The Effect of Polyvinyl Alcohol Concentration on the Growth Kinetics of KTiOPO₄ Nanoparticles Synthesized by the Co-precipitation Method

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Abstract

KTiOPO₄ nanoparticles are known as the best candidate to utilize for second-harmonic generation in multiphoton microscopes and bio labels. Size and shape are important and effective parameters to control the properties of nanoparticles. In this paper, we will investigate the role of capping agent concentration on the size and shape control of KTP nanoparticles. We synthesized KTP nanoparticles by the co-precipitation method. Polyvinyl alcohol with different mole ratios to titanium ion (1:3, 1:2, 1:1) was used as a capping agent. Products were examined by X-ray diffraction patterns and scanning electron microscopy analyses. X-ray diffraction patterns confirmed the formation of the KTP structure. The biggest (56.36 nm) and smallest (39.42 nm) grain size were obtained by 1:3 and 1:1 mole ratios of capping agent, respectively. Dumbly, spherical and polyhedral forms of KTP nanoparticles were observed by the change in capping agent mole ratio. The narrowest size distribution of KTiOPO₄ nanoparticles was obtained at 1:1 mole ratio of capping agent.

Keywords: Co-precipitation Method; Nanoparticles; Potassium Titanyl Phosphate; Size Control; Shape Control.

1. Introduction

Potassium titanyl phosphate (KTiOPO₄ or KTP) single crystals are excellent nonlinear optical materials [1-3]. Also, they have important technological applications in laser frequency mixing and waveguides [4]. They are a good ionic conductor [5, 6] and a piezo-optic material [3]. Many valuable properties of this crystal have made it a standard material in many industrial, medical, and other applications. A study on the growth conditions of KTP single crystals to improve in their properties for different applications [7-9], especially for SHG, was started in the late nineteenth century. Now, these crystals are industrialized, but there are a few reports of the same studies on KTP nanocrystalline. In recent years, nanoscience and technology have potential applications in the field of science and technology. Because of it, the attention of scientists has been focused on production of KTP nanostructures. Different applications were reported for these nanoparticles, such as second harmonic generation [10], charged nanofiltration membranes [11], and bio-labels [12]. The size and shape of nanocrystals act as critical parameters for determining materials properties. Therefore, precise control of the size and shape of nanocrystals, results in desired chemical and physical properties. Pechini [13], Sol-gel [14], mechanochemical mixing [15], combustion [16], co-precipitation [17, 18], and hydrothermal [19] methods have been used to prepare KTP nanostructures. Mechano chemical, sol-gel, and pechini are primitive methods for the synthesis of KTP nanoparticles. Among these methods, there are problems such as expensive raw materials, the presence of OH^- ions in products, and weakness in the shape control of nanoparticles.

The co-precipitation is known as an appropriate, cheap, and simple method for controlling the size and shape of nanoparticles [20-22]. In this method, by controlling the relative rate of nucleation and growth during the nanoparticles synthesis process, shape, size, and its distribution will be controlled. For nanocrystals prepared by solution-based chemical methods, a capping agent, generally is added to control the size and shape of nanocrystals. Capping agents with selective adsorption to specific crystal faces could be used to kinetically control the single-crystalline growth. Also, it plays an important role in the formation of nanocrystals morphology. When we use polymers as capping agents, the length of their polyol's hydrocarbon chain can determine solution viscosity. Therefore, polymers as a capping agent can greatly control the diffusion, growth process, and morphology of obtained nanoparticles. In this paper, we report a low-temperature aqueous solution based co-precipitation method for the synthesis of KTP nanoparticles and selected polyvinyl alcohol (PVA) as capping agents. PVA generally acts as a holding matrix and is expected to control the size of nanoparticles and their distribution. The average grain size, particle size, and morphology of obtained nanoparticles were studied by X-ray diffraction (XRD) patterns and scanning electron microscopy (SEM) analysis.

