Biomimetic Synthesis and characterization of polymer template Mn@CaCO₃ nanomaterials using natural carbonate sources

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Abstract : PMMA templateMn doped $CaCO_3$nanomaterials were synthesized bybiomimetic method using calcium rich natural carbonate sources. The following, techniques have been used to recognize the mineralogy (FTIR), morphology and elemental composition (SEM-EDX) and structure and crystallites size (XRD). The synthesized products are in rhombohedral structure within the crystallite of 20-40 nm range. It has monodispersed spherical shape and aggregated crystalline with flower like morphology. The revealed characteristics show that the transition metal doped biomimetic products may be used for various industrial applications. This eco-friendly method is very easy for large scale production in lower cost without any impurity.

Keywords : Manganese; Nano $CaCO_3$; Natural sources; Calcite; Mineralogy.

1. Introduction

The study of nanomaterials with controlled shape, size and morphology is very important in newly developing material with novel properties. Different type of inorganic materials plays an important role in industrial applications.Among them $CaCO_3$ is an essential material and availability in low cost. A great attention has been paid to artificially synthesize in regular structure of $CaCO_3$ during recent decade[1-3]. On other side, due to the outstanding properties such as optical, mechanicaland thermal properties[4], it is used in many industries like papermaking, plastics, paints, cosmetics, etc. to enhance these kinds of properties.

The polymers play vital role to contrast the high surface area. Especially, Poly (methyl methacrylate), (PMMA), is asignificant commercial plastic and it is odorless, tasteless, and nontoxic material.So that, it is used in many fields such as in aircraft glazing, signs,lighting, dentures, food-handling equipment, contact lenses,etc[5].

In this work, thecalcium rich natural carbonate source is mainly used as one of the precursors. The main focus is to on synthesis of transition metal doped nano calcium carbonate using natural carbonate resources.
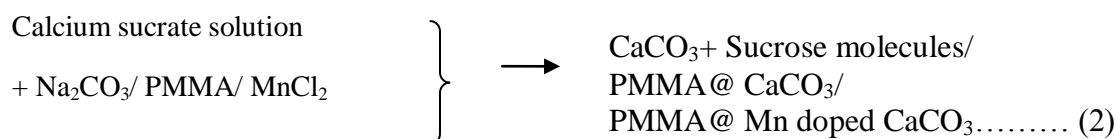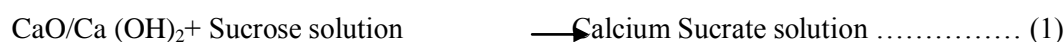
2. Materials and methods

2.1 Chemicals

Manganese chloride salt, sucrose, sodium carbonate and Poly methyl methacrlyate (polymer) analytical grade with 99% purity were used without further purification. All the glassware's used in this work were acid washed. Ultrapure water was used for all dilution and sample preparation.

The high-grade natural calcium rich carbonate rock samples collected from Padaivedu, Salem district,Tamilnadu, India were used in this work as raw material.

2.2 Biomimetic synthesis

All samples were crushed, ground using ball mill and filtered through ASTM 230 (62.5 micrometers) mesh sieve. The powdered sample was calcined at 900 °C for 2 h in a muffle furnace to get CaO. 10.00 g of CaO powder was dissolved in 100 ml of 1.00 M sucrose solution and vigorously stirred for an hour at room temperature. The soluble calcium sucrose solution wascollected under suction.

The prepared calcium sucrose solution was placed in a 500 ml three-necked rounded bottom flask and 10 ml of PMMA, 80 ml of 1M sodium carbonate and mole concentration of Mn solution were added drop wise to get Mn doped $CaCO_3$ nanomaterial, while the solution vigorously stirred, maintained at 80°C for two hrs. The possible mechanism to synthesize nano PCC as follows [4]. Natural calcitic rock calcined at 900 °C yielded $CaO/Ca(OH)_2$.

$CaO/Ca (OH)_2$+ Sucrose solution $\longrightarrow$ Calcium Sucrate solution …………… (1)

Calcium sucrate solution

+ Na_2CO_3/ PMMA/ $MnCl_2$ $\longrightarrow$ $CaCO_3$+ Sucrose molecules/ PMMA@ $CaCO_3$/ PMMA@ Mn doped $CaCO_3$……… (2)

2.3 Characterization Techniques

The mineralogical assessment was examined by FT–IR (SHIMADZU–8400), with a resolution of ±4 cm^{-1}, in the region 4000-400 cm^{-1}. The crystal structure and phase purity was investigated by X–ray diffractometer (XPERT-PRO) with CuK_α radiation (λ = 1.5406 Å), an operating voltage 40 mA, and current of 40 kV.

