



**Storing renewable**  
wind energy for use  
on still days is one of  
today's energy  
problems that cannot  
be solved with  
today's materials.  
New materials are  
needed.

## Watching Nanoparticles Grow

New approach shows particles and ensembles follow different growth patterns, explaining a frustrating discrepancy in experimental results

### RESULTS

Individual silver nanoparticles in solutions typically grow through single atom attachment, but importantly, when they reach a certain size they can link with other particles, according to scientists at Pacific Northwest National Laboratory (PNNL), the University of California, Davis, and Florida State University. This seemingly simple result has shifted a long-held scientific paradigm that did not consider kinetic models when explaining how nanoparticle ensembles formed.

Conventional methods have either 1) been limited to “post-mortem” analysis long after the growth subsided, 2) “cherry picked” the particles being examined, thereby missing the mesoscale implications, or 3) analyzed only the population average and missed the individual particle variances. By considering the kinetics of the average growth rate and the distribution of particle sizes, the team explains why scientists see what they see when nano-particle ensembles form via non-classical mechanisms.

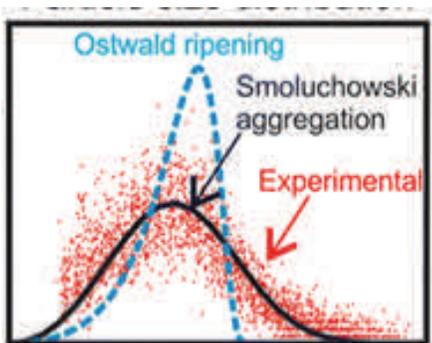
“The team’s findings shed light on previously unexplained observations of aggregative nanoparticle growth,” said Dr. Louis Terminello, who leads the Chemical Imaging Initiative at PNNL, which funded much of the work. “Such understanding of mesoscale interactions provides more precision in material synthesis, bringing us closer to tailored materials for catalysis, energy storage, and other uses.”

### WHY IT MATTERS

Whether storing renewable energy for later use or designing longer lasting batteries for electric-powered vehicles, many of today’s energy problems will not be solved with today’s materials. New materials are needed. The key to avoiding time-consuming trial-and-error research is to tightly control nanoparticle growth to build the materials needed, from the bottom up. This study provides important information about nano-ensembles grown by non-classical mechanisms, including aggregation and coalescence.

### METHODS

Since the early 1960s, scientists have interpreted nanoparticle growth quantitatively using a model called Lifshitz-Slyozov-Wagner (LSW). This model addresses the dissolution of small crystals and deposition of the dissolved material onto larger ones—a process called Ostwald ripening. But until now, little attention has been paid to modeling the corresponding particle size distribution—a global property that



The Smoluchowski model quantitatively captures the mean growth rate and particle size distribution of a silver nanoparticle, while Ostwald ripening does not. By considering the kinetics of the average growth rate and the distribution of particle sizes, scientists can explain what they see when nanoparticle ensembles form via non-classical mechanisms.

often dictates important functional properties, such as catalytic activity.

“At the atomic scale, Ostwald ripening fits the observed growth. But at the mesoscale, we need to know more about particle size distribution,” said Dr. Nigel Browning, Chief Science Officer for the Chemical Imaging Initiative and lead of this project.

The scientists used in situ liquid scanning transmission electron microscopy to grow and directly observe silver nanoparticle ensembles. The team found that the Smoluchowski aggregation kinetic model quantitatively matched the mean growth rate and the particle size distribution of the ensemble. The researchers also used an algorithm created by Dr. Chiwoo Park at Florida State to capture all the particles and analyze all the data, another difference from previous methods.

“Using the combined imaging and analytical approach, we can map out

the complete particle size distribution, and see how one mechanism takes over from the other,” said Browning.

Although the mean growth rate observed during the in situ growth experiments was consistent with the LSW model and suggested that Ostwald ripening was the dominant growth mechanism, the Smoluchowski model showed that the ensemble-scale mean growth rate is ~20% larger than for non-aggregating nanoparticles. The corresponding particle size distribution is broader and more symmetric (see figure) than that predicted by Ostwald ripening in the LSW. And, it more closely matches the experimental data. The team’s results suggest that the particles must reach a certain size before they are capable of growing into bigger ensembles.

“Our results really highlight the need for the field to consider both classical and non-classical growth mechanisms when trying to understand and ultimately control the final characteristics of nanoparticles,” said Dr. James Evans, a coauthor and scientist within the Environmental Molecular Sciences Laboratory.

## WHAT’S NEXT?

This study is a first step in allowing researchers to accurately predict and tune nanoparticle size distributions in lab-scale syntheses based on physical theories and empirical observations. The team will continue to answer fundamental questions about mesoscale phenomena.

## ACKNOWLEDGMENTS

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