Characterisation of Sol-Gel Synthesis of Phase Pure CaTiO$_3$ Nano Powders after Drying

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Abstract: According to a few recent studies, calcium titanate (CT) is a material that is similar to hydroxyapatite in biological properties. However, calcium titanate is not currently being used in the biomedical applications as to hydroxyapatite. The objective is to prepare nano calcium titanate powders from the equimolar solution of calcium oxide, ethanol and Titanium (IV) isopropoxide via sol-gel synthesis. The phase analysis and morphology of powder particles were studied by X-ray diffraction (XRD), while the composition and size of powder particles were determined by Transmission electron microscope (TEM) attached with energy dispersive x-ray spectrometer (EDS). As results, XRD confirm the presence of phase pure crystalline CaTiO$_3$ after drying at 100°C for 24 hours, while TEM analysis confirms about 13 nm sizes of CaTiO$_3$ particles and some agglomerated particle of 20-30 nm. Moreover, EDS analysis indicates that the approximately stoichiometric Ca/Ti ratio 1:1 was obtained in the CaTiO$_3$ powders. Finally, it can be concluded that described sol-gel synthesis could be novel method for the production of nano CaTiO$_3$ particles at lower temperature compared to any other methods of production.

1. Introduction
Currently, researchers in chemistry, physics, biochemistry, and material engineering are interested in new class of nanosized materials for electronic and biomedical applications. In this regard, calcium titanate (CaTiO$_3$) was reported as good substrate for apatite growth in vitro with the potential to enhance osseointegration and osteoconductivity.[1-2] Furthermore, some researchers suggested that CaTiO$_3$ possess large dielectric constant (~190) and high dielectric loss (~3.5).[3-4] The beneficial effect of addition of CaTiO$_3$ to HA encourages the development of electrically active biomaterial for bone replacement.[5-6] Apart from this, CaTiO$_3$ is widely used as synthetic rock for immobilization of high level nuclear wastes.[7] Several special methods are known for the synthesis of CaTiO$_3$ nanomaterials such as sol–gel [8], coprecipitation [9], organic–inorganic solution [10], and combustion [11] etc. CaTiO$_3$ is one of the materials that were initially synthesized via the mechanochemical route from the varying mixture of CaCO$_3$, CaO and TiO$_2$. The major drawbacks of this processes are contamination and energy consumption. However, the study on sol gel synthesis effect on fine particles and uniform distribution of particles have been created much interest among researchers because of its several advantages to downstream processes like reducing the sintering time and temperature, reducing the phase transformation temperature, decreasing the thermal decomposition temperature, and increasing the particle reactivity.[12-14] In addition, small sizes of nanoparticles can affect the sintering or miscibility properties of the material relatively at lower temperatures.[15] On the whole, in nanoparticles high numbers of atoms are located on the surface of the grains or interface boundaries which lead to an increase in surface activity between materials and host bodies.[16]
The objective of the present work is to synthesis of phase pure CaTiO$_3$ using sol-gel process in which calcium oxide (CaO) and Titanium (IV) isopropoxide (Ti(OC$_3$H$_7$)$_4$) as starting materials, ethanol as the dispersed medium, nitric acid (HNO$_3$) as catalyst for the reaction and distilled water as used for the hydrolysis reaction. During this process, Titanium (IV) isopropoxide and CaO were hydrolysis into Ti(OH)$_4$ and Ca(OH)$_2$ gels. As result, with their combined reaction of gels were decomposed into precipitates CaTiO$_3$. The precipitate was dried at 100°C for 24 hours to obtain crystalline CaTiO$_3$ powders. X-ray diffraction (XRD) and Transmission Electron Microscopy attached with energy dispersive X-ray spectroscopy (TEM-EDS) analysis were carried out to study the microstructural and morphological behavior of dried CaTiO$_3$ sol-gel powders.

2. Experimental procedure

2.1. Materials and methods

The precursor materials used for the synthesis of CaTiO$_3$ were calcium oxide (CaO) and Titanium (IV) isopropoxide (Ti(OC$_3$H$_7$)$_4$), ethanol and nitric acid (HNO$_3$) and distilled water. Initially, CaO was dispersed in ethanol. The dispersed medium was kept on a hot plate and the suspension was stirred by an electromagnetic stirrer. Following this, an equivalent amount (keeping the Ca/Ti ratio same as CaTiO$_3$) of Titanium Isopropoxide solution (0.17M) was added drop wise in the dispersed CaO medium. The total solution was stirred at 80°C for 3-4 hrs to allow the reaction to take place towards completion. Then, distilled water and concentrated HNO$_3$ was added drop wise till the pH of the solution increases to 10. For the production of 25g CaTiO$_3$, the amount of CaO, ethanol, distilled water, and HNO$_3$ solution were required for according to the stoichiometric molar ratio of (Ti(OC$_3$H$_7$)$_4$:C$_2$H$_5$OH:H$_2$O:HNO$_3$:1:20:4:0.8). Subsequently, the solution was kept at room temperature for one day to precipitate the reaction product, which was further dried at 100°C for one day in a drying oven. After drying, the powder lump was crushed by using an agate mortar to make the material in powder form.

