



Received: 28-10-2025  
Accepted: 08-12-2025

ISSN: 2583-049X

## Synthesis of Nano Calcium Carbonate Structure and Characteristics

**Normuradov Nurbek Fayzullo Ugli**

Junior Researcher, Uzbekistan Academy of Sciences, Institute of Polymer, Chemistry and Physics, Tashkent, Uzbekistan

Corresponding Author: **Normuradov Nurbek Fayzullo Ugli**

### Abstract

The precipitation and formation of calcium carbonate ( $\text{CaCO}_3$ ) nanostructures from  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  solutions were studied. Maintaining a high pH level was shown to be a key factor in ensuring the stable presence of carbonate ions and preventing the formation of soluble bicarbonate

forms. DLS data indicate that the formed calcium carbonate consists of nano-sized structures. The results obtained confirm the importance of controlling pH, reagent ratio, and carbonate ion concentration to purposefully control the morphology and structure of nanocrystals.

**Keywords:** DLS,  $\text{CaCl}_2$ ,  $\text{Na}_2\text{CO}_3$ , Nano- $\text{CaCO}_3$ , Nanoparticle

### Introduction

Nanostructured inorganic compounds can be used as fillers in polymer composite materials, improving their mechanical, thermal and technological properties [1]. Nano calcium carbonate ( $\text{CaCO}_3$ ) is one of the most common types of fillers due to its chemical inertness, heat resistance, low density, availability of raw materials and relative cheapness [2, 3]. The introduction of nano-sized  $\text{CaCO}_3$  particles into the structure of thermoplastics helps to increase impact strength, hardness, thermal stability, and also increases resistance to atmospheric influences [4, 5].

One of the most convenient methods for the production of nano calcium carbonate is the exchange reaction between soluble calcium salts and carbonates in aqueous media [6, 7]. However, without special additives, the synthesized nanoparticles are prone to aggregation, which reduces their effectiveness as fillers. Organic additives, including polycarboxylic acids, amino acids, and surfactants, are widely used to stabilize the particles and control their growth [8]. Citric acid (citrate) as a tricarboxylic organic acid effectively adsorbs on the surface of growing  $\text{CaCO}_3$  particles, forms a stable shell and prevents their aggregation. In addition, it has the ability to form complexes with calcium ions, thereby affecting the rate and direction of crystal growth [9, 10]. The use of citric acid allows obtaining particles with a narrow size distribution and stable spherical morphology, which is considered an important approach for polymer modification [11].

Calcium carbonate nanoparticles were synthesized by precipitation from sodium carbonate and calcium chloride solutions in the presence of citric acid as a stabilizer. The obtained materials were characterized by dynamic light scattering (DLS). The effect of synthesis conditions on particle size was studied. The aim of this study was to determine the effect of sodium carbonate concentration on the precipitation process, phase composition, crystal size and morphology of calcium carbonate nanostructures obtained as a result of the exchange reaction between  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  solutions.

### Materials and Methods

#### Materials

Anhydrous sodium carbonate, calcium chloride, citric acid monohydrate, "pure food" grade, manufacturer - Medkhimfarmstroy, Russia.

#### Synthesis of nanocalcium carbonate

The calculated amount of citric acid was placed in a beaker and dissolved in distilled water. Then the calculated amount of  $\text{Na}_2\text{CO}_3$  was added to this solution and dissolved until a clear solution was obtained. In another beaker, a specified amount of calcium chloride was dissolved in distilled water. Next, the beaker containing the  $\text{Na}_2\text{CO}_3$  and citric acid solution was placed on a magnetic stirrer. The solution containing calcium chloride was placed in a burette and  $\text{Na}_2\text{CO}_3$  was gradually added to the solution. The pH of the medium was controlled by the volume of calcium chloride solution added. After mixing the

solutions, stirring was continued for 5 minutes, after which the particle size was determined using the DLS method. The precipitate containing calcium carbonate nanoparticles was separated from the solution by centrifugation, washed with distilled water and dried at 80 °C until constant weight.

