Surface modification of high-volume micro-nanoparticles with atomic accuracy

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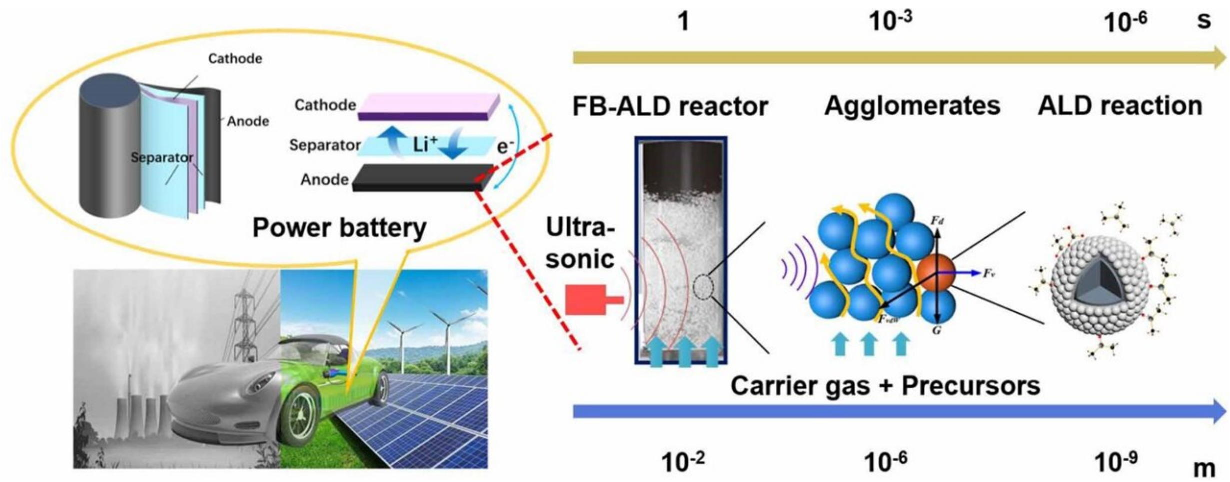

This approach provides the nanoparticle application in power batteries for electric vehicles and the schematic of the ultrasonic vibration-assisted FB-ALD process. The ultrasonic vibration can break the large agglomerates, which facilitates the precursor diffusion and improve the overall particle coating efficiency. Credit: Zoushuang Li et al

Surface modification of micro-nanoparticles at the atomic and close-to-atomic scales is of great importance to their applications in a variety of fields, such as energy storage, catalysis, sensors, and biomedicine. In order to meet the industry requirements in these areas, it is urgently necessary to develop high-volume manufacturing of atomically precise coatings on particulate materials. As an advanced extreme manufacturing method, atomic layer deposition (ALD) is a thin film deposition method which offers pinhole-free films with precise thickness control at the angstrom level and exceptional homogeneity on complex structures. Fluidized bed ALD (FB-ALD) has shown great potential in atomically ultrathin films on large amounts of particles.

In a new paper published in the *International Journal of Extreme Manufacturing*, a team of researchers, led by Prof. Rong Chen from the State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China, have comprehensively investigate the effect of ultrasonic vibration on the hydrodynamics and the particle agglomeration behavior in an FB-ALD reactor via CFD-DEM simulation. The bed pressure drops and expansions, fluid turbulent kinetic energy, distribution of particle velocities and solid volume fraction as well as the agglomerate sizes are presented to characterize the fluidization quality. Different amplitudes and frequencies of ultrasonic vibrations are investigated to find the optimal conditions for enhancing the fluidization quality and the coating efficiency of FB-ALD process.

In order to investigate the effect of ultrasonic vibration on the general fluidization behaviors, a typical ultrasonic vibration with a frequency of 20 kHz and an amplitude of 20 μm is applied to the FB after the fluidization reaches a steady state. With the induce of the ultrasonic vibration, the velocity of the particles close to the vibrating wall increases immediately. The number of particles with high velocities also increases, leading to more particle–particle collisions. Besides, the bed height increases gradually as time increases, which implies that the ultrasonic vibration can effectively promote particle dispersion. Moreover, channeling is also reduced by the ultrasonic field. These improvements of fluidization behaviors are beneficial to the particle coating process, since the precursor molecules can diffuse faster and more uniformly into the agglomerates, thus increasing the overall coating efficiency.

