A Novel Approach to Synthesize Hollow Calcium Carbonate Particles

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Hollow calcium carbonate particles were synthesized by a novel and facile approach which involves bubbling the CO_2/N_2 mixed gases into $CaCl_2$ solution. The hollow particles were formed by the aggregation of nano-sized spherical particles on bubble surface. The formation mechanism was firstly proposed and the interaction of particles with bubbles was discussed.

In recent years, there has been keen interest in the fabrication of micrometer- and nanometer-sized hollow particles. The hollow particles usually exhibit special properties that are substantially different from dense particles, such as low density, large surface area, stability, and surface permeability. Hollow oxide particles have been widely used for lightweight and thermally insulating fillers, composite materials, dyes and cosmetics,[1] catalyst supports, separation media,[2] and drug delivery agents.[3] Some optically hollow shells have extensive applications in the fields of optics, electronics, chemistry, and coating system due to a large refractive index contract between core and shell materials.

Inorganic hollow particles have been synthesized by different methods, such as organic bean template,[3,4] emulsion template,[5] surfactant-assembled template,[6,7] colloid array template,[8,9] and so on. All these methods involve two steps. First is to cover the template by inorganic materials, forming the solid shell. Second is to remove the template by calcinations or decomposition to solvent. The limitations of these methods are the pollution of organics and the complexity of process. It is therefore, necessary to develop a simple and low-cost process for the preparation of hollow particles, especially for the industrial production.

We proposed a new and simple process to prepare hollow calcium carbonate particles by using bubbles as templates. The advantage of this new approach is to simplify the synthesis of hollow particles by leaving out the removal of template. The fabrication procedure can be described as the following. Firstly, calcium chloride (Wako Pure Chemicals, Japan) and ammonia (Wako Pure Chemicals, Japan) were mixed and diluted to form a solution ($C_{Ca} = 0.05$ M, $C_{NH_3 \cdot H_2O} = 0.5\%$). The freshly prepared solution reacted with the mixed gas ($CO_2 + N_2$) that was introduced to the bottom of the solution through a wood filter which is a natural wood for bubbles production, at a flow rate of 0.9 L/min and CO_2 content of 33.3%. The reaction temperature was kept 25 °C by a water bath. During the precipitation, the solution was continuously stirred at a constant rate of 400 rpm by means of Teflon-coated magnetic stirring bar. The total volume of the working solution was 500 mL and the pH value of the solution was measured by a pH meter (Cyberscan, made in Singapore). The pH value decreased continuously with the proceeding of precipitation. There was no change in pH after the precipitation was completed. The prepared solids were collected by filtering through membrane filters (0.2 µm) and dried at 120 °C. SEM (JEOL JSM-6100) was used to observe the morphologies of samples. XRD (RINT, Rigaku, Japan) measurements were conducted using Cu Kα radiation (40 keV, 30 mA) to identify the composition of products. Spherical particles with a diameter of 3–5 µm were synthesized, as shown in Figure 1. The XRD measurements, as shown in Figure 2, revealed that the spherical particles were primarily composed of vaterite with minor phase of calcite.

Some broken particles were observed with void inside surrounding by solid shell with the thickness of several hundred nanometers. These particles were called hollow $CaCO_3$ parti-

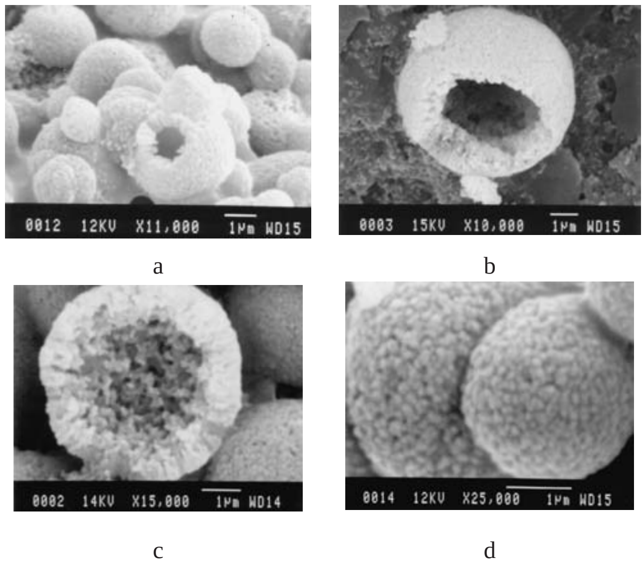

Figure 1. SEM image of hollow calcium carbonate particles.

