UNIVERSITI TEKNOLOGI MARA

PHASE STABILITY OF CALCITE NANOCRYSTALS SYNTHESIZED BY ADDITIVE-FREE THERMAL CHEMICAL VAPOR DEPOSITION AND PRECIPITATION

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ABSTRACT

Calcium carbonate ($CaCO_3$) nanocrystal mostly occur naturally micro sized in unstable mixed phases making it unsuitable for critical biomedical application. Hence many attempts to synthesize them with the use of additives to gain stable single-phase calcite nanocrystal. However, the toxicity of most additives could cause it not suitable for a more sensitive application. Therefore, in this study, a few different methods were used to synthesize $CaCO_3$ in single-phase calcite without using any additives. A few different methods were attempted such as novel thermal chemical vapor deposition method (CVD), hydrothermal method, gas diffusion method and titration-precipitation method. The novel thermal CVD method was first time ever reported to synthesize single-phase nanocrystal optimally on fluorine tin oxide substrate in steady flow of 100 sccm CO_2 gas at 400 °C however in less stable $CaCO_3$ phase. The hydrothermal method at 150 °C produced a mixture of phases of less stable phase of $CaCO_3$, with the presence of impurities. Whereas gas diffusion method synthesized single phase calcite nanocrystal at 168 h in 25 °C nevertheless produced significantly lower yield. This work concludes that titration – precipitation method is most feasible to synthesize single-phase calcite nanocrystal. It was found that even at low concentration titration-precipitation method successfully synthesized single-phase calcite nanocrystal. The crystallite size was determined to be 86 nm under the optimal conditions of a 0.5 M concentration of calcium chloride and ammonium carbonate precursors, mixed in a 1:1 ratio at 25 °C. With each method, elemental analysis was done to confirm its chemical composition and phase whereas surface morphology analysis was done to describe its structure. It was explained how precursor concentration affects its structural morphology more specifically demonstrated by the presence of micro strain and change of lattice parameter in the crystal lattice. Other parameters sensitive to each different method affecting ion availability, and molecular interaction were also discussed. This study effectively outlined an innovative, additive-free technique for producing stable, single-phase $CaCO_3$ nanocrystals that may be used in sensitive biosensor or biomedical applications.

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CHAPTER 1
INTRODUCTION

1.1 Nanomaterials: Past, Present, and Future

Research and development in nanotechnology are growing rapidly throughout the world. There are different types of nanomaterials comprised of organic, inorganic, carbon, and composite-based [1, 2]. It is based on the study and development of new or existing materials with one or more external dimensions measuring less than 100 nm to create materials with fundamentally new properties and functions [1, 3-6]. The areas where nanomaterials are encompassed are extensive involving from small domestic scale to the big industrial-scale [7-9]. Although nanomaterials have been around since the geological period, it is only recently that strong interest revolves around them. This is related to the concerns surrounding how it affects the health and safety [6-9] and the conjecture of how nanomaterials' overall properties are greatly enhanced. Among them are physical, chemical, and biological characteristics that are improved immensely compared to the bulk materials [1, 6]. They are also known to have superior optical, electrical, and magnetic properties [3].

There are many types of nanomaterials ranging from nanosphere, nanoclusters, nanofibers, nanowires, nanorods, networks, nanofilms, and many more fields [3]. The past of nanomaterials is part of the substance civilization [5] from as early as the Big Bang where nanostructures are found in the meteorite [3]. Around 5000 years ago, there was evidence of carbon nanotechnology used as a black pigment for house bases in Gansu Province of China made from pine soot [5]. Whereas silver and gold nanomaterials were being used in Mesopotamia in ninth century [1] and by the Romans in AD 400 [1]. From AD 300 to AD 1700, the Damascans and Romans used nanomaterials to improve their steel swords' properties. At AD 800, one of the most popular uses of nanomaterials was used in Mayan City of an indigo dye in clay nanopores called Maya Blue [1].