process has many disadvantages. Quality variation occurs with every operation. Operational cost is high and productivity is low. It is therefore necessary to construct a continuous process.

In this paper, an improved continuous process is proposed in which a small reactor for controlling the nucleation rate is connected in series with an aging tube for controlling the growth of particles. The hydrolysis rate is controlled by the vaporization of H_2O and the feed rate of TEOT solution, respectively. In addition, by controlling the parameters affecting to the particle size

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in the aging tube, nanoparticles can be obtained. The objectives of this work are: (1) to suggest a new method for the synthesis of TiO_2 nanoparticles, (2) to compare the particle size and standard deviation of TiO_2 particles prepared by batch, semi-batch and continuous reaction method, respectively.

2. Experimental procedure

2.1. Starting solutions

In this present work, the starting solutions were TEOT (99%, Aldrich Chemical Co.), ethanol (99.9%, Sigma Chemical Co.) solution with hydroxypropylcellulose (HPC, molecular weight ~100,000, Aldrich Chemical Co.), and water-ethanol solution. HPC was used as a dispersant to prevent agglomeration during particle growth. The reactants were used without any purification. The solutions were prepared in a glove box at room temperature under dry air. The humidity in the glove box was kept below a few percent.

2.2. Preparation and analysis of TiO_2 nanoparticles

Monodispersed spherical TiO_2 nanoparticles were prepared by the hydrolysis of TEOT using a batch, semi-batch and continuous reaction method, respectively. A schematic diagram of the continuous synthesis reactor system designed for this work is shown in Fig. 1. The apparatus consists of the following sections; (1) small reactor (100 ml) for two feed reagents (vaporized water and TEOT) with an ethanol solvent, (2) a syringe pump (Kd scientific, Model 100) to supply the vaporized H_2O/Et(OH) solutions with a constant feed rate (0.040–0.306 ml/min) and a micro feed pump (EYELA, MP-3) to supply the TEOT/ Et(OH) solutions with a constant feed rate (0.66–1.10 ml/min), (3) a heating tape for vaporizing the H_2O, and (4) a long silicon tube (diameter: 3.0 mm) for aging of the particles. The aging tube is placed in a water bath at a constant temperature and can be changed for desired length and diameter. At the entrance of the aging tube, there is a valve to control the flow rate of solutions after mixing of TEOT and vaporized H_2O. The two feeds are continuously supplied to the small reactor. Primary nuclei of titanium dioxide are generated by the polymerization of the hydrolysis product while passing through the small reactor. A part of them is grown to fine particles while passing through the aging tube.

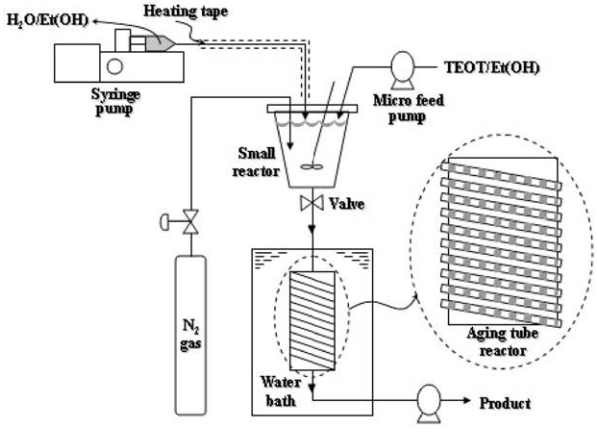

Fig. 1. Schematic arrangement of continuous reactor set-up.

In this continuous reactor system, two methods for preparing nanoparticles with narrow size distribution were used. One is the vaporized H_2O/Et(OH) solution by which slower hydrolysis rate of TEOT is induced, resulting in prevention of agglomeration of particles. The other is intermittent flow in the aging tube described as shown in Fig. 1. The possibility of an increase in particle size and agglomeration can be minimized by using this intermittent flow. The ways for changing the flow type in the aging tube are N_2 gas injection and valve handling. Firstly, at the entrance of the aging tube, there is another inlet to feed the N_2 gas. So, the feed liquids and the injected N_2 gas form an intermittent flow in the aging tube. Secondly, the flow type of solution in the aging tube can be controlled by adjusting the valve placed in the middle of the small reactor and the entrance of the aging tube. By using these two methods, the continuous flow in the aging tube can be separated into small portions. In this study, the latter is applied because the N_2 gas injection method is not suitable to mass production.