The morphology of the as-synthesized material was examined through scanning electron microscopy (JEOL- 6610 and Zeiss). Energy–dispersive X–ray analysis (EDX) measurement was carried out using Brucker 129 eV.Gold coating method is used for sample preparation by sputtering technique before the measurement.

3. Results and discussion

3.1 Functional group analysis

FTIR spectroscopy is the most prominent and precise method to identify different phases of organic and inorganic compounds and, generally, calcium carbonate has three differentphases such as calcite, vaterite and aragonite. Carbonate ions have four normal modes of vibration peaks: υ_1 (1083 cm^{-1}) - symmetric stretching; υ_2(909-833 cm^{-1}) - out-of-plane bending; υ_3 (1420-1480 cm^{-1}) - doubly degenerate planar asymmetric stretching; and υ_4 (769-666 cm^{-1})- doublydegenerate planar bending[6-7].
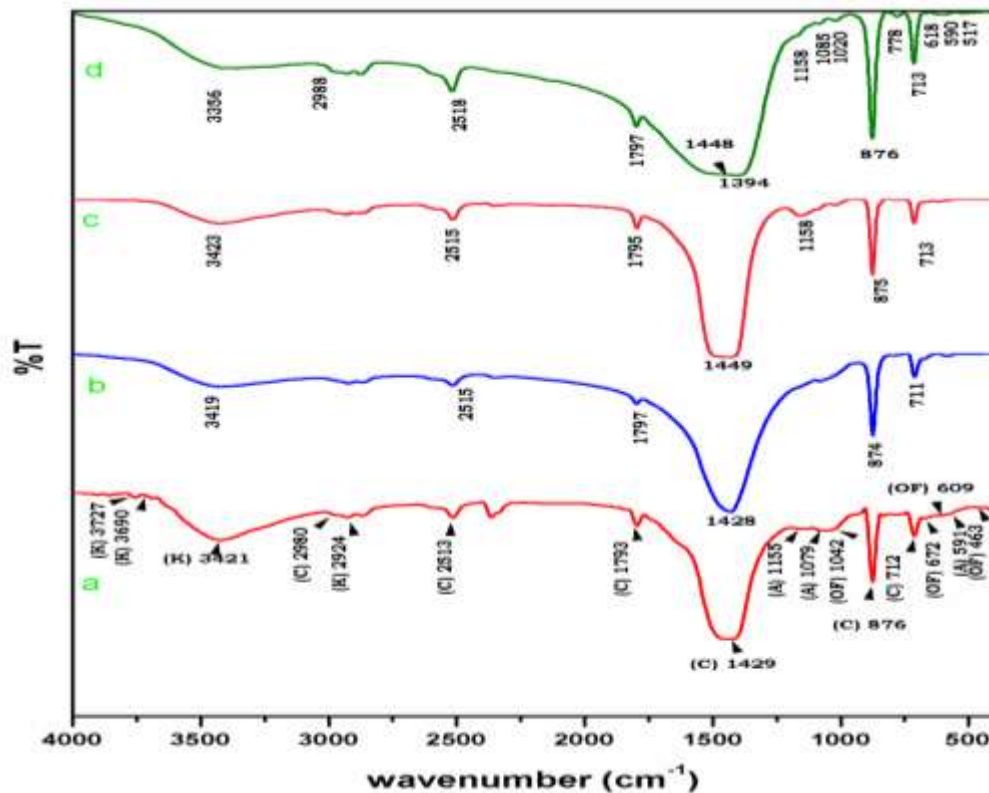
Figure.1 FTIR spectra of raw carbonate rock sample   (a), synthesized nanoCaCO$_3$ (b), PMMA@ nanoCaCO$_3$ (c) and PMMA @ Mn dopednanoCaCO$_3$ (d)

Figure. 1(a-f)shows the FTIR spectra of raw carbonate rock, synthesized calcium carbonate without polymer, PMMA mediated CaCO$_3$ and PMMA mediated Mn doped CaCO$_3$ materials.

