

Novel method for synthesis of unstable vaterite polymorph of hollow calcium carbonate nanoparticles and encapsulation of anticancer drug cisplatin

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Calcium carbonate particles have widespread technological applications in paper, pharmaceutical, textile, rubber, plastic, paint, cosmetic, toothpaste, glove and other industries. Calcium carbonate mineral has several polymorphic forms of which calcite is the most stable form. Other polymorphic forms include aragonite and vaterite which are less stable. The use of nanoparticles instead of micro or macro particles in industries drastically reduces the material requirement and hence development of methods to prepare nanoparticles is important. However, usual sol-gel synthesis of calcium carbonate nanoparticles results in the formation of the stable polymorph, i.e., calcite, or amorphous calcium carbonate. In this research, we have developed a novel method to prepare thermodynamically unstable vaterite nanoparticles using a soft-template method and to stabilize them under ambient laboratory conditions. In this method, the soft-template is formed using ethylene glycol and water and calcium carbonate is prepared in the aqueous solution of the soft template. The hollow, spherical hydrogen-bonded structures formed from water and ethylene glycol molecules lead to the arrangement of calcium and carbonate ions in a spherical structure thus leading to the formation of vaterite. This has been confirmed by SEM images taken without heat treatment, X-ray diffractogrammes and FT-IR spectra of the product. SEM images also show the porous nature of nanoparticles. Particularly, the FT-IR absorption bands at 877, 745.8 and 1084 cm^{-1} confirm the presence of the vaterite polymorph of CaCO_3 . Absence of absorption bands at 854, 712, 700 cm^{-1} and 848, 714 cm^{-1} indicates the absence of calcite and aragonite polymorphs. BET surface area analysis indicates 60% porosity in the particles. Particle size analysis in the solution phase reveals that the colloidal solution prepared contain three discrete sizes of particles with diameters 25 nm, 35 nm and 50 nm. The vaterite nanoparticles prepared are dispersed in the aqueous solution of cisplatin in saline water and stirred for 24 h. The product separated from centrifugation followed by filtration is washed several times with distilled water and dried under ambient laboratory conditions. The FT-IR of the product contains N-H stretching, N-H wagging together with CO_3^{2-} vibrations. XRF spectrum shows Ca, Pt and Cl peaks with Pt:Cl atomic ratio close to 1:2. Both these information suggest the presence of both vaterite and cisplatin in the product. Since the product was thoroughly washed it is impossible to have a mixture of two or cisplatin adsorbed onto external surfaces of vaterite particles. Hence cisplatin is encapsulated within the hollow nanoparticles of vaterite. This product has a significant medicinal use as a safe anticancer drug since the cytotoxicity of cisplatin can be drastically reduced in this way.