2. Materials and Methods

The aqueous solution of titanyl chloride, high purity of potassium dihydrogen phosphate (KH_2PO_4), potassium carbonate (K_2CO_3) and PVA as capping agent in different mole ratios to titanium ion (1:3,1:2 and 1:1) were used for the synthesis of KTP nanoparticles. The aqueous solution of titanyl chloride was produced by dissolving $Ti(OH)_4$ powder in HCl (6 N) solution. Capping agent-mixed titanyl chloride solution was reacted with an aqueous solution of KH_2PO_4 with solution concentration equal to 0.5M. Solution pH was regulated at pH≈6 using K_2CO_3 to obtain white precipitate. The obtained powders were washed by distilled water several times to remove chloride ion from them and finally dried at 100°C under ambient condition. The initial amorphous phase, after precipitation, was calcined at 700 °C for 2h. The synthesis steps to obtain $KTiOPO_4$ nanoparticles are shown in Figure 1.
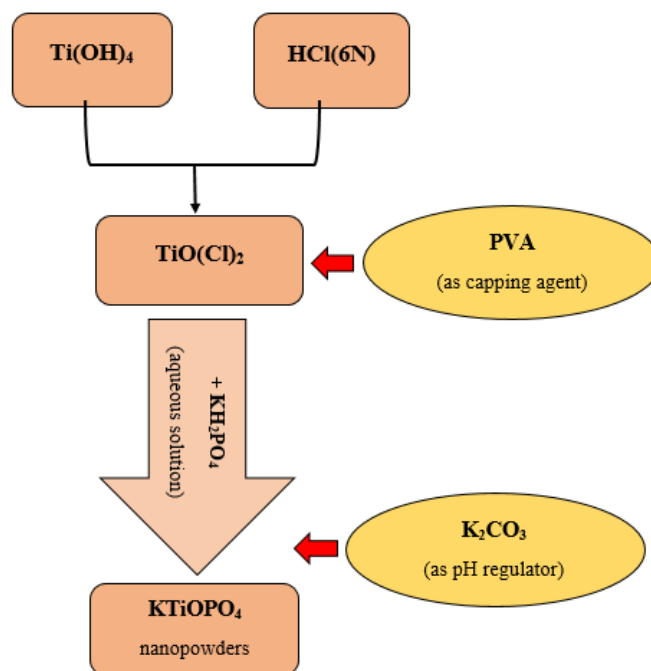

**Figure 1. The synthesis diagram of KTP nanoparticles by co-precipitation method**

3. Results and Discussion

3.1. X-Ray Diffraction Studies

Figure 2 shows the XRD patterns of KTP nanoparticles synthesized without using capping agent and with different mole ratios of PVA as capping agent after calcination at 700°C. For all the samples, diffraction peaks were well assigned to orthorhombic structure of KTP. X-ray analysis showed crystal lattice rotation at 1:2 mole ratio of PVA as capping agent. Lattice parameters were calculated equal to a= 10.58A°, b= 12.81 A° and c=6.40 A° for 1:3 and 1:1 mole ratios of PVA, which are in consistent with the values in the standard card of ASTM (35-0802). One's values for PVA1:2 sample were obtained equal to a=12.82, b=6.40 and c=10.59 (card No. 01-079-1569). The average crystallite size of produced samples was calculated by measuring the broadening of the XRD peaks using the Scherrer equation.