From **Fig 1a,**the observed major frequencies such as 712 (υ_4), 876 (υ_2)and 1429 cm^{-1} (υ_3), minor bands at 1793 ($\upsilon_1 + \upsilon_4$), 2513($\upsilon 2 + \upsilon_4$)and 2980cm^{-1} (2υ_3) are due to the presence of calcium carbonate in rhombohedral form[8]. Some other frequencies are observed such as 463, 672 and 1042 cm-1, which indicates the presence of orthoclase feldspar (OF)[9]. The peaks observed at 591, 1079 and 1115 cm-1 indicates the presence of anorthite (A). According to Mackenzie and rahman (1987)[6], theabsorption peaks observed at 2924, 3421, 3690 and 3727 cm-1 are due to the presence of kaolininte (K). Based on the number of peaks and intensity, calcite occupies major portion. The other accessory minerals such as orthoclase feldspar, anorthite, and kaolinite occupies minor portion.

From 1b shows the characteristic peaks at 711, 874 and 1428 cm^{-1} and minor peaks at 1796, 2515 and 3419 cm^{-1}, indicates the presence of CaCO$_3$ alone. No other peaks are observed. After the synthesis, the product is in pure form. The other impurity minerals are completely filtered or eliminated thorough this biomimetic method.

From figure 1c an additional peak at 1158 cm^{-1} is observed along with the characteristic peaks of pure CaCO$_3$ which is due to the presence of PMMA. The influence of PMMA alters the position of the peak from 1427 cm^{-1} to 1448 cm^{-1}[10]

Figure 1d shows three additional peaks at 517, 590, 617, 778, 1085 cm^{-1}and 1020 cm^{-1} (sugar) along with characteristic peaks of pure CaCO$_3$ and PMMA. According to Liping Kang et al, 2007this may be due to the influence of Mn doping[11-13]. This confirmed that the Mn occupied the CaCO$_3$ lattice.

3.2 XRD- Structuralanalysis

Figure 2(a-d) depicts the XRDdiffraction pattern of raw carbonate rock, synthesized CaCO$_3$without polymer, polymer mediated CaCO$_3$ and polymer mediated Mn doped CaCO$_3$.

The diffractogram of raw carbonate rock shows the characteristic planes such as (012), (104), (006), (110), (113), (202), (018), (116), (211), (122), (214) and (300) at an angle (23.13), (104), (31.65), (36.18), (39.62), (43.41), (47.85), (48.86), (56.85), (57.69), (61.05) and (65.06)of calcium carbonate in rhombohedral structure (JCPDS card no: 01-086-2335). No other additional planes are observed. The same planes are observed for all other synthesized product (JCPDS card no: 47-1743). However the intensities are decreased and FWHM is increased with respect to fig. 2a.The increase in broadness of the planes suggests that the products are in lower crystallites. It is due to quantum confinement effect.
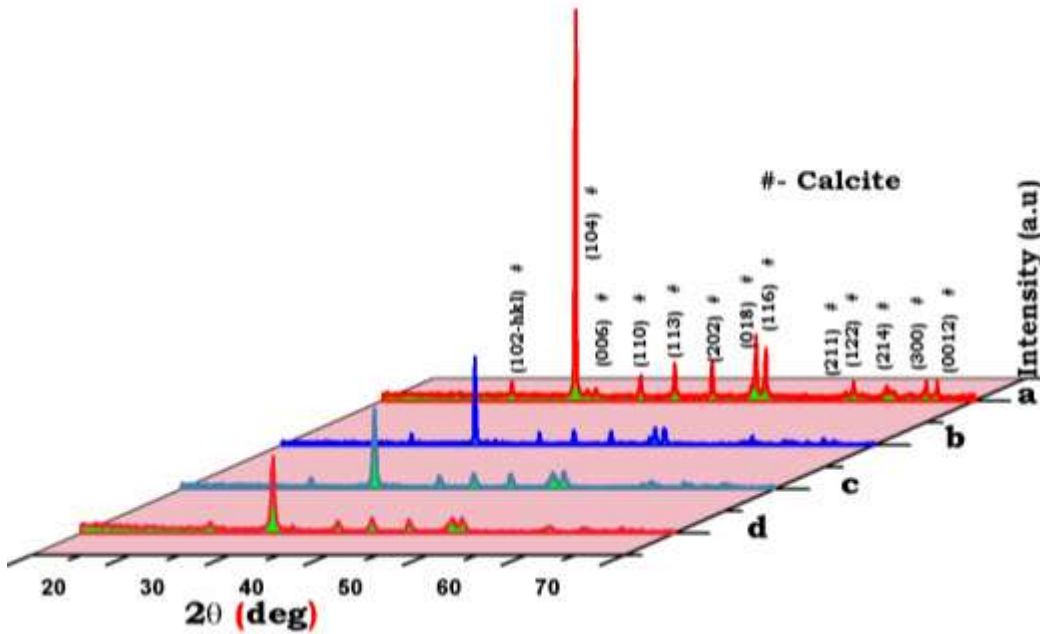