A schematic diagram of the batch and semi-batch reaction method is shown in Fig. 2, respectively. For the semi-batch reaction, a micro feed pump with a constant flow rate (1.1 cm^2/min) fed the starting solution A (TEOT, HPC, and ethanol) into the reactor with another solution B (water and ethanol). The reaction mixture was vigorously stirred for 60 min. The TiO_2 alcosols were transferred out of the reactor and the powders were washed with ethanol by repeated centrifugation (at 3000 rpm for 5 min) and dried at 70 °C for 12 h. A laser particle size analyzer (Otsuka electronics, LPA-3000, 3100) was used to determine the particle size and size distribution presented in Figure 2 of this paper. To confirm the results,a scanning electron microscope (SEM, JEOL JSM-T330, Japan) was also used.

3. Results and discussion

3.1. Effect of HPC dispersant on particle size and standard deviation

With the HPC dispersant used during the particle formation, the resulting particle nucleation, particle size, number density, and agglomeration are all greatly

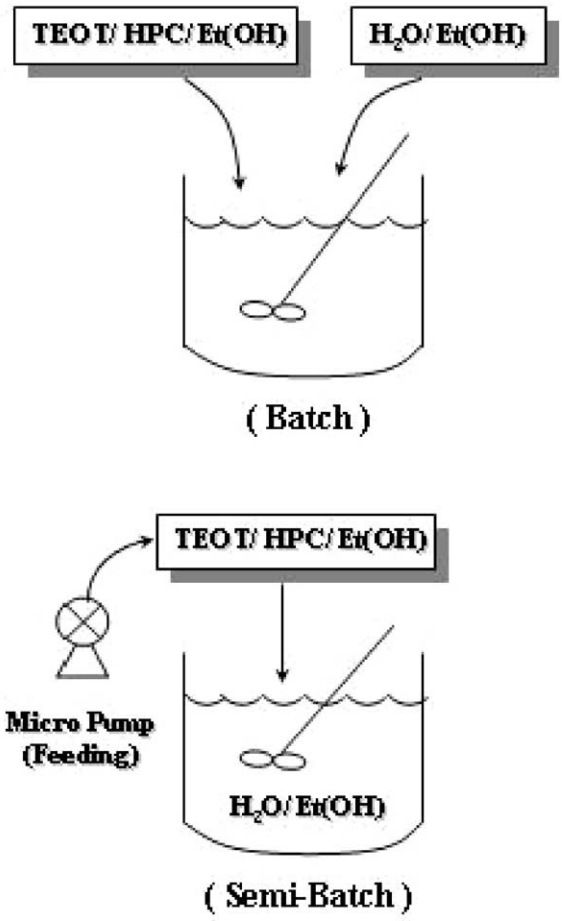

Fig. 2. Schematic diagram of batch and semi-batch system.

affected. The enhanced nucleation is caused by the association between the nuclei and the dispersant, which reduce the capture rate of the existing particles and increase the particle formation rate. Moreover, the interfacial free energy between the TiO_2 aggregate and the solution is reduced by the adsorption of the dispersant onto the aggregate surface. This then reduces the activation energy for homogeneous nucleation. The effect of HPC concentrations on the particle size and the standard deviation using a batch and semi-batch reactor for 0.075 M TEOT and 6.0 M H_2O is given in Figs. 3 and 4, respectively. The particle size was 315.3 nm (batch) and 127.3 nm (semi-batch), respectively, for the solution without HPC. When the HPC (0.01 g/100 ml) was added, however, the particle size decreased to 112.3 nm (batch) and 56.3 nm (semi-batch), respectively. Fig. 4 shows the same results. When the dispersant HPC was used, the standard deviation of particle size decreased to ± 5–7% for all reaction methods (batch and semi-batch).

These results can be explained by Fig. 5. Fig. 5 schematically depicts how HPC has a noticeable effect on the resulting particle morphology. TiO_2 particles made without HPC are agglomerated, but those made with

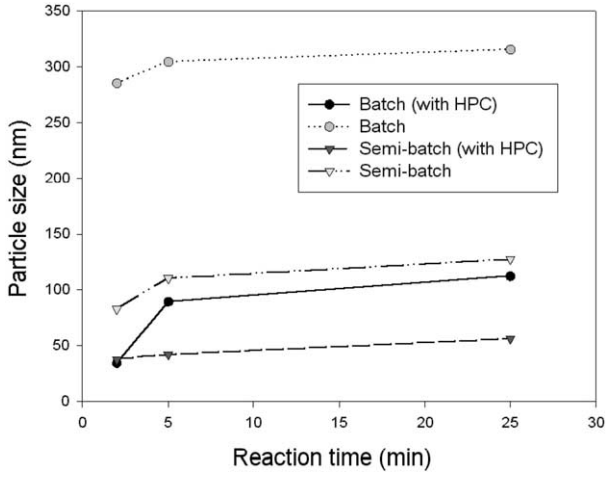

Fig 3. Effect of HPC dispersant on particle size under batch and semi-batch reaction.