#### Methodology pH

A glass electrode pH meter 150 MI (NPO Izmeritel'naya tekhnika, Russia) was used to control the pH level of the medium.

#### Methodology Centrifuga

It was carried out using a CB-2200 (1000-7000 rpm) centrifuge from HT Machinery, Tokyo (Japan).

#### Methodology DLS

Otsenka razmerov chastitsy providolim metodom dinamicheskogo svetorasseyaniya s pomoshchyu pribora Photocor compact (OOO "Fotokor", Russia). Measurements are carried out at temperature  $T=298$  K, thermostabilized semiconductor laser, long wave 635.6 nm, s moshchnostyu 25 mW.

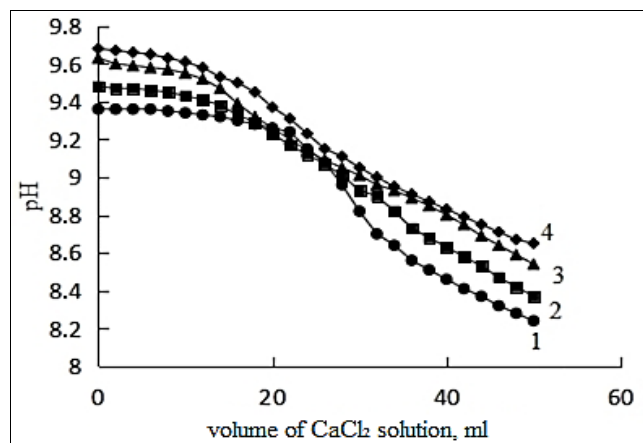
#### Results and Discussion

Maintaining an alkaline pH is essential for the production of calcium carbonate nanoparticles ( $\text{CaCO}_3$ ) via the exchange reaction between  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  solutions. Alkaline conditions help maintain a high concentration of carbonate ions ( $\text{CO}_3^{2-}$ ) required for efficient precipitation of  $\text{CaCO}_3$ . When the pH decreases, the carbonate ion can protonate to form bicarbonate ( $\text{HCO}_3^-$ ), which reduces the saturation of the solution with  $\text{CaCO}_3$  and reduces the yield of the target product.

In neutral or slightly acidic media, soluble calcium bicarbonate  $\text{Ca}(\text{HCO}_3)_2$  can be formed, which prevents the precipitation of insoluble carbonate. The alkaline medium also helps to stabilize the resulting nanoparticles, reduces the aggregation rate, and allows for control of particle morphology and size. Thus, controlling pH, reagent concentration, and the presence of organic additives has a significant impact on the phase composition, stability, and morphology of the synthesized  $\text{CaCO}_3$ , including the equilibrium between  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  [12].

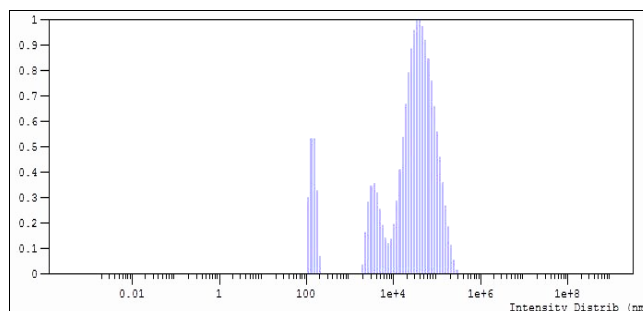
The experiments were carried out at room temperature. The concentration of the  $\text{CaCl}_2$  solution was 0.05 mol/l, the concentration of citric acid was 0.0313 mol/l. The samples were synthesized at different concentrations of  $\text{Na}_2\text{CO}_3$  (starting from a concentration of 0.081 mol/l and increasing from 13.5, 19.7, and 26 mass percent).

