Mechanochemical and Sonochemical Synthesis of Bio-Based Nanoparticles

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ABSTRACT

Nanoparticles have been widely used in engineering applications because of their unique thermal, electronic, and mechanical properties. Due to the high cost and environmental hazard of the petroleum and mineral derived products, a growing effort has emerged in recent years on the research, development, and application of bio materials obtained from renewable resources. In this study we explore the synthesis and characterization of bio based nanoparticles derived from different sea shells that have a high content of inorganic components that can offer great materials for industrial and structural applications. Sea shells used in this research include littleneck and quahog clams, as well as Mussels. Mechanochemical and sonochemical methods were employed for size reduction of these materials to nanometer scale and surface modification for better dispersion. The particles were characterized for their chemical structure, size and morphology using different characterization techniques including X-Ray diffraction and scanning electron microscopy.

Keywords: Calcium silicate, Bio Nanoparticles, Eggshell and Sonochemical method.

1 INTRODUCTION

Nanoparticles have been a major research interest in the last few decades. Physical properties of materials at a micrometer scale are the same as of bulk form; however, nanometer size materials exhibit many physical and chemical properties that distinctively differ from their bulk counter parts. The transition from atoms to molecules to bulk form takes place in the nanometer size range. This is why materials in this size range demonstrate various remarkable specific properties. Moreover, the nanometer scale range is where fundamental physics of property and characteristic length scale (i.e. morphology) intersect, which is a potential to realize significant property improvements. Property changes follow from structural changes and size effects. Wide ranges of properties are possible, as opposed to just a narrow band or single value property for bulk materials. Many material properties, such as the strength, dielectric constants, and reactivity, depend on the crystalline size [1-6]

Surface to volume ratio is one of the size-dependent characteristics; at the nanometer scale, the number of surface atoms and ions becomes a significant fraction of the total number of atoms or ions. Exploring the unique properties of nanostructures and nanomaterials and realizing their potential application starts with the ability to synthesize fabricate and process them. The explosive growth of nanoscience and nanotechnology in the last decades has been possible because of the rising number of novel methods of synthesis and fabrication of nanomaterials as well as tools of characterization and manipulation. A number of innovative methods of synthesizing nanostructure materials are now available. Nanostructured materials with at least one dimension in nanometer scale include nanoparticles, nanorods and nanowires, thin films, and also bulk materials that are made of nanometer scale units or consisting of nanometer structures. Many technologies have been introduced to fabricate nanostructures and nanomaterials. The two major approaches to the synthesis and fabrication of nanomaterials are top-down approach and bottom-up approach. Bottom-up approach refers to the buildup of a material from the bottom; atom-by-atom, molecule by molecule or cluster by cluster such as the synthesis of nanoparticles by the use of colloidal dispersion. Top down approach refers to slicing or successive cutting of a bulk material to get nanometer-sized particles like mechanical attrition or ball milling. [7-8] In this method powders with typical particle diameter on the order of 50-100 μm are placed in a sealed container along with hardened steel balls. The container is shaken, rotated, or agitated to induce ball-ball and ball-wall collisions involving the powder particles. The powder deforms, facture, or gets crushed as a result of ball collisions and the particles size decreased drastically.[9-11]

Sonochemical processing is considered as of one of the most efficient techniques for generating novel materials with remarkable properties. Sonochemistry arises from the acoustic cavitation phenomenon, that is, the formation, growth, and implosive collapse of bubbles in a liquid medium [12]. The extremely high temperatures (>5000K), pressures (>20 MPa), and very high cooling rates (>10^7 K S^{-1}) [13] attained during cavity collapse lead to many unique properties in the irradiated solution. Using these extreme conditions, researchers have been able to synthesize various novel materials.

2 EXPERIMENTATION

2.1 Materials

This study focuses on the size reduction of sea shells to produce bio-nanoparticles. Sea shells used in this study include Mussels, Littleneck, and Quahog Clams which were purchased from the Farmer's Market in Dekalb County, Atlanta, GA. Littleneck and Quahog Clams are classified as "Hard Clams", with Littleneck being of the smallest in this class and Quahog being the largest. Mussels are different from most shells in that they can be found in both salt and fresh water in addition they have an elongated shell, making it easy to distinguish them from Littleneck and Quahog clams.

2.2 Procedure

Sea shells were subjected to cleaning and size reduction processes in order to produce bio-particles in nano scale. The shells were boiled in distilled water for 1 hour and then the contents were removed. In the next step the shells were grinded using a steel mortar and then using a coffee grinder to prepare fine see shell powders. The powders were collected and soaked in acetone for 2 hours then dried by heating in the oven at 60°C for 2 hours for further processing.

