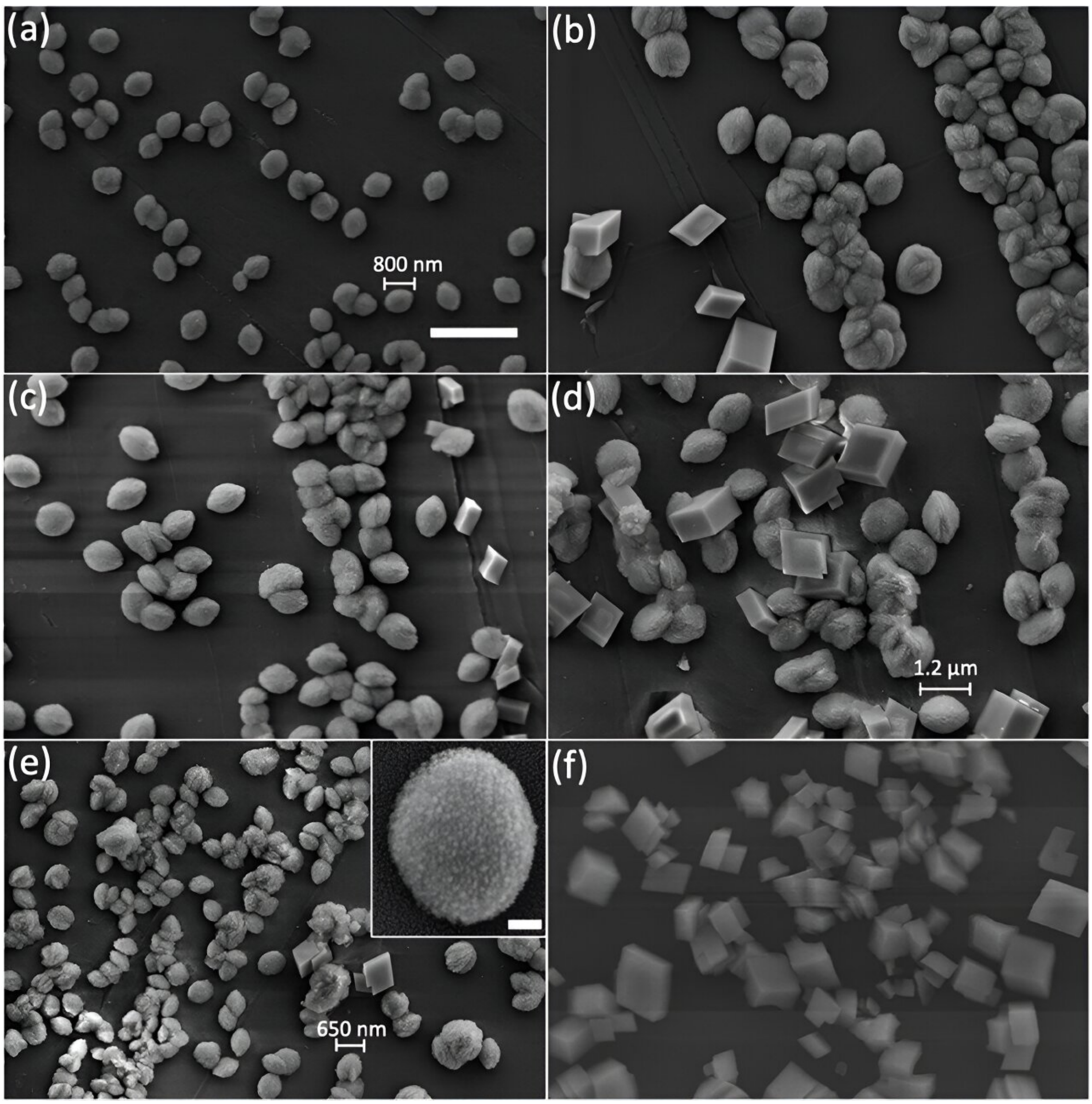
Not all calcite crystals perfect; synthesis methods can alter internal structure, affect chemical reactivity

June 25 2024, by Lea E. Radick



(a–e) Representative SEM images of the calcium carbonate samples grown from supersaturated solutions on Kapton films after 1, 2, 3, 4, and 5 min of reaction, respectively, and f) after 24 h in contact with CSS. The scale bar in panel (a) represents 2 µm. The same magnification is used for panels (a)–(f). The scale bar in the inset of panel (e) is 200 nm. Credit: *Advanced Materials* (2024). DOI: 10.1002/adma.202310672

When looking at calcite under a microscope, a scientist would immediately recognize the crystalline form of calcium carbonate by its rhombohedral appearance. That is, calcite is shaped like a distorted cube. One of Earth's most abundant minerals, calcite is a major component of limestone and marble. It is also the most stable of the three common, naturally occurring crystal forms of calcium carbonate; the other two forms are aragonite and vaterite.