The  $\text{Na}_2\text{CO}_3$  solution is characterized by an alkaline reaction ( $\text{pH} \approx 9.5$ ) resulting from the hydrolysis of carbonate ions to form hydroxide ions. Adding the calculated amount of  $\text{CaCl}_2$  solution leads to a decrease in pH to 8.5. This is due to the formation of poorly soluble calcium carbonate and a shift in the equilibrium with a decrease in the concentration of hydroxide ions in the solution.



**Fig 1:** Dependence of NaCl solution on volume.  $\text{Na}_2\text{CO}_3$  concentration = 0.081 mol/l (1), 13.5, (2), 19.7 (3) and 26 (4) mass percent

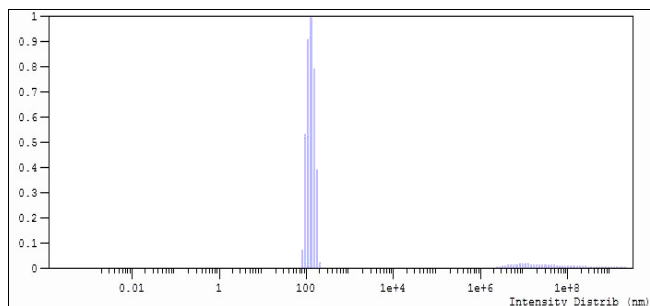
It was also interesting to study the particle size of the obtained samples using DLS. The results are shown in Figure 2.



**Fig 2:** (a) DLS results of calcium carbonate nanoparticles ( $\text{CaCO}_3$ ) formed by the exchange reaction between  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  (0.081 mol/l) solutions

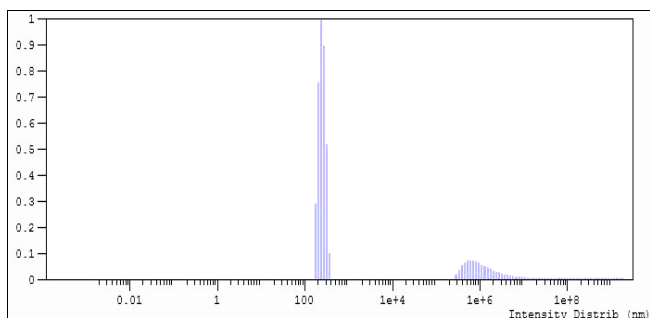
This graph shows that there are three distinct peaks in the particle size distribution of your  $\text{CaCO}_3$  sample, indicating that the sample is polydisperse. The average size of 142.1 nm represents very small (10.3%) individual nano-sized  $\text{CaCO}_3$  particles formed as a result of the stabilizing effect of citric acid. This size is considered optimal for the synthesis of high-quality nanostructures. 3845 nm (12.2%) indicates that some of these nanoparticles coalesced in the initial step, forming small agglomerates. This indicates that growth and coalescence reactions occurred simultaneously during the synthesis process. 54  $\mu\text{m}$  (77.5%) represents very large agglomerates or large micron-sized particles that make up the bulk of the sample. The dominance of this peak in the intensity distribution indicates that even at relatively low  $\text{Na}_2\text{CO}_3$  concentrations and in the presence of a stabilizer, the precipitation process occurred very quickly, with uncontrolled particle growth and aggregation into large clusters.  $\text{CaCO}_3$  shows the complexity of the precipitation process.  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions reacted rapidly to form very small primary particles (nanoparticles) (Peak 1). Citric acid

(0.0313 mol/l) was able to stabilize only a small fraction of the particles (Peak 1). The 0.081 mol/l concentration of  $\text{Na}_2\text{CO}_3$  (and a higher amount of  $\text{Ca}^{2+}$ , since  $\text{CaCl}_2$  is 0.05 mol/l) created a high saturation level, which led to the adhesion and rapid growth (agglomeration) of the particles, resulting in Peak 3 (77.5%).