Mechanical attrition technique was used to reduce the particle size of sea shells. See shell powders were ball milled in polypropylene glycol for 10 hours using SPEX SamplePrep 8000D Mixer/Mill. The powder was placed in a stainless steel container along with the liquid polymer and 4 stainless steel balls (5 mm in diameter) and the container was rotated and shaked, with the mixture of powder, liquid polymer and milling balls inside. The resultant materials was washed repeatedly with ethanol and separated by centrifuge process then dried by heating at 60ºC for 24 hours. The particles were then separated according to their size using a set of sieves (95 and 20 µm) and a Retsch sieve shaker for 6 hours. Sonochemical technique was also used for size reduction of eggshell powder. The resultant material was mixed with Decahydronaphthalene in a stainless steel reaction vessel and irradiated with high intensity ultrasonic horn (Ti-horn, 20 kHz, 100 W/cm^2) for 2 hours at 10ºC. The reaction mixture was then washed with hexane repeatedly and centrifuged at 15000 rpm at 5ºC using Beckman Coulter Allegra 64R Centrifuge. The particles were separated and then dried under vacuum for 24 hours the later characterization.

2.3 Characterization

The X-ray diffraction (XRD) study was carried out with Rigaku D/MAX 2200 X-ray Diffractometer. The XRD sample was prepared by uniformly spreading the resultant powder on a quartz sample holder. XRD test was conducted at room temperature from 10 to 80 degree of two thetas.

Scanning electron microscopy (SEM) analysis was carried out using a JEOL JSM 5800 scanning electron microscope. Sea shell powder samples for SEM studies were prepared by spreading a small amount of the powder on a double sided adhesive conductive carbon tape and coated with a thin layer of gold/palladium mixture (Au/Pd) using a sputter coater Hummer 6.2 to prevent charge buildup by the electron absorption by the specimen. A 5 kV accelerating voltage was applied to accomplish desired magnification.

3 RESULTS

To investigate the crystal structure and impurities in the sea shells, the XRD analysis was conducted at various states of size reduction processes including ball milling and sonochemical method.

Figures 1 is the XRD results for littleneck clams. As seen in the figure all the XRD pattern peaks matched very well that of aragonite $CaCO_3$ (JCPDS card No. 41-1475). These results clearly indicate the presence of high content of inorganic calcium carbonate in the littleneck clam shells, and no impurities were observed. The full width at half maximum (FWHM) of 100% peak at 26° of 2θ of ball milled particles are much larger (0.407 of 2θ degrees) than the grinded shells (0.327 of 2θ degrees). This clearly suggests that the ball milled particles are much smaller as compared to the ground littleneck clams. Furthermore FWHM value of the sonicated particles after 2 hours of ultrasonic irradiation have increased to 0.420 of 2θ degrees indicating a further size reduction of the particles.

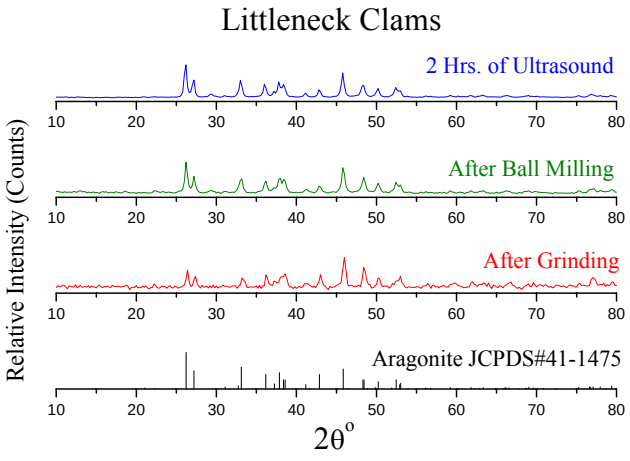

Figure 1: XRD results for littleneck clams particles

The XRD pattern of quahog clams showed similar results as seen in figure 2. All the diffraction peaks of are also assigned to aragonite $CaCO_3$ (JCPDS card No. 41-1475). The diffraction patterns also show an increase in the

FWHM values of the 100% intensity peaks at 26° of 2θ with the steps of size reduction procedure indicating the formation of smaller particles.

