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Experimental and theoretical spectroscopic studies of branchlet-like $SrCO_3$ superarchitecture

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Abstract. Novel $SrCO_3$ superarchitecture was prepared by a simple and inexpensive wet chemical method at room temperature has been investigated. The $SrCO_3$ super architecture is in branchlet-like morphology with diameter of 1 μm and composed of numerous well-aligned nanorods of 52 nm in diameter. It was found that the morphology of the product strongly dependent on the experimental parameters, such as the concentration of aqueous NaOH solution and the reaction temperature. The synthesized nanostructure has been characterized by Field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), FT-IR and Raman spectroscopies. The vibrational frequencies of the fundamental modes of the compound have been precisely assigned and theoretical results were compared with the experimental vibrations. Theoretical information of the vibrational frequencies (FT-IR and Raman) was obtained by means of Density functional theory (DFT) calculations using DGDZVP basis set. HOMO-LUMO energy gap has been calculated. The Molecular Electrostatic Potential (MEP) analysis reveals the sites for electrophilic attack and nucleophilic reactions in the molecule.

Keywords: Morphology, XRD, Vibrational analysis, DFT, FMOs, MEP.
PACS: 68.37.Hk, 61.72.Dd, 31.15.E**,** 33.20Tp, 81.05.ue.

INTRODUCTION

Nano Strontium carbonate ($SrCO_3$) is an important raw material in modern glass and electronic industries [1]. In other hand the inorganic nano-materials strongly depend upon their size and morphologies. Therefore, it is very important to note that the design and controlled synthesis of nano-structures with different size and morphology from the viewpoint of basic science and technology [2]. $SrCO_3$ nanostructures with various morphologies, such as nanowires, nanorods and sphere-like and elliptical-like particles were successfully synthesized by a microemulsion-mediated solvothermal method [3]. In the present work, branchlet-like $SrCO_3$ super-architecture was synthesized by a simple wet chemical method by the reaction of strontium nitrate and sodium hydroxide at room temperature and they were characterized by XRD, FTIR, Raman Spectroscopy and FESEM. Density functional theory (DFT) approach has been used to study the theoretical construction of IR and Raman spectra, HOMO-LUMO and MEP analysis of $SrCO_3$ superarchitecture with the DGDZVP basis set.

MATERIALS AND METHODS

All the reagents were of analytical grade and were used as received without further purification. Synthesis was carried out by a wet chemical process using Strontium nitrate (Sr $(NO_3)_2$), sodium hydroxide (NaOH) as source materials. In a typical preparation, solution of 0.2 M Strontium nitrate was prepared in 50 ml of deionized water and then the solution of 0.2 M sodium hydroxide was added to the solution which was kept on stirring using a magnetic stirrer at room temperature for 12 h. The resultant product was finally dried at 100° C for 6 h. The structure of the $SrCO_3$ superarchitecture was characterized by XRD measurements were performed using a Philips diffractometer of X'pert Company with

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monochromatized Cu Kα radiation (λ=1. 5406 Å), with 2θ ranging between 20° and 80°, FTIR by using Perkin Elmer spectrophotometer in the range of 400-4000 cm^{-1} and micro-Raman spectrometer (Jobin Yvon LabRAM HR800 UV. The morphology was analyzed by field-emission scanning electron microscopy (FE-SEM S-4800, Hitachi).

COMPUTATIONAL DETAILS

The structure was optimized by DFT/B3PW91 method with DGDZVP basis set using Gaussian 09 program [4]. The FTIR and Raman spectra were simulated for the optimized geometry of $SrCO_3$. Gauss View 05 is used to visualize the Frontier Molecular Orbital (FMOs), vibrational spectra and molecular electrostatic potential (MEP) surface.

RESULTS AND DISCUSSION

SEM analysis

The typical $SrCO_3$ superarchitecture synthesized in wet chemical method at room temperature were observed by field-emission SEM. Fig. 1 displays a representative overview of the $SrCO_3$ superarchitecture with a scale of 1 μm, which shows morphology of individual branchlet-like SrCO3 superarchitecture. The field-emission SEM of the superarchitecture indicates that the superarchitecture was composed of uniform nanorods with a diameter of about 52 nm. All the nanorods were self assembled to construct the branchlet-like superarchitecture.

XRD analysis

The phase structures of the SrCO3 superarchitecture were examined by its XRD patterns as shown in Fig. 2. The strong and sharp diffraction peaks in Fig. 2 indicates that the as obtained $SrCO_3$ superarchitecture was principally crystalline. All of the diffraction peaks can be perfectly indexed to the orthorhombic phase of $SrCO_3$. The patterns match with the standard patterns of $SrCO_3$. The lattice parameter for SrCO3 was close to the reported values with JCPDS Nos. 05-0418. Estimated from the sheerer formula, $D = 0.891\lambda/\beta\cos\theta$. The average crystalline size of the particles for $SrCO_3$ was calculated 52 nm. The XRD results indicating that the as-synthesized product has high phase purity.

