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In situ Raman spectroscopy of crystallization: One crystal nucleation at a time

Crystallization is an important topic in science and has many applications in fundamental and industrial research. Understanding the microscopic picture of crystal nucleation is crucial for rational control of crystallization processes and crystal polymorphs. A major challenge for experimentalists to study crystal nucleation is its stochastic and heterogeneous nature at the nanoscale: it is impossible to predict where and when a nucleation occurs. Particularly, probing the details of the nucleation dynamics by optical spectroscopy has been difficult. To this regard, there is a well-established powerful concept to deal with a stochastic, complex and heterogenous system: Single molecule spectroscopy [1]. The key to bring optical spectroscopy to the field with its full potential is to probe single nucleation event at a time, if we can predict precisely where a nucleation occurs.

Recently, we developed a method called Single Crystal Nucleation Spectroscopy (SCNS) that spectroscopically probes crystallization process in aqueous solution one crystal nucleation at a time [2]. SCNS is based on an extension of optical trapping Raman microspectroscopy combined with optical trapping induced crystallization (OTIC). OTIC allows us to spatially control a single crystal nucleation event (i.e. at a focused laser spot), so that a probe beam can be placed at the same position to track the nucleation process. We achieved measuring Raman spectral evolution of a single glycine crystal formation in aqueous solution with 46 ms time resolution at room temperature.

Even if glycine is the simplest amino acid, the glycine crystallization in solution is subject to a lot of debate on its nucleation pathway: the existence of aggregates and the alteration of polymorphs by addition of additives. Raman spectral evolution during a single glycine crystal nucleation in water measured by SCNS and analyzed by a non-supervised spectral decomposition technique uncovered the Raman spectrum of pre-nucleation aggregates as well as its critical role as an intermediate species in the dynamics. The kinetical data showed that the spectrum of prenucleation aggregates were replaced by that of β-glycine which then quickly converted to α-glycine. The comparison between the Raman spectrum of pre-nucleation aggregates and our simulated spectrum from glycine solutions further suggested that there is a broad structural distribution of glycine linear networks that are held together by hydrogen-bonding interactions, and they play an important role as pre-nucleation aggregates toward glycine crystallization in water.

References

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