

***In-situ* micro-spectroscopy technique for chemical bonding during nucleation: A transition from soft bond to stiff bond**

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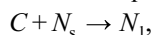
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In-situ technique has been widely used in recent years since the advent of high-resolution spectroscopy systems, which stimulates us to probe into the time-dependent, dynamic behaviors and relevant mechanisms during a series of physical processes [1]. Especially, *in-situ* analysis presents a unique real-time glimpse into the fascinating physical phenomena [2], which are very important to develop the materials for subsequent applications. Generally speaking, the nucleation process involves dynamic changes in the cluster structures, as well as the formation and transformation of chemical bonds, which requires *in-situ* analysis urgently [3].

The idea of chemical bonding provides novel insights into the nucleation process [4,5] which can be expressed as a chemical equation as follows:



where C is the cluster, N_s is the small size nucleus and N_l is the large size nucleus. This model contains two fundamental assumptions: entropy change approximation and chemical bond softening. In the first assumption, entropy change may be assumed negligible when individual small size clusters are combined into larger clusters. This means that reduction of the whole system energy comes from the released energy via forming chemical bonds when clusters become combined. This also makes it possible to use bond energy (bond enthalpy) [6] to describe free energy variation of the system. In the second assumption, ions with similar resonance status

[7] often combine to form clusters, and the clustering structure is constantly changing due to chemical bonds softening. Different chemical bonding is the key to distinguish the state of the system. As shown in Figure 1, the as-formed clusters via those soft chemical bonds belong to a kind of amorphous state. When the size is large enough, the soft chemical bonds transform into stiff ones, resulting in a further reduction in energy. This marks the formation of a nucleus with a crystalline structure which has the lowest energy and therefore no longer changes dynamically.

We have proposed and experimentally demonstrated the *in-situ* micro Raman characterization technique of chemical bonding behaviors driven by electronegativity [8]. As shown in Figure 2, in a modified setup, the emission from a single droplet can be excited *in-situ* under a laser scanning. The sample information about chemical bonding in aqueous system can be characterized *in-situ* by a series of spectra. High spatial resolution and the design of the bottom droplets make it possible to observe nucleation in real time. Raman signal increased obviously with the increase of the laser intensity [9,10], and the use of droplet inversion and ultra-thin glass expand the application of high magnification short focus objectives in solution Raman testing, which further significantly improves the signal. Figure 3 is a typical Raman spectrum of hexahydrate nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) aqueous solution which is divided into two regions to analyze variations of sulfate ions and water molecules [11,12]. Through rapid and continuous scanning of these two regions,

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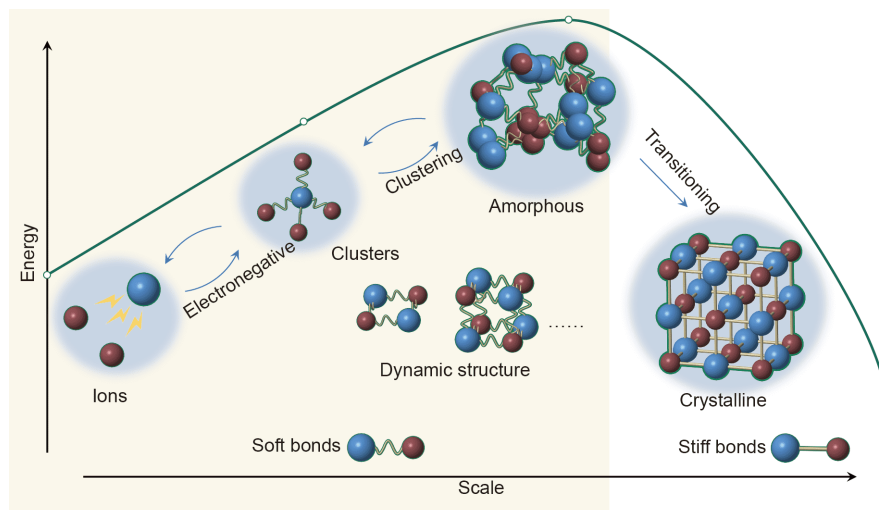


Figure 1 (Color online) Schematic drawing of chemical bonding during nucleation. Ions form clusters with dynamic structure due to electronegativity. As the supersaturation increases, the cluster size increases to a critical amorphous state. This process is the chemical bond softening which produces soft chemical bonds that are easy to recombine. Finally, the soft bond changes to stiff bond and thus becomes crystalline which the structure no longer changes dynamically.