Fluid turbulent motion is the primary reason for particles to achieve random motion, and turbulence kinetic energy is the key factor for evaluating the breakage energy for particle agglomerates. Without the ultrasonic vibration, the turbulence kinetic energy is quite small, and it remains unchanged. However, once the ultrasonic vibration is applied, the maximum turbulence kinetic energy increases sharply. It is shown that the maximum turbulence kinetic energy increases with the frequency or amplitude increasing.

Characterizations of the coordination number and agglomerate size distribution for all cases are also carried out to quantitatively investigate the particle agglomeration and breakage behaviors. When the ultrasonic frequency is set as 20 kHz, the de-agglomeration effect of the ultrasonic field increases with the ultrasonic amplitude. When the ultrasonic frequency increases from 10 kHz to 20 kHz, the probability for the agglomerates formed by two primary particles increases rapidly, while the agglomerates formed by three to ten primary particles all decrease. This indicates that the ultrasonic vibration with the frequency of 20 kHz can further break the small agglomerates into the smallest agglomerate or even individual particles.

To verify the simulation results, comparative coating experiments have been performed with ultrasonic vibration-assisted FB-ALD reactor on NCM811 particles, which can offer high energy density in automotive lithium-ion batteries (LIBs). The SEM images of the coated nanoparticles also show that, the particles in the ultrasonic vibration-assisted FB-ALD have been effectively dispersed, leading to more conformal layers and a higher coating efficiency. The experimental data agree well with the simulation results, which has verified the effectiveness of the dynamic multiscale CFD-DEM model.

Professor Chen Rong and other researchers in her group answered questions about several key points when performing the ultrasonic vibration-assisted FB-ALD technology:

Is the current CFD-DEM model of FB with a size of a few millimeters precise enough to predict the particle behaviors in a scale-up ultrasonic-vibration assisted FB-ALD reactor?

"Although the current multiscale CFD-DEM model covers scales only from the simple agglomerates to the FB with a size of a few millimeters, it has successfully revealed the particle agglomeration and breakage behaviors with ultrasonic assistance. With the development of the multiscale theory and computational science, this model is believed to be further developed for a better investigation from lab-scale to manufacturing-scale."

How does the ultrasonic vibration influence the agglomerate breakage? Is it always better to use higher ultrasonic frequencies?

"There exists a critical value of the ultrasonic frequency. When the ultrasonic value is lower than the critical value, the average particle velocity and the agglomerate size increase with the ultrasonic frequency increasing. However, when the ultrasonic frequency exceeds this critical value (e.g. 40 kHz) the particles begin to agglomerate near the vibrating wall."

What aspects should we consider when optimizing the process parameters or designing the ultrasonic-

vibration FB-ALD reactor for the coating of large amounts nanoparticles?

"The selections of the ultrasonic frequencies or amplitudes depends on many factors, such as the reactor pressure, the equivalent inter-particle cohesive forces, as well as the particle size distribution in the whole FB. For the optimal design reactor, knowledge from adjacent fields such as hydromechanics and mechanical engineering is further required."

Researchers have suggested that various kinds of particulate materials are going to benefit a lot from the ultrasonic vibration-assisted FB-ALD technology. The assistance of ultrasonic vibration can effectively accelerate the velocity of fluid and particles near the vibrating wall. Enhanced fluidization quality of nanoparticles is also bound to facilitate the heat transfer and precursor diffusion in the whole FB-ALD reactor and the agglomerates, which can largely improve the coating efficiency.

More information: Zoushuang Li et al, A combined multiscale modeling and experimental study on surface modification of high-volume micro-nanoparticles with atomic accuracy, *International Journal of Extreme Manufacturing* (2022). DOI: 10.1088/2631-7990/ac529c

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