$$D = \frac{k\lambda}{\beta \cos \theta} \tag{1}$$

Where D is the crystallite size, λ is the wavelength of the CuKα radiation (1.542Å), K is a constant (0.9), β is the full-width at half-maximum and θ is the Bragg angle. The crystallite size of obtained KTP nanoparticles under different conditions is given in Table 1. Crystallite size decreased with an increase in the mole ratio of the capping agent. At 1:2 and 1:3 mole ratios of PVA, the number of ligands is fewer than Ti^{+2} ions. This parameter results in fewer nucleation and bigger grain size. Optimum condition to kinetically control the nanoparticle grain size was observed at the 1:1 mole ratio of PVA. This concentration showed the smallest grain size of the obtained KTP nanoparticles.
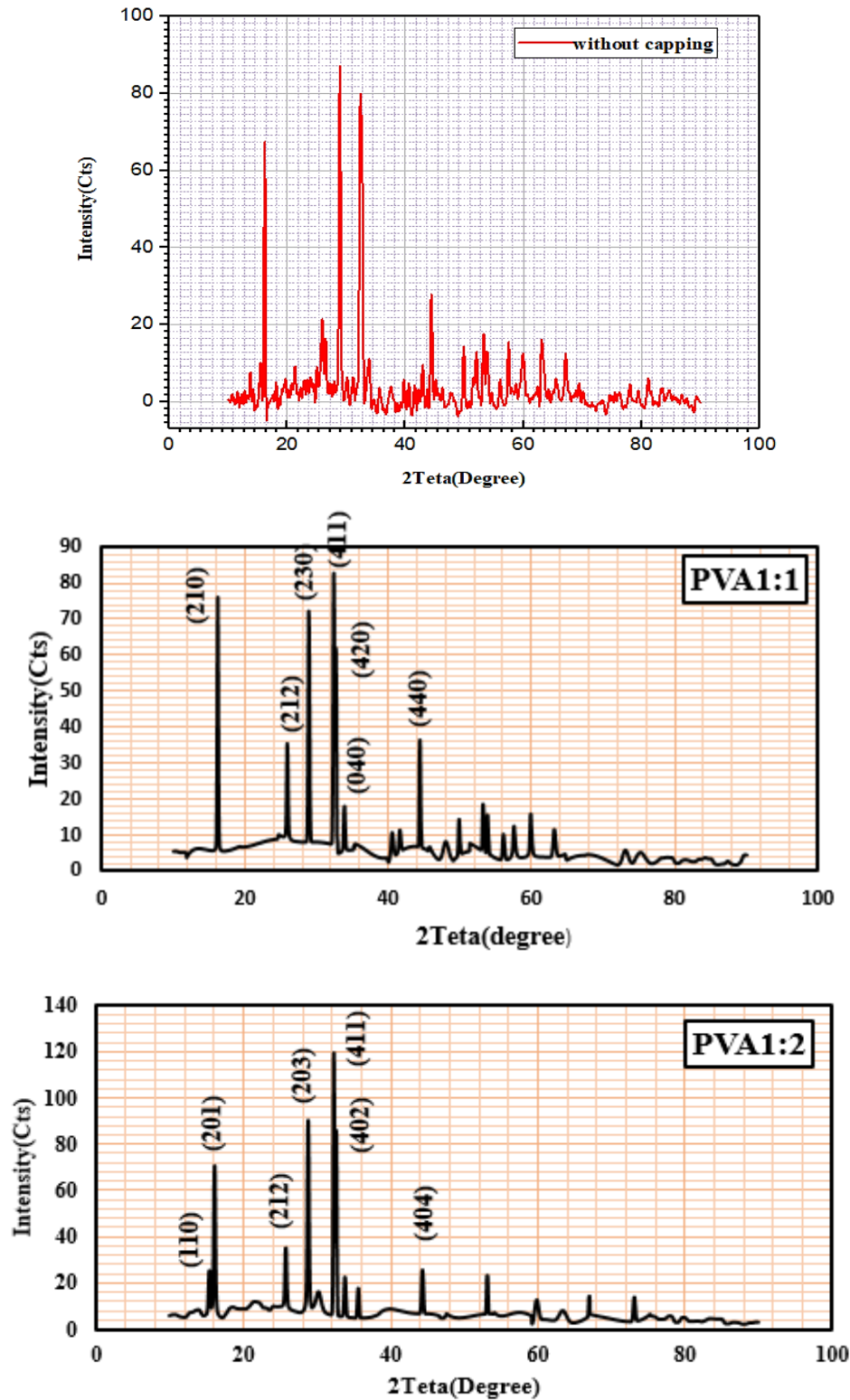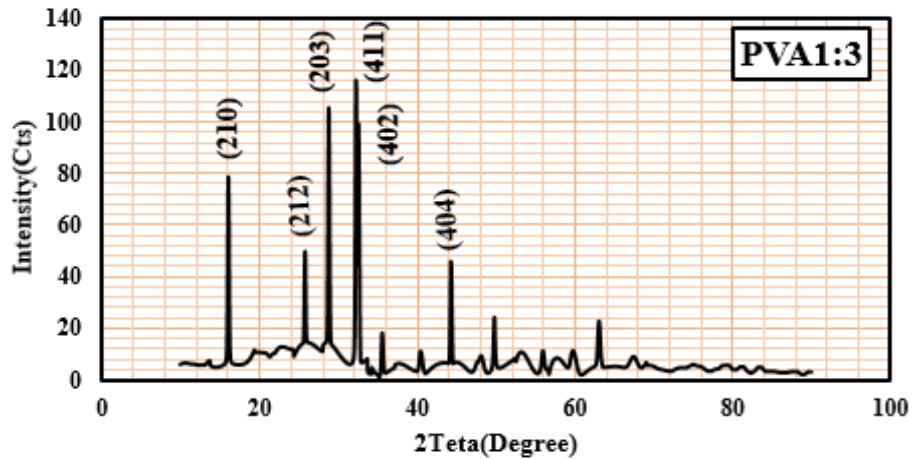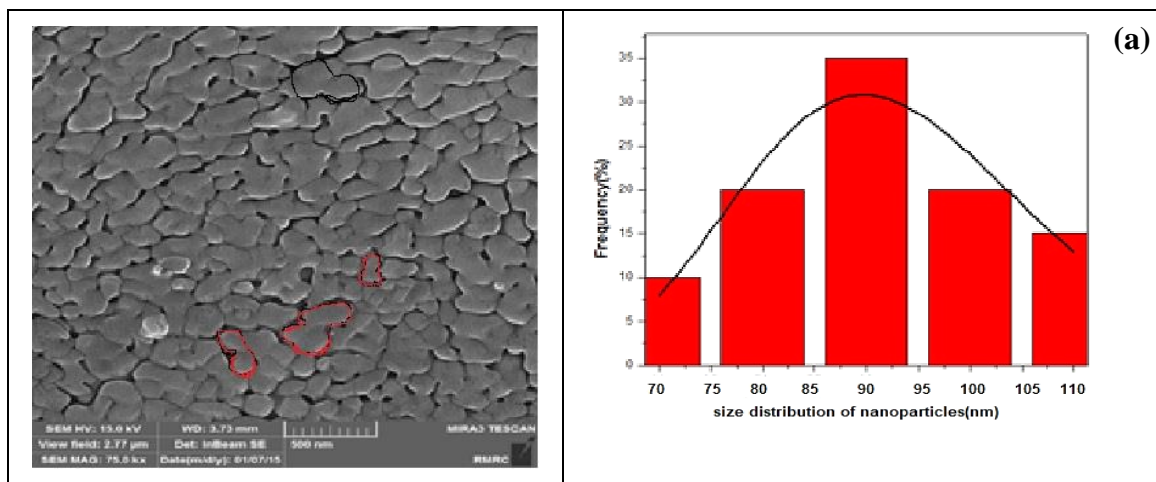
Figure 2. XRD patterns of KTP nanoparticles synthesized without and with different mole ratios of PVA as capping agent