**Fig 2: (b)** DLS results of calcium carbonate nanoparticles ( $\text{CaCO}_3$ ) via the exchange reaction between  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  (13.5 mass percent) solutions

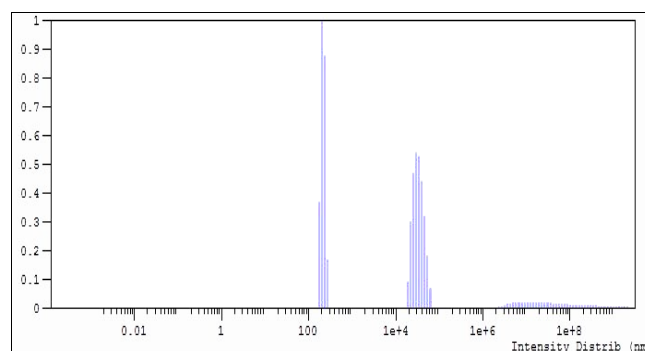
This graph most likely reflects a well-dispersed sample. The main and only dominant peak is located in a very narrow range of about 100 nm to 200 nm. The intensity of the peak is almost 1.0, which indicates that particles of this size are the main component of the sample. This indicates that the majority of the sample consists of nano-sized particles (nanoparticles), the distribution is narrow and monodisperse (of the same size). The citric acid has done its job very well as a stabilizer and has effectively prevented the particles from growing and coalescing into large agglomerates. The presence of a small peak is accompanied by a small scattering of very low intensity on the right side of the graph, located in the range of about 106 to 108 nm (i.e., 1 to 100 micrometers). The intensity of this small scattering is very small (less than about 0.02) compared to that of the main nanopeak. This distribution indicates the presence of minimal agglomerates or very few large particles. Since the DLS method is very sensitive to large particles, this low intensity practically means that there are very few large agglomerates.



**Fig 2: (c)** DLS results of calcium carbonate nanoparticles ( $\text{CaCO}_3$ ) via the exchange reaction between  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  (19.7 mass percent) solutions

This graph also shows a two-peak distribution, similar to the graph analyzed above (Fig. 2c), indicating the zones of nanoparticles and agglomerates. It is located in the range of approximately 100 nm to 200 nm. The dominant intensity (almost 1.0) indicates that the main part of the light in the sample is scattered by these nano-sized particles. As a result of the action of the citric acid stabilizer, well-dispersed and

almost monodisperse nanoparticles (primary particles) are formed. The second peak contains agglomerates located in the range of approximately 105 nm to 107 nm. The intensity is much lower (reaching about 0.1). This low intensity indicates that some nanoparticles, even if present in very small quantities in the sample, have coalesced during the synthesis process and formed micron-sized agglomerates. At low  $\text{Na}_2\text{CO}_3$  concentration (0.081 mol/l) and in the presence of citric acid,  $\text{CaCO}_3$  was synthesized with a majority of nano-sized particles (100-200 nm). Citric acid effectively prevented the rapid growth of particles, resulting in a narrow and dominant distribution. The presence of a second low-intensity peak indicates that agglomeration could not be completely eliminated since the synthesis process was carried out under high saturation conditions.



**Fig 2: (d)** DLS results of calcium carbonate nanoparticles ( $\text{CaCO}_3$ ) via the exchange reaction between  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  (26 mass percent) solutions

There are two similar graphs above for this sample, both showing almost the same result. Primary nanoparticles (100-200 nm) are still forming (Peak 1). This indicates that the nucleation control effect of citric acid is maintained. The intensity of the second peak increases sharply as agglomeration increases. This indicates that a higher saturation level of the solution is reached as a result of the increase in  $\text{Na}_2\text{CO}_3$  concentration and the precipitation rate increases. Citric acid was not able to fully control this rate. As a result, the sample contains a mixture of nano-sized particles and a significant amount of micron-sized agglomerates (the polydisperse distribution is more clearly visible).