Figure.2 XRD pattern of raw carbonate rock sample (a), synthesized nanoCaCO$_3$ (b), PMMA@ nanoCaCO$_3$ (c) and PMMA @ Mn dopednanoCaCO$_3$ (d)

The average crystallite size of synthesized products is calculated   by Scherer' formula [14-15]

$$D = \frac{k\lambda}{\beta cos\theta}(\text{Å}) \dots\dots\dots\dots\dots. (4)$$

Where D - crystallite size (nm) λ - wavelength of the CuK$_\alpha$ (1.5406 A°), K – constant (0.94), β - FWHM (full-width half maximum) and θ is the diffracted angle.

The calculated crystallites sizes of the products are in the range of 20-40nm. Hence the obtained products are in the nanoregime.

3.3 Morphological and elemental composition analysis

The SEM with EDX technique has been used to analyze the surface morphology and elemental composition of all the samplesandis shown in figure 3 (a-d).
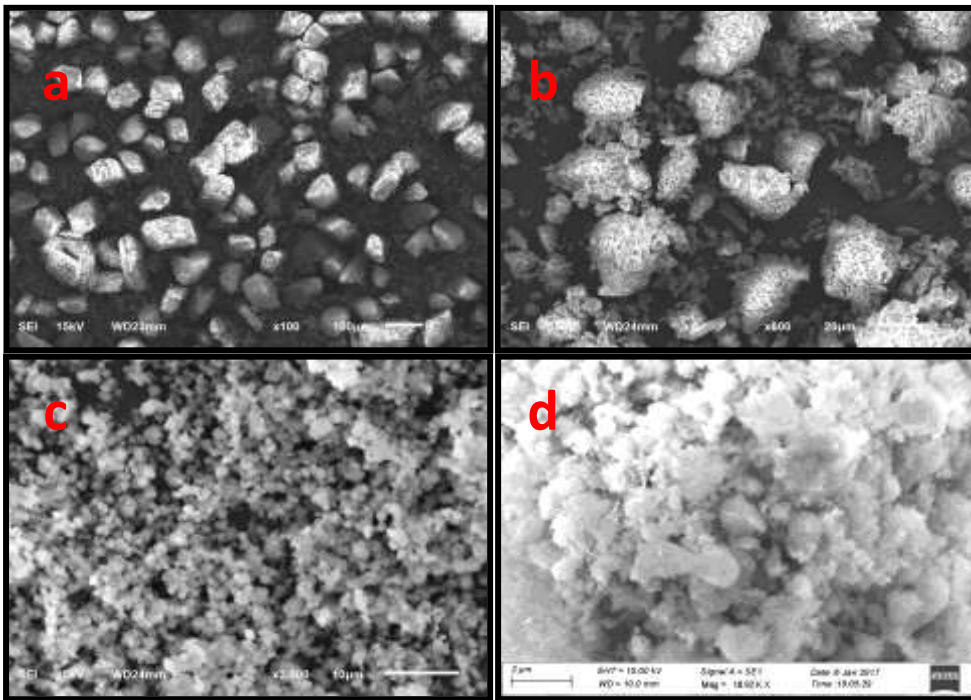

Figure.3 SEM image of raw carbonate rock sample (a), synthesized nanoCaCO$_3$ (b), PMMA @ nanoCaCO$_3$ (c) and PMMA @ Mn dopednanoCaCO$_3$ (d)

The micrograph of raw carbonate rock sample (fig.3a) depicts the well crystal morphology with monodispersion. Figure 3b of nanoCaCO$_3$ (without polymer) shows the aggregation of particles with flower like structure. The monodispersed spherical morphology was observed in figure 3c of PMMA mediated CaCO3. This may be due to the presence of polymer, which controls the growth of the particle, and makes the changes in sample surface of the particle. The addition of polymer and Mn in the CaCO$_3$ matrix (figure 3d) shows the changes in spherical shape with aggregation.