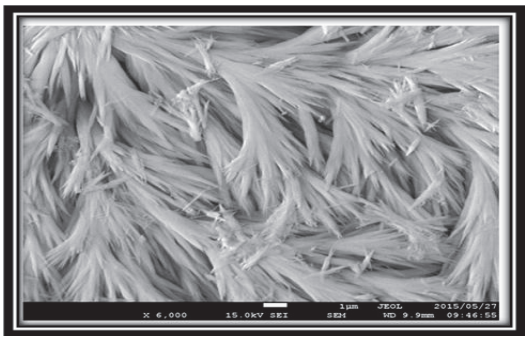

FIGURE 1. FESEM image of $SrCO_3$ superarchitecture

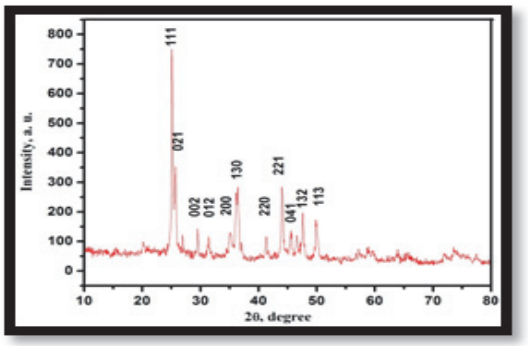

FIGURE 2. XRD pattern of $SrCO_3$ superarchitecture

FMOs analysis

There are several ways to calculate the excitation energies. The key parameter to determining the molecular properties is the simplest one involves the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The Eigen values of HOMO and LUMO and their energy gap reflect the chemical activity of the molecules. The HOMO-LUMO energy gap of $SrCO_3$ was calculated at DFT-B3PW91 methods using DGDZVP basis set and they are shown in Fig. 3.

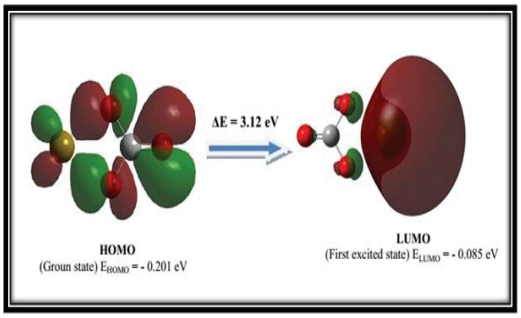

FIGURE 3. The FMOs of $SrCO_3$ superarchitecture

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Vibrational analysis

The Experimental and theoretical FTIR and Raman spectra of $SrCO_3$ superarchitecture are shown in Fig. 4 and 5.The assigned vibrational frequencies are shown in Table 1. The $SrCO_3$ was confirmed from the local lowest point on the potential energy surface by observing the absence of negative frequencies in the calculated frequencies. The calculated frequencies belong to same symmetry species due to its c_1 point group symmetry [5,6].

TABLE 1. The assignment of experimentally observed and calculated vibrational frequencies (cm^{-1}) based on the potential energy distribution (PED) analysis

S. No	Wavenumber (cm^{-1})			Assignment with PED (%)
	Calculated	FTIR	Raman	
1	1143	1071	1071	ν_{as} CO_2 (88)
2	978	856		ν_s CO_2 (86), ν C=O (10)
3	829			φ C=O (91)
4	732	705	700	δ CO_2 (89)
5	660			β C-O (63)
6	368		180	ν Sr-O (89)
7	324		146	β Sr-O (64), ν Sr-O (26)
8	101			φ Sr-O (91)

ν- Stretching, ν_s – Symmetrical Stretching, ν_{as} – Assymmetrical Stretching, β- Inplane Bending, δ – Scissoring φ- Out of Plane Bending

MEP analysis

The region around strontium was found to be electron deficient and the region around C=O was predicted as slightly electron rich which is shown in Fig. 6.

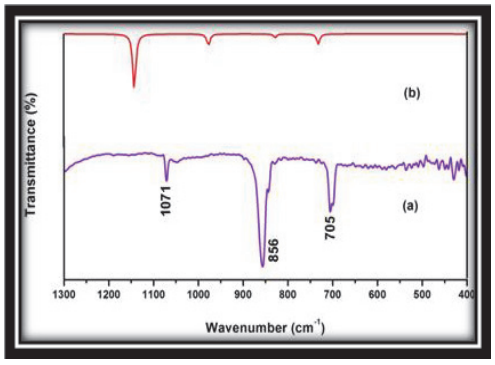

FIGURE 4. FTIR spectra of $SrCO_3$ superarchitecture (a) Experimental (b) Theoretical

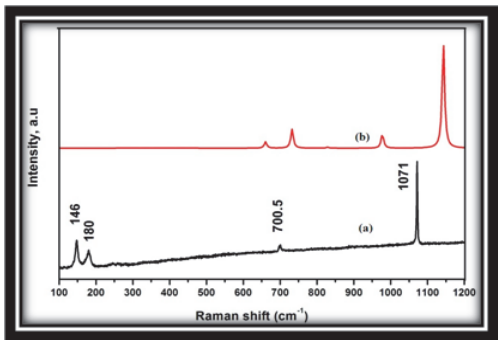

FIGURE 5. Raman spectra of $SrCO_3$ superarchitecture (a) Experimental (b) Theoretical

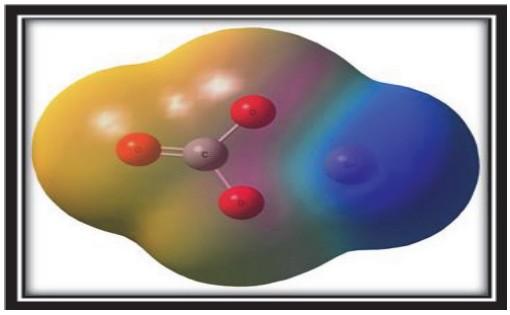

FIGURE 6. MEP diagram of $SrCO_3$

CONCLUSION

The assembly of branchlet-like SrCO3 superarchitecture has been demonstrated by a simple wet chemical route with the average diameter of 52 nm. The calculated frequencies are very closer to experimentally observed frequencies. The frontier molecular orbital analysis was carried out and charge transfer characteristics were studied. The detailed vibrational assignments were performed with a high degree of accuracy on the basis of the PED calculations using VEDA 4.0 program. The MEP analysis shows the reactive regions of $SrCO_3$

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