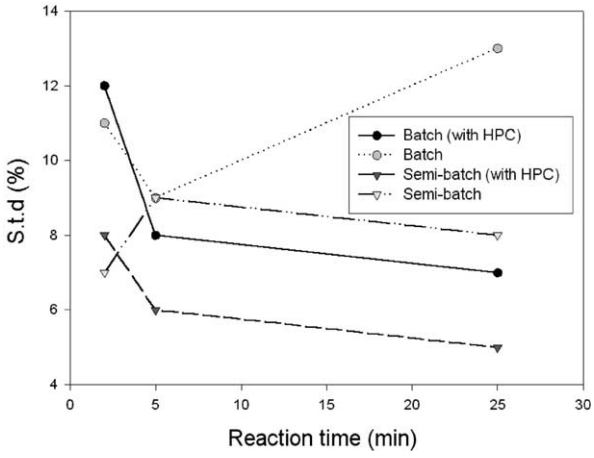

Fig. 4. Effect of HPC dispersant on standard deviation under batch and semi-batch reaction.

HPC have a narrower particle size distribution. Because the HPC adsorbed on to the TiO_2 particles during growth, provides a steric barrier to aggregation.

3.2. *Effectiveness of continuous reaction method for reducing the particle size*

Fig. 6 (a) and (b) shows how the reactor system has a remarkable effect on the particle size and size distribution. TiO_2 fine particles through a batch process (a) were not enough to obtain the particles with a narrow size distribution. On the contrary, a semi-batch process (b), in which system reactants are fed into the reactor with a constant feed rate is easier than a batch process in controlling the size, shape, and size distribution because of the short nucleation and slow hydrolysis rate.

The effect of the flow type in the aging tube is shown in Table 1. If the flow type in the aging tube was inter-

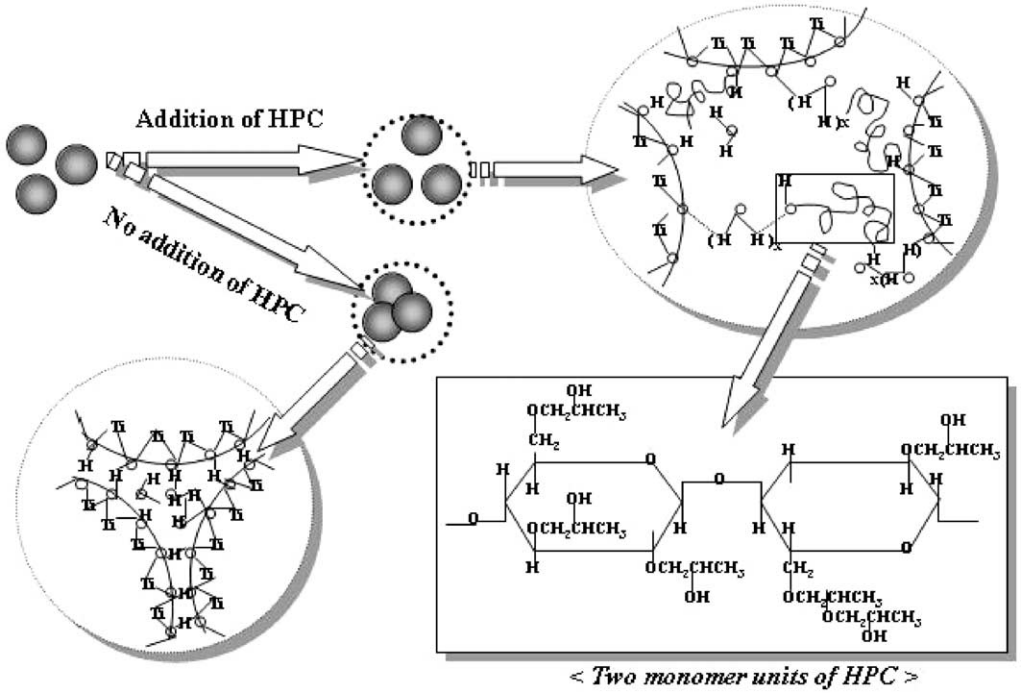

Fig. 5. Schematic diagram of the effect of HPC dispersant on particle size and standard deviation.