Table 1. Crystallite size, particle size and PDI for KTP nanoparticles obtained under different conditions

sample	Type of capping agent	Mole ratio of capping agent	Grain size (nm)	Particle size (nm)	PDI
S	Without capping agent	-	39/49	100	1/26
PVA1:3	PVA	1:3	56/36	115	2/25
PVA1:2	PVA	1:2	42/50	110	2/23
PVA1:1	PVA	1:1	39/42	90	1/53

3.2. Scanning Electron Microscopy (SEM) Studies

The FE-SEM images of KTP nanoparticles synthesized without and with using different mole ratios of capping agent are shown in Figure 3. Poly dispersity index (PDI) [18] was calculated via Image-J software. PDI and particle size of obtained KTP powders with different mole ratios of polyvinyl alcohol are given in Table 1. It is observed that size, size distribution, and the shape of produced nanoparticles have been affected by mole ratios variation of PVA. The particle size of the obtained KTP nanoparticles increased with a decrease in the mole ratio of PVA. Table 1 shows using PVA as a capping agent only at 1:1 mole ratio results in a decrease in grain size and particle size compared with the S sample. Morphology of KTP nanoparticles for the S sample was dumbly-form but using PVA as a capping agent resulted in spherical-form for PVA1:3 and PVA 1:2 samples and polyhedral-form for PVA1:1 sample. PDI decreased with increasing the PVA mole ratio for obtained samples. PVA generally has the role of the holding matrix. The OH functional group of PVA may temporarily bind with the metal ions through Vander Waals forces [23]. The amount of PVA as a capping agent plays a definite role in determining the growth habit of the various crystal faces, so in determining the morphology of KTP nanocrystals. The selective adsorption of capping agents on the crystal surface results in the formation of nanoparticles with certain morphology.
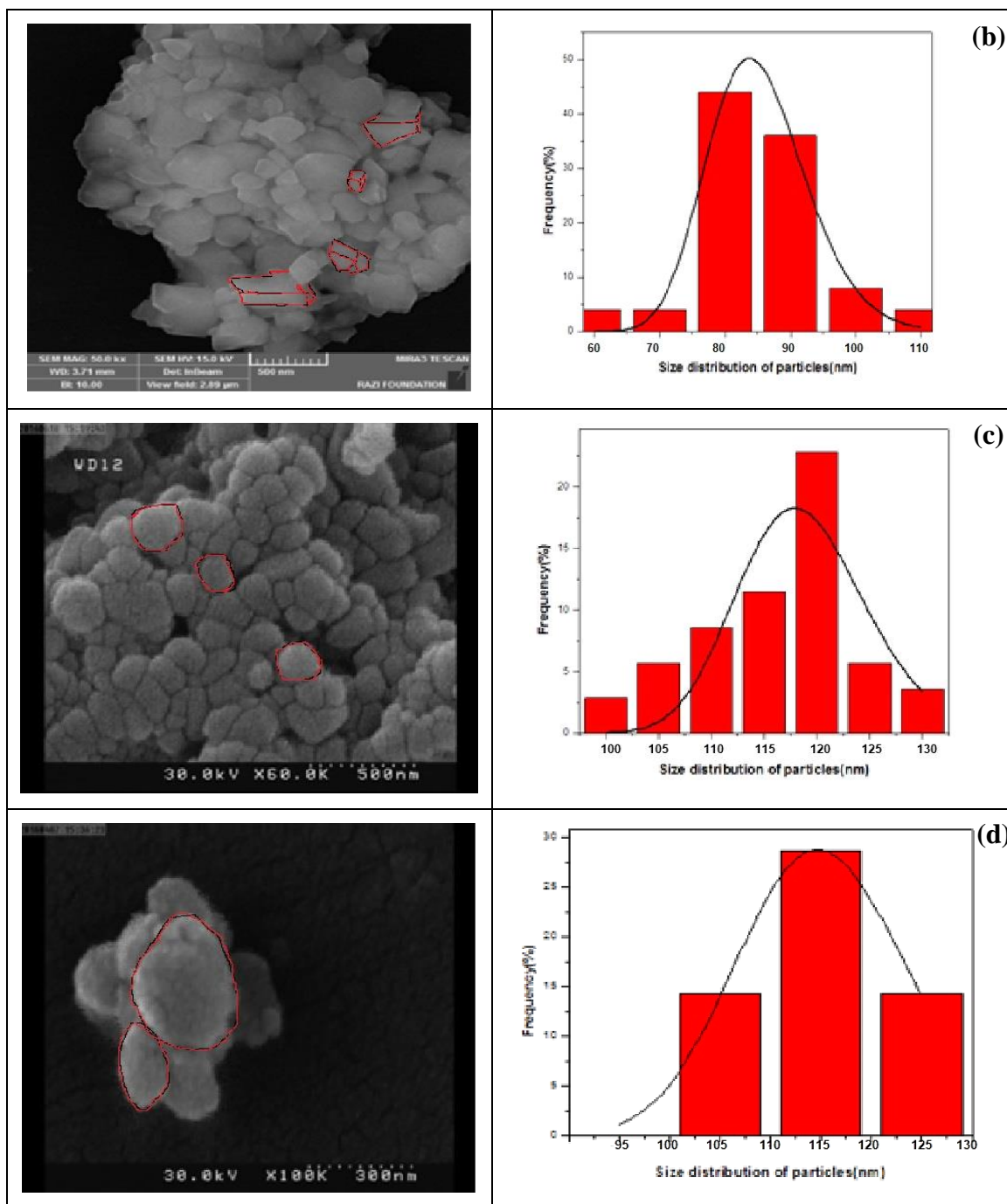
Figure 3. FE-SEM images of KTP nanoparticles synthesized (a) without capping agent and with PVA as capping agent with mole ratio, (b)1:1, (c) 1:2, (d) 1:3, accompanied by size distributions curve of obtained samples with different mole ratio

