Synchrotron Diffraction Study

of Nanostructures Nucleating in Solutions

Dissertation

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Ahmed Shaban Abdelfadil Mohammed

aus

Ägypten

Promotionskomitee

Prof. Dr. Johan Chang (Leitung der Dissertation)

Prof. Dr. Titus Neupert

Prof. Dr. Piero Macchi

Dr. Antonio Cervellino

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Abstract

Synchrotron Diffraction of Nanostructures Nucleating in Solutions

The nature of the entities present at the early stage of the precipitation pathways from solutions is largely debated in the literature. These entities might drive the entire nucleation and growth mechanisms of the precipitation. Understanding the formation of these entities is of fundamental relevance in order to achieve an appropriate control at the macroscopic level of the solid formation, for instance in terms of morphology, physicochemical properties, and crystalline phase. In this thesis, targets of investigations of the early stage of the precipitation kinetics (i.e. pre-nucleation stage) from supersaturated solutions are calcium carbonate (CaC) and phosphate (CaP), being the most studied biominerals. Despite the high scientific relevance across a broad spectrum of applications, little is known about their early stage formations.

In order to investigate the precipitation pathway from CaC and CaP systems, a series of synchrotron wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) experiments were performed at the MS-X04SA beamline of the Swiss Light Source (SLS) at the PSI, Villigen, Switzerland. In particular, the SAXS signal is

important for detecting amorphous entities in suspension such as clusters or nanodroplets with a density higher than that of the solvent and their size and shape. For the CaC and CaP systems, *in-situ* SAXS experiments were performed with horizontal liquid microjet specifically designed for such measurements. The jet was generated using a capillary connected to a mixer, where four HPLC pumps were delivering solutions in order to obtain the desired pH and saturation level of the systems. The saturation level was evaluated thanks to an accurate thermodynamic-kinetic precipitation model of CaC and CaP systems. The liquid was collected in a catcher where the temperature (T) and pH of the solution, under stirring, are monitored on line. The microjet was highly stable, with tunable diameter, pulsation-free and the delay between the mixing point and measuring point can be tuned. Time-resolved measurements using the WAXS regime were also conducted on calcium carbonate-forming solutions system in quartz capillary.

A practical procedure for absolute intensity calibration for SAXS studies on liquid microjets was established, using a gold nanoparticle suspension as a standard. In this way, the intercept of the corresponding SAXS scattering curve could provide a scaling reference pertaining to the experiments. The SAXS data collected from liquid

microjets of amorphous calcium carbonate (ACC) and amorphous calcium phosphate (ACP) suspensions were modeled using parametric statistical models. Insights about the size and shape distribution of denser matter in the liquid jet are provided. Theoretical implications on the early stage of solid formation pathway are inferred. Furthermore, the pair distribution function (PDF) analysis was utilized to extract information from the WAXS data about the evolving structure of calcium carbonate. The feasibility of the WAXS data collection yields a clear signal in moderate acquisition times, of the order of minutes−it is able to distinguish between amorphous clumps and crystalline nanoparticles.