ABSTRACT

A simple one pot synthesis method was developed for the synthesis of biocompatible fluorescent ultra-small $CaCO_3$ prenucleation clusters (1.3 nm) using moringa oleifera extract as reducing agent and BSA protein as capping and biomineralization agent. The synthesized $CaCO_3$ prenucleation clusters emit different colors in blue, green, and yellow/red zone having fluorescence lifetime of 1.05, 6.23 and 30.60 ns, respectively. The number of calcium atoms present in one molecular nanoclusters were 16, 50, 73, 222 and 936, as revealed by MALDI MS analysis. When these nanoclusters are incubated with MG-63 cells for a period of 7 days, cell viability started to increase when compared with the control cells. Further, CTCF analysis was utilized to estimate the cell penetration depth of these nanoclusters. Blue and green emitting nanoclusters traversed 6 μm, while red emitting clusters traversed 4 μm. The relative quantum yield of these nanoclusters are determined to be 0.0175 in solvent water relative to Rhodamine 6G (0.92). The synthesized nanoclusters displayed eminent photostability, long term stability (four months) and excellent pH stability. These nanoclusters synthesis process uses environmental friendly, low cost, and green synthesis approach that relied on the biomineralization technique. Furthermore, the current research includes results obtained through sophisticated characterizations such as XRD, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), MALDI-MS, UV-visible absorbance analyzer, fluorescence lifetime measurements, fluorescence spectroscopy, transmission electron microscopy, fluorescence and confocal microscopy. Furthermore, to understand the thermodynamic and kinetic properties of ultra-small $CaCO_3$ prenucleation clusters, for computation of nucleation rate at high temperature (>100°C), thermogravimetric analysis (TGA) was utilized for the first time. The examination of such nucleation rate at various temperature levels especially at high temperature greater than 100°C offers valuable quantitative information

about the formation of sub molecular size nuclei, which can ultimately help to produce crystals of desired morphology (size and shape). The precise determination of nucleation rates, thermodynamic properties, and interfacial energy for nanoclusters (1-2nm) continues to hold a great challenge at elevated temperatures. Herein, E_α (activation energy of nucleation), $\Delta G, \Delta H, \Delta S$ (thermodynamic parameters) and A_α (preexponential kinetic factor) are typically used to compute the kinetic, thermodynamic and frequency factor analyses, which ultimately utilized to compute nucleation rate of such ultra-small $CaCO_3$ prenucleation clusters at elevated temperatures (>100℃). TGA experimental values are used from 555 to 795K to estimate activation energy of nucleation by using the most precise iterative iso-conversional method and subsequently random nucleation dependent differential function f(α), respectively, in a small interval of conversion (0.005). Based on the aforementioned analyses, this study introduces four different mathematical models that can be utilized to calculate nucleation rates$(\text{nuclei}\,\mu m^{-2}min^{-1})$ and interfacial energy(mJ/m^2) of $CaCO_3$ nanoclusters against conversion and specific temperature. In addition, experimental verification is also conducted to evaluate the presence of nucleation in $CaCO_3$ pre-nucleation clusters at elevated temperatures (500℃), employing X-ray diffraction pattern and experimental z(α) master plots. Therefore, thermogravimetric analysis (TGA) technique can be employed to forecast and comprehend rates of nucleation in diverse range of nanoclusters. On the same lines, tin (Sn) element exhibits eminent biocompatibility as similar to alkaline earth metal such as calcium. Tin (Sn) is commonly exists in two different phases, abbreviated as alpha tin (α-Sn) and beta tin (β-Sn). The exceptional semiconducting properties of diamond-cubic tin (α-Sn) render them an astonishing material among diverse scientific communities. However, to synthesize substrate-free α-Sn nanocrystals at room temperature remains a great challenge. To address this challenge, herein an

advanced reduction technique is developed that produces ultra-small α-Sn nanocrystals alongside β-Sn in solvent water, at normal room temperature. Due to presence of high NIR light to heat conversion efficiency (42.4%), these nanocrystals are utilized for *in-vitro* cancer cell treatment, on exposure to a low-power (0.5 W) continuous wave (CW) laser that emits near-infrared (NIR) light at a wavelength of 980 nm. A highly advanced mathematical model is proposed to predict the extent of damage to malignant cells both pre- and post-photothermal therapy, by using FFT-weighted bright-field imaging. The presence of non-toxicity and astonishing biocompatibility of tin nanocrystals have been conclusively established through *in-vivo* experiments on Wistar rats, and by MTT assay. The synthesis of tin nanocrystals without any type of substrate like InSb, CdTe, holds a significant potential for their utilization not only in the field of healthcare but also for diverse applications.