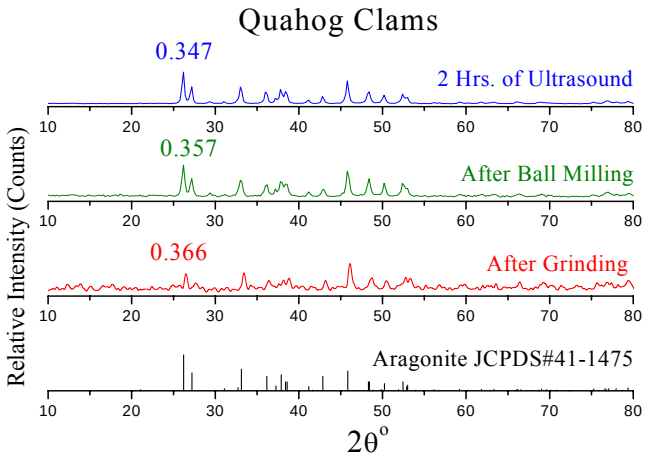

Figure 2: XRD results for quahog clams particles

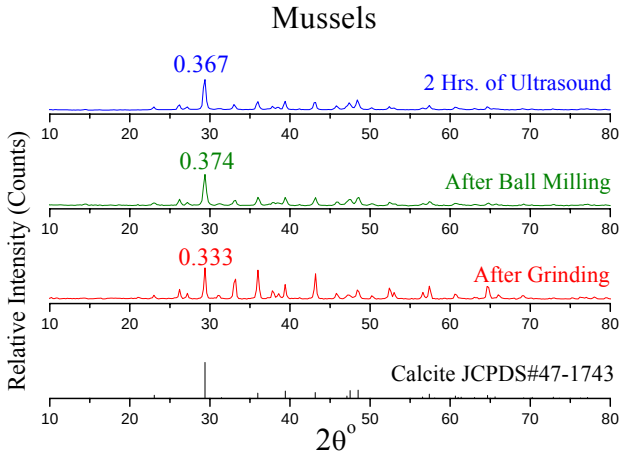

Figure 3: XRD results for mussels particles

The XRD pattern of the mussel shells particles is presented in Figure 3. The diffraction peaks are assigned to the $CaCO_3$, and they match very with JCPDS card no. 47-1743 of calcite, another form of $CaCO_3$. The values for FWHM of the 100% intensity peaks at 29.4° of 2θ were increased after ball milling of the sample from 0.333 to 0.374 of 2θ degrees suggesting the reduction of the particle sizes. However the FWHM of the sample after 2 hours of ultrasonic irradiation have decreased to 0.367 of 2θ degrees. The reason for the increase in FWHM may be due to the agglomeration of the particles after the sonication process.

To investigate the efficiency of the cleaning and size reduction processes of sea shells, scanning electron microscopy (SEM) analyses were carried out. Figure 4 shows SEM micrographs of as-prepared sea shell particles after the ball milling process. The SEM studies have shown that sea shell particles have no contaminations, and their size have been drastically reduced to few micrometer scale particles with large particles size distribution. Figure 4 shows SEM micrographs of as-prepared sea shell particles. As seen in figure 4(a), littleneck clams particles have irregular shapes and sizes with a large particles size distribution; however, all the particles presented in the image are in the micrometer scale.

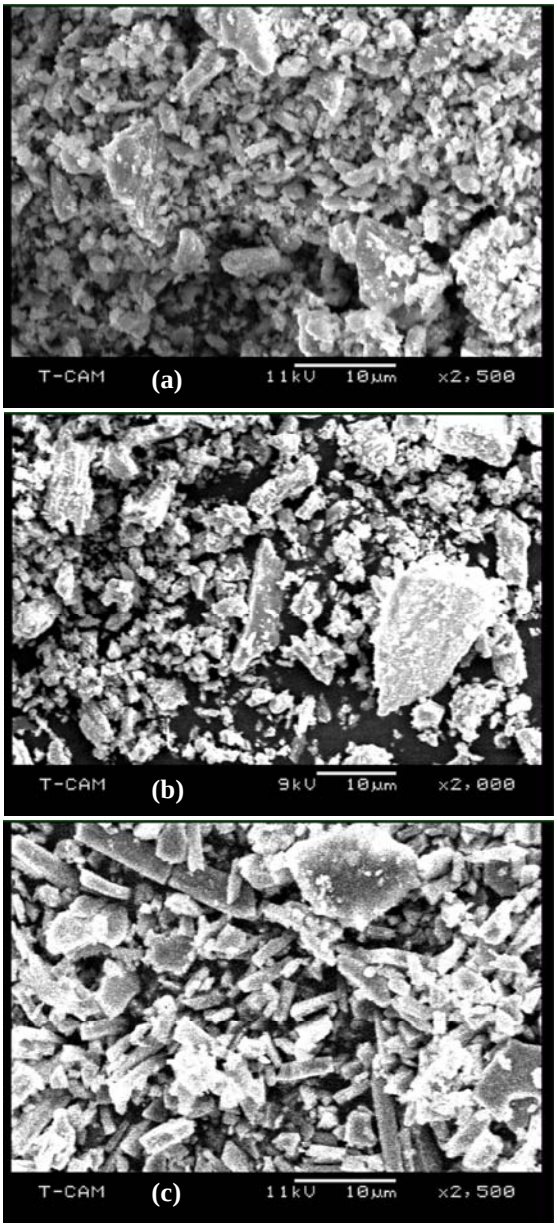

Figure 3: SEM micrographs of (a) littleneck clams (b) quahog clams and (c) mussels particles

Similar results were obtained for the quahog clams and mussels as seen in figures 4(b) and 4(c) respectively. The quahog clams particles have irregular shapes with particles sizes in the range of 1 - 10 µm as seen in the SEM image presented in figure 4(b). Mussel shells powder also have irregular shapes; however, large number of particles can be

seen to have a rod shape with particle sizes vary from > 1μm to ~ 10 μm.

These results show that ball milling is an efficient method for size reduction of sea shells to produce smaller size particles. However further transmission electron microscopy studies are needed to determine the shape and particles sizes for the as-prepared particles using the sonochemical process.

4 CONCLUSIONS

- The XRD results confirmed that the high content of calcium carbonate of different forms including calcite and aragonite in the sea shells.
- The size reduction process of sea shell particles can be efficiently used for the production of Calcium Carbonate bio-based nanoparticles.

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