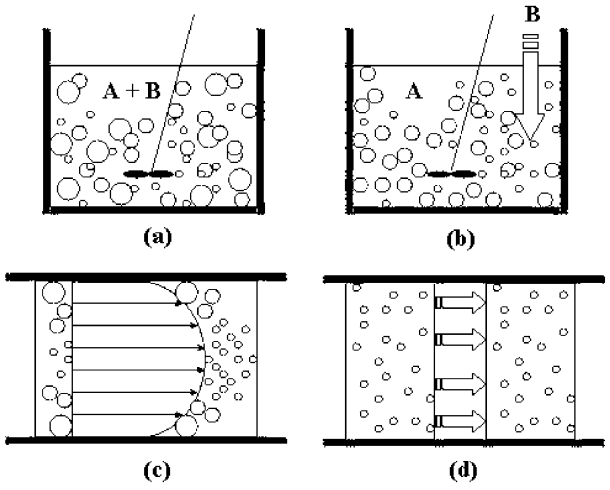

Fig. 6. Comparison of particle growth in the aging tube (a) batch, (b) semi-batch, (c) continuous flow and (d) intermittent flow.

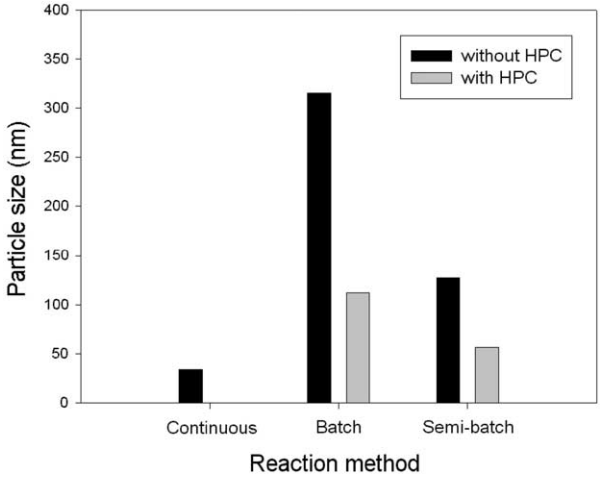

Fig. 7. Comparison of particle size according to the reaction method.

Table 1
Effect of flow type in the aging tube during growth period

	Continuous flow	Intermittent flow
Particle size (nm)	162.6	34.0
S.D. (%)	±8.4	±5.0

mittent, nanoparticles (34 nm) with a narrow particle size distribution (±5.0%) were synthesized. In contrast, for continuous type in the aging tube, the particle size of TiO_2 increased to 162.6 nm with a broad particle size distribution. The explanation for this result is schematically shown in Fig. 6(c) and (d). Continuous flow in the aging tube [Fig. 6(c)] is responsible for a rather wide range of the residence time distribution of the particles. Particles flowing in the center region of the tube have a shorter residence time, which means that they flow out for a shorter reaction time and smaller particles are generated. On the other hand, particles flowing in the vicinity of the tube wall grow to a larger size due to the longer residence time. By controlling the valve into the inlet of the aging tube, as shown in Fig. 6(d), the continuous liquid feed is separated into small portions. This intermittent flow in the aging tube is analogous to many

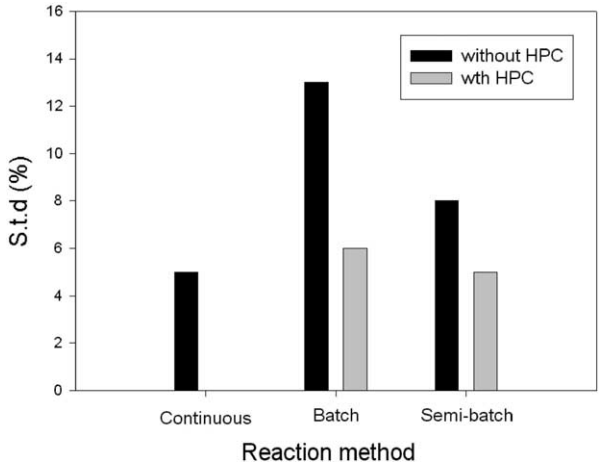

Fig. 8. Comparison of standard deviation according to the reaction method.

small batch reactors passing through the aging tube at constant velocity, so the residence time of the liquid suspension in the aging tube leads to the same reaction time for all particles.