From another perspective, viscosity is increased with increasing the PVA solution concentration. An increase in the viscosity results in difficult diffusion and migration of ions within the solution. So, the nucleation process becomes slower and the nucleation number was decreased. Decreasing the nucleation alongside used stirring rate can provide the required conditions to steady growth at appropriate PVA concentration. In this work increasing the amount of capping agent and a used relatively high-speed stirring lead to decrease the grain and particle size and increase the structural quality of obtained nanocrystals in the PVA1:1 sample. In the absence of a capping agent, we will usually have dumbly-form nanoparticle. In the crystal growth process, the capping agent effectively reduces the surface energy of crystal faces, which can effectively decrease the grain adhesion. As a result, agglomeration reduced and KTP nanoparticles with certain crystal faces are obtained at the 1:1 mole ratio of PVA. On the other hand, the shape of the nanoparticles is very sensitive to the stirring rate. Low capping agent concentration and relatively high stirring rate result in a spherical form of KTP nanoparticles at 1:3 and 1:2 mole ratios of PVA.

4. Conclusion

Nanoparticles properties are affected by different parameters such as size, shape, and structural quality of them. These parameters have been controlled by growth kinetics. $KTiOPO_4$ nanoparticles were synthesized by the co-precipitation method as a known method for shape and size control of the nanoparticles. PVA as a capping agent was selected to control the growth kinetics. Change in PVA concentration resulted in a variety of sizes, morphologies and size distributions of nanoparticles. For KTP nanoparticles synthesized with 1:3, 1:2, and 1:1 mole ratios of PVA, grain size and particle size were obtained at the range of 39.42 – 56.36 nm and 90-115 nm, respectively. The smallest grain and particle size belongs to the 1:1 mole ratio of the capping agent. For a constant stirring rate, at the 1:1 mole ratio of PVA, the growth condition was more stable rather than other concentrations. This mole ratio resulted in the development of crystal faces and the polyhedral-form of KTP nanoparticles. Other concentrations of PVA showed spherical-form of nanoparticles. Shape of KTP nanoparticles synthesized without capping agent was dumbly-form. Size distribution increased with a decrease in the capping agent mole ratio. Narrowest size distribution was obtained by 1:1 mole ratio of PVA.

5. Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

6. References

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