Studying calcite is important as it has broad relevance in several ways. When calcium carbonate is synthesized, it transforms carbon dioxide (CO_2) into solid carbonate, the final reaction product needed for long-term carbon storage in the fight against climate change. Additionally, as researchers recently discovered, the presence of defects in calcite can be controlled by how it is synthesized and can alter many of its properties. For example, defects can affect calcite's ability to soak up harmful substances in the environment like heavy metals. They can also affect the mechanical strength of calcite—which has implications for the development of more durable materials—and the ability to improve catalysts used in industrial processes.

On the surface, calcite appears "transparent and shiny," resembling a crystal you might hang in a window, according to Sang Soo Lee, a geochemist at the U.S. Department of Energy's (DOE) Argonne National Laboratory. Inside, calcite is composed of orderly, repeating patterns of atoms, or so the scientists thought.

Recently, Ana Suzana, an assistant scientist, working with Lee and other researchers at Argonne, discovered that how calcite is synthesized, or chemically transformed, can dramatically alter the internal structure of individual mineral particles. In turn, this affects calcite's reactivity.

A paper on the study, "Visualizing the Internal Nanocrystallinity of Calcite Due to Nonclassical Crystallization by 3D Coherent X-Ray Diffraction Imaging," appears in *Advanced Materials*.

Thus far, the influence of synthesis approach on the internal structure of crystals has received little attention. To better understand the mechanistic impacts, Suzana compared the external shape and internal structure of calcite particles grown by two synthesis approaches using scanning electron microscopy (SEM), powder X-ray diffraction and a technique known as Bragg Coherent Diffraction Imaging (BCDI).

To conduct the BCDI experiment, which provided a high-resolution view of calcite's internal crystallinity, researchers used the facilities at beamline 34-ID-C at Argonne's Advanced Photon Source (APS), a DOE Office of Science user facility.

"Using brilliant, coherent, hard X-rays delivered by the APS, which are essential for BCDI, we were able to image localized features within individual tiny mineral particles instead of capturing averaged values throughout the particles," said Wonsuk Cha, a physicist at APS who was involved with this research.

For one synthesis approach, calcite crystals were grown slowly. SEM images of these crystals showed rhombohedral, or distorted, cube-like shapes, consistent with what the scientists expected to see. Then, BCDI was used to create a 3D map of the crystal structure inside the calcite particles. These images also showed the orderly, repeating patterns scientists expected to see.

Using another synthesis approach, crystals were grown very quickly. SEM images once again showed distorted, cube-like calcite crystals. However, when BCDI was used, it revealed a more complex internal structure. Each perfectly shaped calcite crystal was composed of countless ultrasmall (nanosized) crystalline fragments, or defects.

The term "nano" means one billionth of something, and a "nanometer" is a measure of length that scientists use to describe the size of extremely small particles like atoms or molecules. One nanometer is about 100,000 times smaller than the width of a human hair.

These nanoscopic defects in the interior structure of the calcite likely reflect the granular substructures that are often seen in vaterite. Vaterite, a less stable form of calcium carbonate, slowly transformed into stable calcite after the mineral was synthesized using the quick approach for this experiment, according to Suzana.

The results of this research reveal new ways of understanding how these internal defects alter calcite reactivity. This discovery is important because it demonstrates a way to distinguish between particles that are perfect from ones that are composed of nanosized internal fragments.

When calcite is fragmented, it can have a very different functionality than it would in its "perfect" crystalline form. This would also influence how it reacts chemically. For example, the defects in calcite can alter how carbonate material grows and dissolves, which affects its ability to absorb toxic chemicals such as heavy metals.

"Most people don't have the tools to distinguish whether it's perfect calcite or not. So, this result shows very clearly that just because it looks like calcite, it doesn't mean it's perfect calcite," said Argonne Distinguished Fellow Paul Fenter, who was also involved in this research.

"Ultimately, we hope to observe how these defects can be used to control how calcite reacts," Fenter added.

The ability to identify such fragmentation in the crystalline structure of minerals may help in designing materials with optimized strength and toughness.

The findings may be relevant to other fields, as well, such as catalysis. The presence of fragments inside particles might enhance the catalytic activities of materials by increasing the reactive surface areas, Suzana explained.

The results also revealed how imaging techniques such as BCDI give researchers a direct way to examine the features of calcite to determine structure-property relationships in a way they hadn't been able to previously.

In addition to Cha, Fenter, Lee and Suzana, authors include Irene Calvo-Almazán and Ross Harder.

More information: Ana F. Suzana et al, Visualizing the Internal Nanocrystallinity of Calcite Due to Nonclassical Crystallization by 3D Coherent X-Ray Diffraction Imaging, *Advanced Materials* (2024). DOI: 10.1002/adma.202310672