3.3. Comparison of the particle size and standard deviation

The effect of reaction methods using a batch, semi-batch and continuous reactor for 0.075 M TEOT and 6.0 M H_2O on the particle size and the standard deviation is shown in Figs. 7 and 8, respectively. When dispersant HPC was used in batch and semi-batch, particle size and particle size distribution decreased. However, for the continuous reaction without HPC, the particle size (34 nm) was much less than that for the batch (112 nm) or semi-batch (56 nm) processes using HPC. In addition, standard deviation showed almost the same results. The advantages of the HPC dispersant were referred to in the previous section. In spite of these advantages, however, the resulting particles appeared to be formed of agglomerates of much smaller subunits and, because of this low density, they exhibited poor sintering characteristics. Therefore, it is desirable that if possible, dispersant is not used. Fig. 9 shows the comparison of SEM photos according to the reaction method [(a) batch (with HPC), (b) semi-batch (with HPC), (c) continuous reaction method (no HPC)]. From

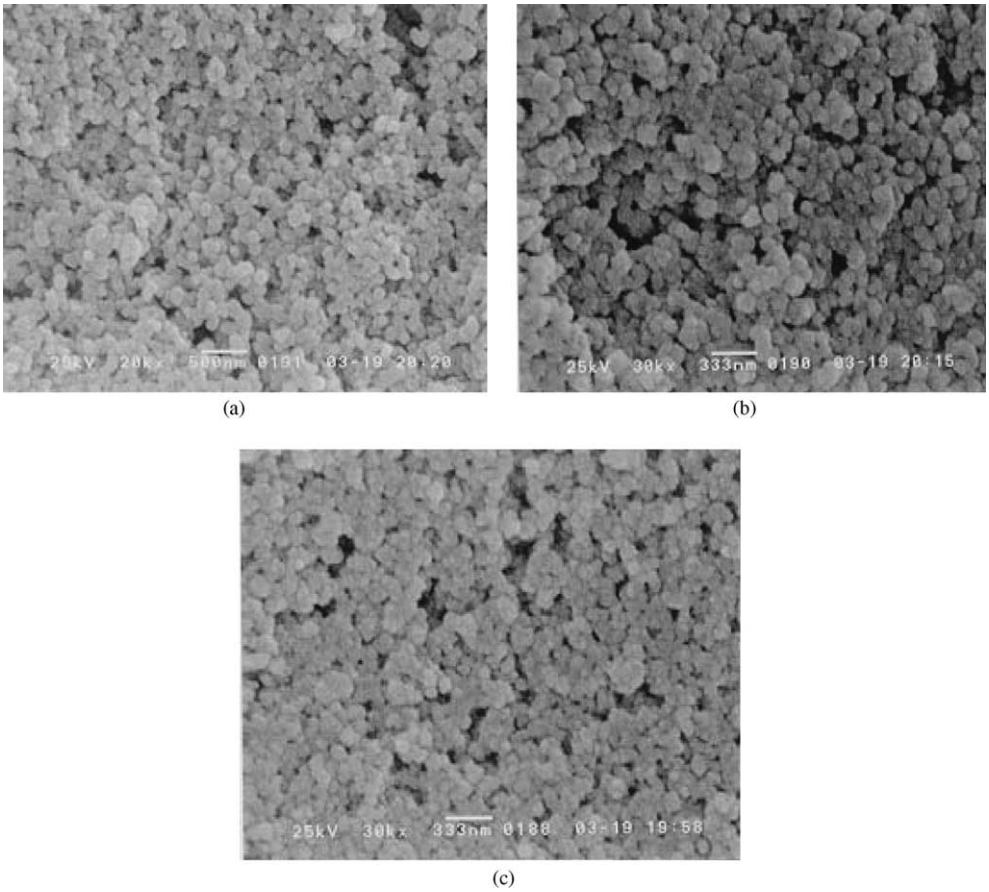

Fig. 9. Comparison of SEM photos according to the reaction method. (a) Batch (with HPC), (b) semi-batch (with HPC) and (c) continuous reaction method (no HPC).

the SEM photos, it was found that the particles prepared by the continuous reaction method without HPC was similar in morphology to particles formed by batch and semi-batch systems using HPC.

4. Conclusions

Continuous synthesis of titanium dioxide by the alkoxide method was compared with batch and semi-batch system, and the following information was obtained. (1) Particle size and standard deviation decreased by using dispersant HPC. Because the HPC was adsorbed on to the TiO_2 particles during growth, it provided a steric barrier to aggregation. (2) An intermittent flow condition in the aging tube of a continuous reactor yields nanoparticles of better quality than continuous flow type. (3) It was found that the particles prepared by continuous reaction method without HPC had a smaller particle size and size distribution than those formed by batch and semi-batch systems using HPC. In addition, the above-mentioned continuous reaction method was used to prepare the particles with minimum particle size (<40 nm) and its standard deviation ($<\pm 5.0\%$), simultaneously.

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