Recent Progress on the Formation Mechanism of Copper Nanoparticle in Oregon Sunstone

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As a high-value gem mineral with unique optical properties, Oregon Sunstone has garnered attention in mineralogical and geochemical research. In our previous studies, we confirmed that its diverse coloration and optical properties arise from copper nanoparticles (NPs) of varying geometries, which induce by localized surface plasmon resonance. In the isotropic (red) zones, NPs manifest as randomly distributed nano-spheres, while in dichroic (green/red) zones, they appear as directionally aligned nano-rods (Wang *et al*. 2025). However, the formation mechanisms of these nanoparticles and the factors controlling their geometries remain unresolved. Resolving these questions will advance efforts to locate, synthesize and identify these gem crystals.

Comparative stability of nanoparticles with different geometries

Both previous studies and our experimental findings demonstrate significant differences in the thermal stability between spherical and rod-shaped nanoparticles. Hofmeister and Rossman (1985) observed that the green color zones in feldspar disappeared after heat treatment at 850°C, whereas the red zones required heating to 900°C for color re-absorption. Our results align with this trend, though the green reabsorption temperature was lowered to 800°C.

Similar instability is observed at the nanoscale: copper nanoparticles exhibit poor electron beam tolerance, rapidly decomposing and undergoing amorphization at visually observable rates during transmission electron microscopy (TEM) observations. Notably, spherical nanoparticles retain metallic Cu^0 even after their geometry and crystal structure are disrupted. In contrast, rod-shaped nanoparticles decompose faster under electron irradiation, and the valence state of Cu in rods increases due to progressive oxidation during decomposition (Figure 1). Both macroscopic and microscopic observations confirm that spherical nanoparticles exhibit superior stability compared to their rod-shaped counterparts.

Color transition by thermal treatment

During thermal treatment of sunstone samples, we serendipitously observed that anisotropic green samples transitioned to isotropic red at 750°C. Intriguingly, this transition could not be achieved when the temperature was lowered or raised. Below 750°C, no color change occurred; while above 750°C, the color completely disappeared (Figure 2). From a phase transition perspective, if rod-shaped and spherical nanoparticles represent distinct mineral phases, their phase transition temperature would be 750°C. However, attempts to reverse the process (converting red to green) proved unsuccessful despite extensive experiments involving multiple thermal pathways: varying temperatures and durations; direct heating at/around the transition temperature; and high-temperature "activation" followed by low-temperature annealing. These efforts either fully dissolved the nanoparticles or re-formed spherical nanoparticles.

This suggests that the interconversion between rod-shaped and spherical nanoparticles is not governed by a simple phase transition mechanism.

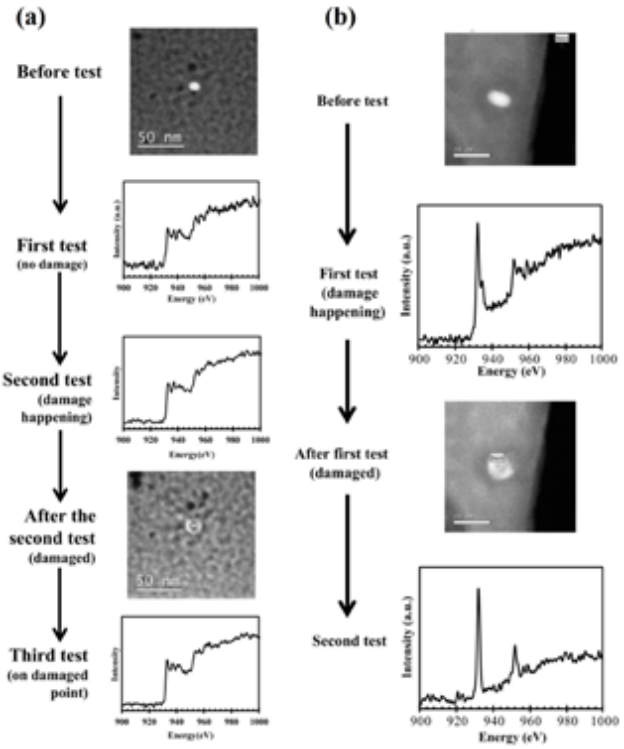

Figure 1. Electron beam damage of NPs during the collection of EELS spectra. (a) In the red zone, the NP was damaged after second test and the valence state of Cu reminded 0.
(b) In green zone, the NP resulted in a valence state about ~1.5 and was significantly damaged thereafter. After the second test, the valence state of the NP turned increased to ~2.