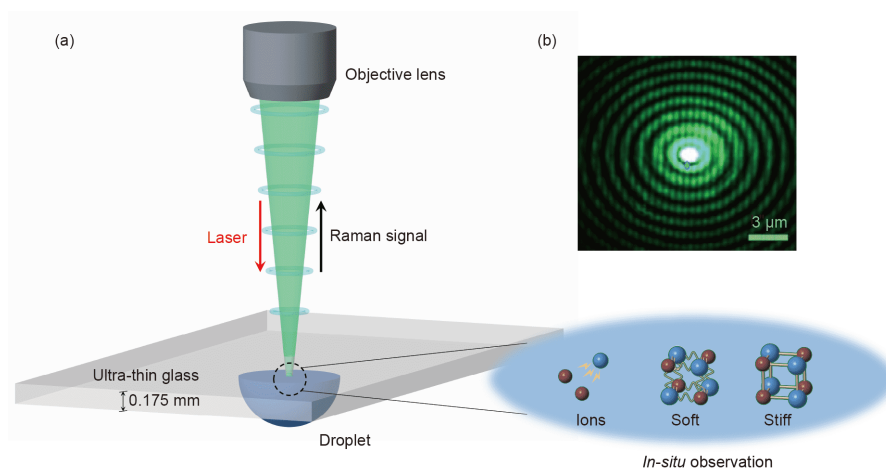


Figure 2 (Color online) (a) Schematic drawing of the *in-situ* Raman characterization setup; (b) enhanced signal of the laser spot focusing onto the sample droplet.

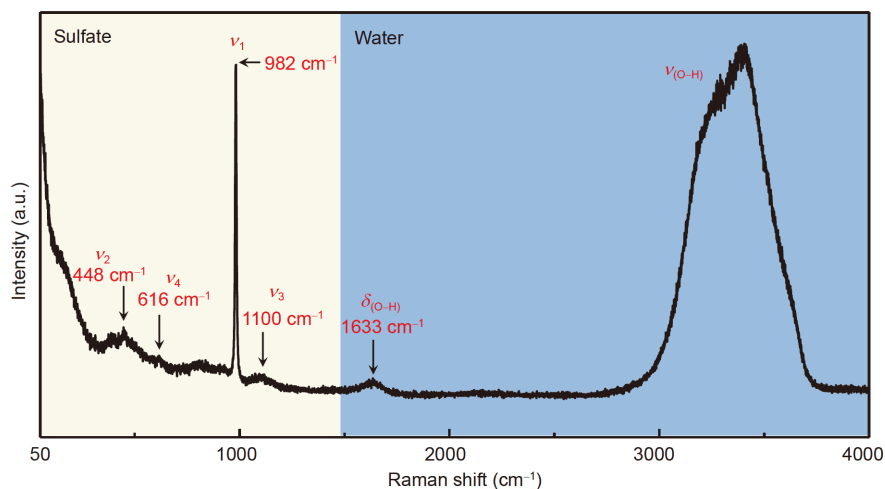


Figure 3 (Color online) Typical Raman spectrum of the $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ aqueous solution sample on the droplet bottom microprobe.

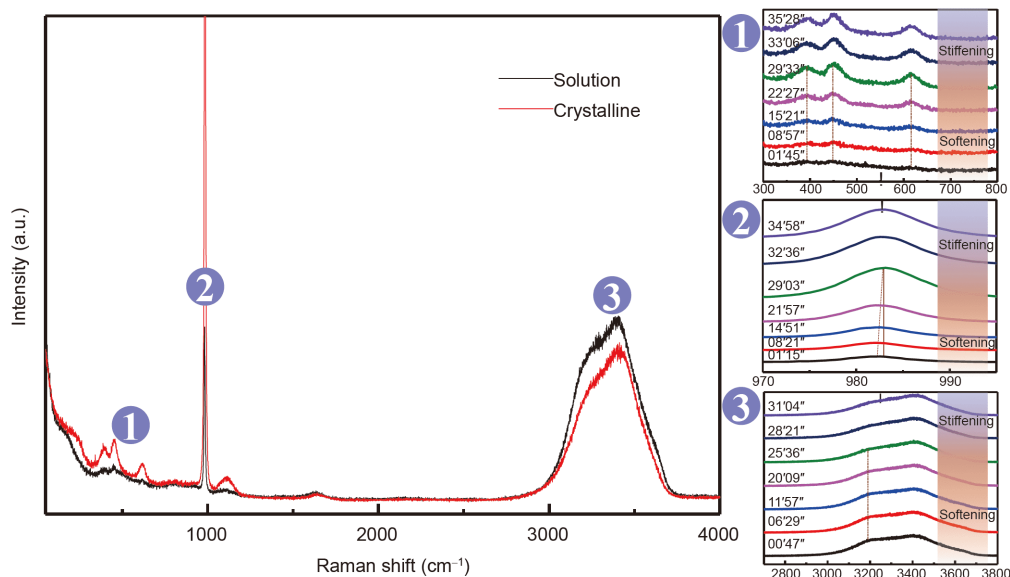


Figure 4 (Color online) Rapid and continuous Raman scanning for three regions of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ aqueous solution. Due to chemical bond softening, the Raman intensity of sulfate ion vibration will gradually increase, and the intensity of water molecules will gradually decrease. After the formation of stiff bond, the intensity no longer changes.

we obtained the changes of sulfate ions and water molecules during nucleation, that is, the variation of solution structure (Figure 4). *In-situ* observations allow us to find the whole process of chemical bond softening and the sharp change, i.e., the transition from soft to stiff bonding. This result shows great importance of chemical bonding during nucleation process. The current strategy and method are quite general and should be applicable to the semi-quantitative research of complex crystallization processes under multiple physical field driving conditions and reaction process of multiple substances.

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