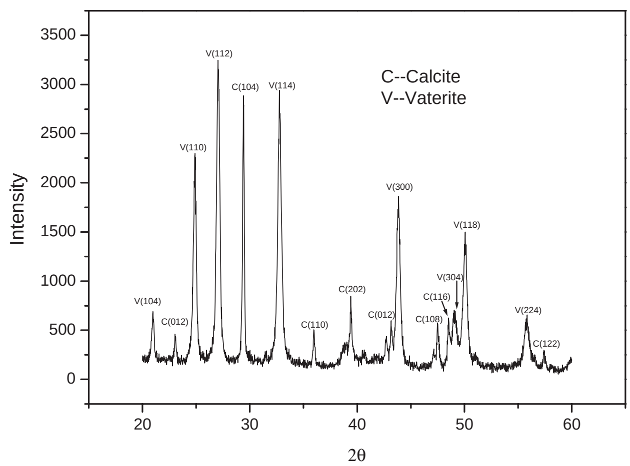

Figure 2. XRD patterns of hollow calcium carbonate particles.

cles. As far as our knowledge is concerned, the hollow $CaCO_3$ particles have not been reported in the carbonation of calcium solution. The formation of hollow particles in our experiments may be attributed to the control of bubbles sizes, bubbles composition, and other precipitation conditions.[10] Figure 1c is a part of the hollow particles, indicating that the inside of hollow particles is porous. Figure 1d is another view of magnified hollow particles. It was found that the particles were formed by the aggregation of fine particles with the diameter of 20–30 nm.

In the carbonation of $CaCl_2$ solution, the initial precipitation is the amorphous calcium carbonate.[11] The initial formed $CaCO_3$ is unstable and quickly transform to two crystalline phases, namely calcite and vaterite. The freshly crystalline particles with a nano-sized diameter are not stable because of its high surface area. The fine particles tend to aggregate to achieve a minimum of total surface free energy. Some fine particles attach to the N_2 bubbles and aggregate together, forming the hollow particles. So the formation mechanism of hollow particles can be depicted as Figure 3. It generally involves 3 steps. First is the formation of fine crystalline particles. Second is the attachment of fine particles to bubbles. Third is the aggregation of fine particles, forming the solid shell.

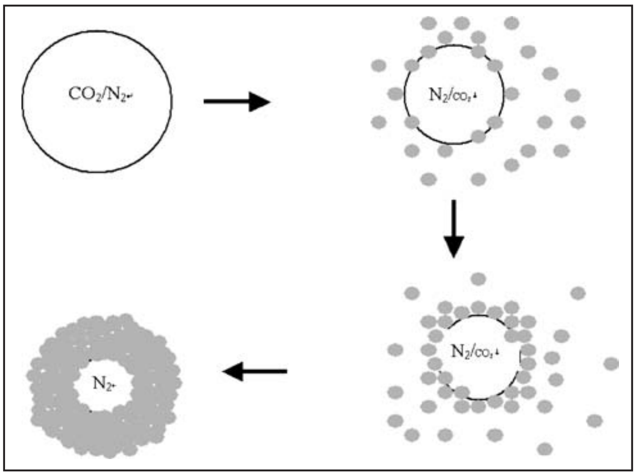

Figure 3. Proposed mechanism for the formation of hollow $CaCO_3$ particles.

In practice, the attachment of solid particles to bubbles is a complex process and is affected by numerous factors, such as particle surface chemistry, particle size, hydrophilic and hydrophobic properties of particle surface, electrostatic interactions, and hydrodynamic conditions.[12] The interaction of particles with bubbles is the key point of this process. At large distance, the interaction between a particle and a bubble is mainly determined by hydrodynamic force. At the distance of 100 nm, surface forces start to play a role.[13] At such a close distance, two regimes can be distinguished, namely before contact state and after contact state. Before a three-phase contact (TPC) is formed, surface forces govern the bubble-particle interaction. Surface forces can be categorized as the electrostatic double-layer force, the van der Waals force, hydration and hydrophobic forces. Electrostatic double-layer interaction contributes to particle-bubble attachment only when the particles and the bubble carry opposite signs of electrostatic potential. Since the air/water interface is negatively charged,[12] the positively charged $CaCO_3$ particle is attracted by bubble.[14] This may be the main reason for the formation of hollow calcium carbonate particles in carbonation. However, the $CaCO_3$ particle is hydrophilic, causing a repulsive force when the $CaCO_3$ particle coming in contact with the bubble, which is one of the reasons for the seldom formation of hollow $CaCO_3$ particles. In the further research, it is necessary to modify the $CaCO_3$ particles with the characteristic of hydrophobic to promote the production of hollow particles. Although the repulsive force is present, the hydrophilic particles can still attach to bubbles in certain condition,[12] which is in good agreement with our results. When the particle encounters the bubble, the TPC is formed. After TPC formation, the capillary force holds the particle in the water/bubble surface. Since the capillary is relatively strong, the adhesive force of the particle is large enough to prevent the destruction of the attachment. The detachment of particles from bubbles probably happen at the strong turbulent fields when the kinetic energy of the particle is greater than the adhesive force.

In a conclusion, hollow calcium carbonate particles were successfully synthesized using bubbles as templates. The prepared particles with the diameter of 3–5 μm were formed by the aggregation of nano-sized spherical particles on the bubbles surface. The formation mechanism was firstly proposed and the interaction of particles with bubbles was discussed. It is warmly expected to apply this method to prepare some other hollow particles, such as SiO_2, TiO_2, by passing bubbles into their colloids.

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