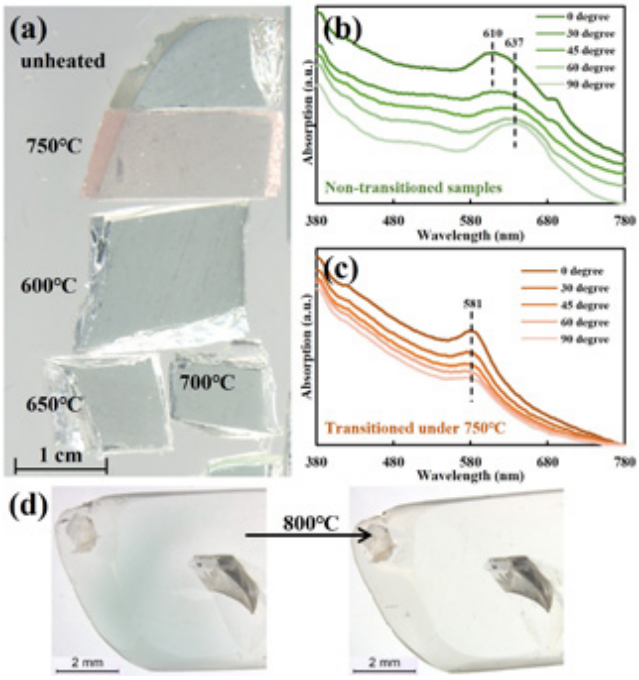

Figure 2. Color transition by thermal treatment.
(a) (d) Photographs for samples which has been heated under different temperatures. (b) Polarized UV-Vis spectra of sample before color transition. (c) Polarized UV-Vis spectra of sample after color transition.

Theoretical model for shape transformation of Cu nanoparticles

Inspired by the shape-control principles in nanomaterial synthesis (Xia *et al*. 2015), a model for shape transformation mechanism was proposed to explain the unidirectional rod-to-sphere transformation and its irreversibility. The most stable geometry corresponds to the global minimum free energy state, typically achieved under thermodynamic dominance. While, local minimum states form when kinetic factors control the pathway. In our system, spherical nanoparticles, represent the global minimum state, while rod-shaped nanoparticles correspond to a local minimum state (Figure 3). Heating rod-shaped NPs to 750°C enables them to overcome the energy barrier between these states, transitioning to the spherical global minimum via thermodynamic driving forces. Conversely, reversing this process (sphere → rod) fails may because rod formation requires the involvement of kinetic factor(s) (e.g., directional structural constraints), which cannot be replicated through thermal activation alone.

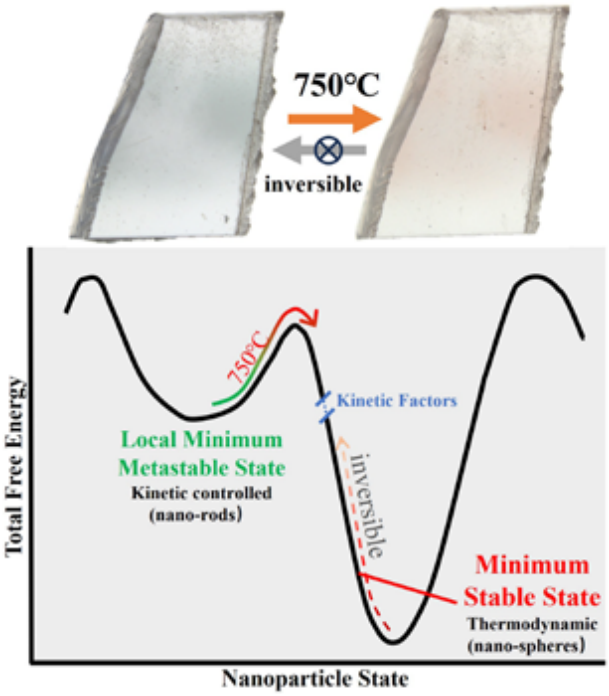

Figure 3. Theoretical model for shape transformation.

References:

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