## Conclusion

The concentration of  $\text{Na}_2\text{CO}_3$  at 0.081 mol/l gave the best result. The relatively low concentration ensured slow precipitation kinetics. Under these conditions, citric acid was sufficiently adsorbed onto the particle surface and effectively prevented their aggregation (agglomeration). As a result, DLS showed that a narrowly distributed, highly monodisperse nano  $\text{CaCO}_3$  (100-200 nm) was obtained. This size is consistent with controlled nanoparticle synthesis. At medium concentrations (13.5%): Increasing the concentration of  $\text{Na}_2\text{CO}_3$  led to a high saturation of the system and rapid nucleation. Due to the increased precipitation rate, citric acid did not have time to stabilize all the newly formed nanoparticles. Although the main nano peak was preserved, a large number of large agglomerates were formed, indicating a limited effect of the stabilizer. The highest concentration of 26 wt%, 0.081 mol/l  $\text{Na}_2\text{CO}_3$ , resulted in the worst dispersion. Such a high concentration

causes very fast precipitation and immediate agglomeration. DLS analysis (Fig. 2a) shows that the main part of the sample (77.5% intensity) is present in the form of very large agglomerates. Under these conditions, citric acid could not control the formation of nano-sized particles and the synthesis product had a polydisperse micro-sized powder-like appearance. The results of the studies have proven that the reagent concentration (in particular,  $\text{Na}_2\text{CO}_3$ ) is the main parameter in controlling the particle size in the synthesis of  $\text{CaCO}_3$  with the presence of citric acid stabilizer. To achieve nano-sized  $\text{CaCO}_3$ , the precipitation rate should be optimized using a low  $\text{Na}_2\text{CO}_3$  concentration, which allows citric acid to fully activate its stabilization mechanism.

### Funding

The research was conducted in 2025–2026 at the Laboratory of Nanostructured Composite Polymer Materials, Institute of Polymer Chemistry and Physics, within the framework of the scientific project “Functional, including nanostructured, polymer composite materials”.

### References

1. Fu SY, *et al.* Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate-polymer composites. *Composites Part B: Engineering*. 2008; 39(6):933-961.
2. Zhang Y, Zhang L. Recent advances in nano- $\text{CaCO}_3$  as functional filler for polymers. *Polymer Composites*. 2019; 40(2):267-282.
3. Meng Y, *et al.* Fabrication of well-dispersed nano  $\text{CaCO}_3$ /PVC composites and their thermal behavior. *Journal of Vinyl and Additive Technology*. 2016; 22(1):36-42.
4. Li K, Qian X. Effect of nano- $\text{CaCO}_3$  on thermal stability and flame retardancy of polypropylene. *Journal of Applied Polymer Science*. 2014; 131(16).
5. Ghosh AK, Naskar K. Surface modification of nano- $\text{CaCO}_3$  and its effect on the performance of rubber composites. *Materials Chemistry and Physics*. 2019; 222:270-278.
6. Hule RA, *et al.* Nanocomposites with polymer grafted nanoparticles. *Macromolecules*. 2007; 40(19):7283-7290.
7. Wang L, *et al.* Preparation and characterization of calcium carbonate nanoparticles from  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  aqueous solutions using reverse microemulsion method. *Powder Technology*. 2010; 197(1-2):68-73.
8. Wang H, *et al.* Modification of calcium carbonate nanoparticles: A brief review. *Materials Letters*. 2012; 67(1):318-321.
9. Jiang Y, *et al.* Role of citric acid in the synthesis of  $\text{CaCO}_3$  nanoparticles: A novel approach to control particle size and morphology. *CrystEngComm*. 2015; 17:8300-8308.
10. Shi X, *et al.* Synthesis of calcium carbonate nanoparticles via citric acid-assisted precipitation: Morphology control and formation mechanism. *Journal of Nanoparticle Research*. 2020; 22:1-13.
11. Lv X, *et al.* Morphology-controlled synthesis of  $\text{CaCO}_3$  nanoparticles with citric acid for polymer composites. *Materials Research Express*. 2021; 8(3):0350e3.
12. Zhou G, Liu X, Pan Y, Wang J, Xu X, Guo Y, *et al.* Morphology Control of Calcium Carbonate Crystals and Application in Papermaking Industry. *Chem. Soc.*

Rev. 2022; 51(5):1983-2030. Doi:  
<https://doi.org/10.1039/D1CS00519G>