2.2. Powders characterisation

The calcined powders were analysis through the different characterisation technique to study the composition, microstructures and morphology. X-ray diffraction (XRD) analysis was performed on a Diffractometer (SHIMADZU, XRD700) using CuK$_\alpha$ radiation for all analyses at 40 kV and 30mA in order to identify the phases of the powders. Crystal size of the calcined powders was calculated with Scherer formula from data of FWHM of XRD spectrum. The XRD patterns were recorded in the 2$\theta$ range = 30–80° using a step size of 0.02° and a counting time of 5s per step. The microstructural and compositional characteristics of powder particles were investigated by TEM (Transmission Electron Microscopy, GEOL GM1400) attached with energy dispersive X-ray spectroscopy (EDS, OXFORD).

3. Results and discussions

3.1. Phase analysis

From the figure 1 show XRD peaks of the crystalline CaTiO$_3$ sol-gel powders after drying at 100°C for 24 hours, which indicates the characteristic peaks corresponding to crystalline CaTiO$_3$ are accurately matched to the three major peaks from JCPDS card number 75-2099. There were no traces of CaO and TiO$_2$ in powder or in calcined CaTiO$_3$ samples. The interesting result is that the crystalline of CaTiO$_3$ gel powders obtained after drying at 100°C for 24 hours. A similar result has been reported for sol-gel derived BaTiO$_3$ powders prepared from the barium alkoxid [17]. Such result indicates that the degree of crystallization of CaTiO$_3$ gel powders is dependent on the mechanisms of hydrolysis and polycondensation reactions of the mixture rather than the calcination temperature of drying powders [18].
The above results clearly indicate that the synthesis of phase pure crystalline CaTiO$_3$ powder after drying can be possible using the equimolar mixture of CaO, ethanol and Titanium (IV) isopropoxide.

3.2. Morphological Analysis

From the figure 2 and figure 3 show the bright field image of TEM micrograph of CaTiO$_3$ particles is in the nanometer range. It can be observed that the average particle size of CaTiO$_3$ nanoparticles is approximately 13 nm. But there are some agglomerated particles of size about 20 nm to 30 nm, as shown in figure 3. The agglomeration of CaTiO$_3$ nano particles is due to the effect of high surface energies between the monolithic CaTiO$_3$ crystals which is evident from the bright field TEM image, as shown in figure 3. Moreover, the results of compositional analysis using EDS attached to TEM show that all the elements are belong to the Ca, Ti and O spectrum, as shown in table 1. This indicates that the presence of impurities was not detected in any more. This suggests that the purity of sol-gel derived CaTiO$_3$ powders is better compared to powders prepared by solid state reaction or mechanochemical route of synthesis.

From the above results, XRD analysis indicates that the pure crystalline CaTiO$_3$ powder can be prepared from the above molar mixture of the starting materials without any traces of CaO and TiO$_2$, which is not possible to achieve through the conventional powder preparation methods such as mechanical chemical synthesis. From bright field TEM micrographs, it was observed that the approximate microcrystals size of CaTiO$_3$ with about 13 nm were obtained after drying at 100$^\circ$C for 24 hours from the mixture of ethanol, CaO and Titanium (IV) isopropoxide for about 3-4 hours. As smaller the particles due to strong surface energy, these microcrystals may grow in size and their average size in reaches about 20 nm to 30 nm, as shown in figure 3. EDS analysis clearly reveals the stoichiometric ratio of CaTiO$_3$ powders, which is merely achieved through the other processing methods. Therefore, it is suggested that crystalline nano CaTiO$_3$ can be produced by described sol-gel process after drying exploit.
better reproducible functional and the structure properties of ceramics for the technological applications.

Figure 2. TEM bright-field images for the sol-gel derived CaTiO$_3$ powders after drying at 100$^\circ$C for 24 hours.

Figure 3. TEM bright-field images showing agglomerated the sol-gel CaTiO$_3$ powders after drying at 100$^\circ$C for 24 hours.
Table 1: Quantitative EDS spectrum of CaTiO$_3$ sol-gel powders.

| Element | Weight% | Atomic% |
|---------|---------|---------|
| O K     | 5.27    | 13.27   |
| Ca K    | 42.98   | 43.21   |
| Ti K    | 51.75   | 43.52   |
| Total   | 100     | 100     |

Figure 4: EDS spectrum of CaTiO$_3$ sol-gel powders was taken from above TEM bright field images.

4. Conclusion
Based on the experimental results and analysis, the following conclusions have been presented.
1. From XRD analysis confirms presence of pure crystalline CaTiO$_3$ phases after drying at 100°C for 24 hours, which cannot be synthesized from grinding the mixtures of CaO-TiO$_2$ powders and it also shows the absences of any trace of CaO and TiO$_2$ powders.
2. From TEM observation, the approximate particle size of the powders is about 13 nm and also it shows the agglomeration of nano particles of size around 30 nm.
3. EDS analysis indicates composition and Ca/Ti ratio of CaTiO$_3$ powders are equal to stoichiometric ratio 1:1.
4. Finally, it can be conclude that phase pure crystalline calcium titanate (CaTiO$_3$) nanoparticles with stoichiometric ratio can be prepared through sol-gel process after drying at 100°C for 24 hours from the equimolar ratio CaO and Titanium (IV) isopropoxide as starting materials.

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