Figure 4(a-d) depicts the elemental composition obtained through EDXspectra of all the samples. This depicts that the addition of Mn is successfully incorporated with the CaCO$_3$ matrix.The impurities are observed in raw carbonate sample (figure 4a). However these are eliminated / filtered through biomimetic synthesis (figure 3b and 3c).No other impurities are observed except Ca, C and O.
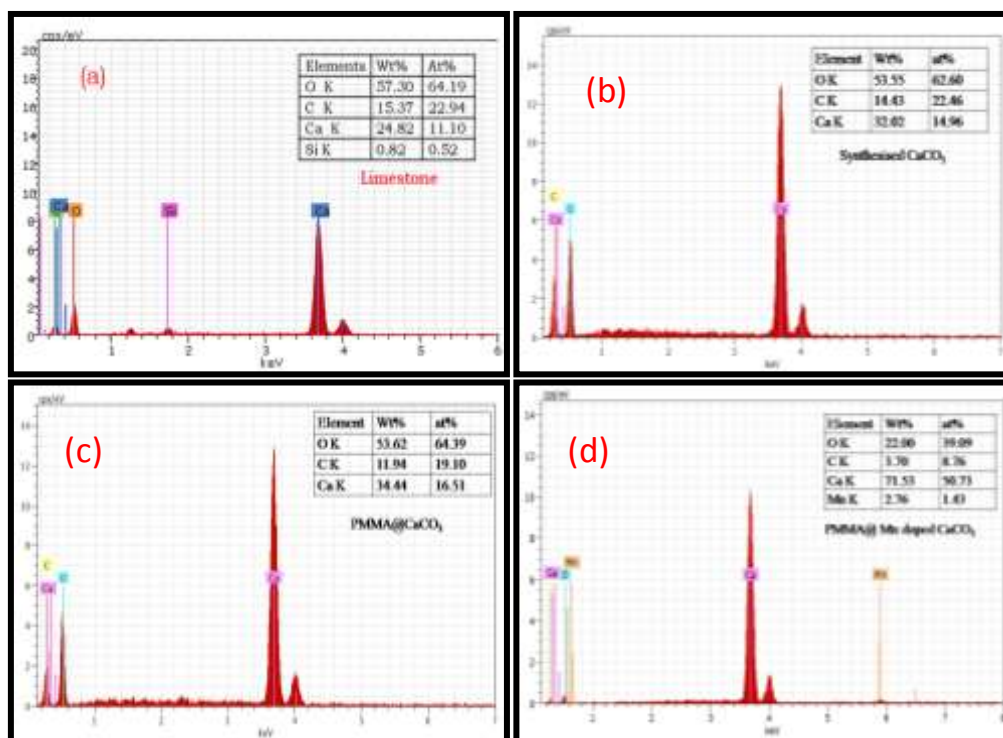
Figure.4 EDX spectra of raw carbonate rock sample (a), synthesized nanoCaCO$_3$ (b), PMMA@ nanoCaCO$_3$ (c) and PMMA @ Mn dopednanoCaCO$_3$ (d)

The doping of Mn is confirmed through the observation from fig 4d.Among these synthesized products, PMMA capped CaCO$_3$ has lower crystallite size than others.However, the increasing in crystallite size of Mn doped CaCO$_3$ product confirms the occupation of Mn in CaCO$_3$ matrix.

4. Conclusion

The PMMA template nano calcium carbonate has been successfully synthesized from natural carbonate sources by biomimetic method. In order to reduce the particle size and to avoid the agglomeration, the polymer (PMMA) has been applied on the surface of the particles. The desired transition metal (Mn) is doped in CaCO$_3$ matrix successfully. The products from this method are in nano regime due to the quantum confinement (XRD analysis). The unwanted minerals, other than calcium carbonate are completely filtered/eliminated through this method.This was proved through FTIR. The synthesized products are in pure form of calcium carbonate with rhombohedral structure. SEM images show that the products havenanoCaCO$_3$ particles. The percentage of pure Ca obtained through this method is very higher than the raw calcitic samples. Thus it is concluded that this method is the best suited procedure for extracting pure nano CaCO$_3$ from any type of natural calcium carbonate with impurities. Since the availability of the calcium carbonate is plenty, one can precipitate the pure form of nanoCaCO$_3$ easily in large scale with less cost using this method.

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