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Anomalous oriented attachment growth behavior on SnO₂ nanocrystals†

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This work reports a detailed characterization of an anomalous oriented attachment behaviour for SnO₂ nanocrystals. Our results evidenced an anisotropic growth for two identical <110> directions, which are equivalent according to the SnO₂ crystallographic structure symmetry. A hypothesis is proposed to describe this behaviour.

Semiconductor nanomaterials have been intensively studied over the last decade due to a number of novel applications in a variety of technological fields. Tin oxide (SnO₂) can be noticed among this group for its use in gas sensors, transparent conductive oxide and solar cell devices. Several works¹ report synthesis procedures for tailoring SnO₂ nanocrystals with controlled morphology and some studies² elucidated the crystal growth behavior for particular synthesis environments. Probing its low solubility in some typical solvents, some works³ further evaluated SnO₂ and its doped forms growth behavior to enhance the oriented attachment (OA) growth mechanism theory.^{4,5} The originally proposed OA mechanism concerns the adjacent nanocrystals self-organization and coalescence, which can occur after the effective collision between particles either with mutual orientation or followed by a particle rotation step.

This communication concerns an anomalous oriented attachment growth behavior that has been repeatedly observed for SnO₂ nanoparticles obtained by a non-aqueous solution synthesis procedure. These results could not be explained using the crystal growth descriptions available in the literature.

The SnO₂ nanocrystals were synthesized in a glovebox under a controlled atmosphere. A total of 5.47 mmol SnCl₄ (99.995%) was stirred in a vessel with 40 ml of benzyl alcohol, after which the reaction vessel was removed from the glovebox and heated at 150 °C for about 48 h in a silicone bath. SnO₂ nanoparticles were collected by centrifugation, washed twice with tetrahydrofuran, and stored in a concentrated THF

dispersion. TEM samples were prepared right after the synthesis procedure by dripping a diluted SnO₂ solution onto copper grids covered with a thin amorphous carbon film. HRTEM characterization was performed using a JEM-3010 URP TEM at 300 kV with a LaB₆ electron gun and equipped with a 1024 × 1024 thermoelectrically cooled CCD camera. HRTEM multislice simulation was performed using JEMS software.⁶

XRD analysis of synthesized material indicated highly crystalline SnO₂ nanocrystals with cassiterite tetragonal *P*₄*2*/*mmm* structure.⁷ Fig. 1a shows a representative TEM image depicting that the nonaqueous synthesis route produces dispersed and crystalline SnO₂ nanoparticles with elongated shape. The size distribution for 200 measurements shown in Fig. 1b reveals elongated particles with a mean length of 29.9 nm, mean width of 10.9 nm, and mean aspect ratio of 3.24.

Fig. 2a and b depict SnO₂ nanocrystals HRTEM images which reveal some relevant features. It can be observed that the SnO₂ particles are single crystals elongated along the [110] direction, according with the aspect ratio indicated by the particle size distribution plot. OA^{4,5} is the expected main crystal growth mechanism due to SnO₂ low solubility in both benzyl alcohol and THF. A similar behavior was observed for SnO₂ nanoparticles synthesized in aqueous solution, however with a different growth direction.⁸ Based on the [001] zone axis projection and the homogeneous contrast along the particle extension, as depicted on Fig. 2b, it is indicated that the {110} facets were the most favorable OA growth sites. According to the allowed symmetry operations for this tetragonal crystalline structure, an identical growth rate would be expected for the four equivalent {110} facets. However, it is important to notice that the observed aspect ratio is related to the two <110>

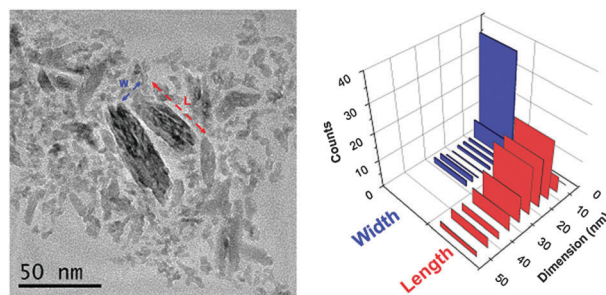


Fig. 1 (a) Low-magnification TEM micrograph illustrating SnO₂ nanocrystals with large aspect ratio, which can be noticed on (b) particle size distribution plot for 200 counts.

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† Electronic supplementary information (ESI) available: Detailed information about XRD analysis, SnO₂ *ab initio* calculated surface energies and Wulff construction, and the Monte Carlo complete model. See DOI: 10.1039/c0cc04570e

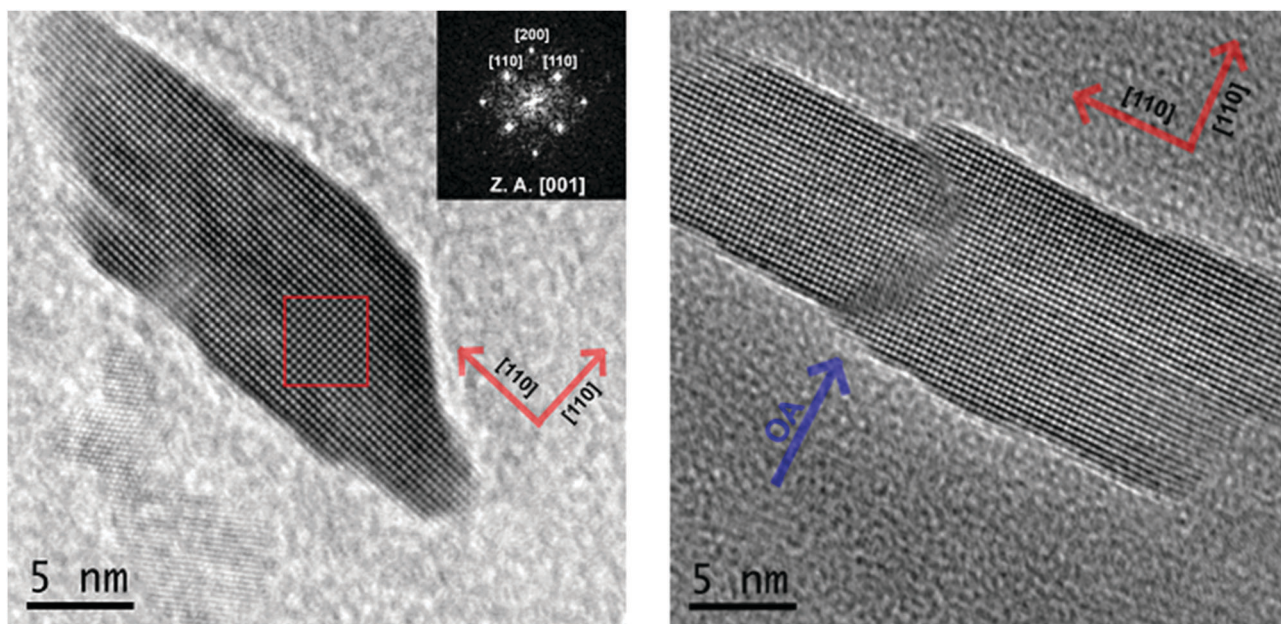


Fig. 2 (a) SnO₂ nanocrystal HRTEM micrograph with an indexed FFT inset (upper right corner) and a HRTEM multislice simulation (red square). Two $\langle 110 \rangle$ directions are identified either as lengthening or shortening nanocrystals axes. (b) OA along the $\langle 110 \rangle$ is identified as the main growth mechanism.

directions, configuring thus an anisotropic growth behavior for identical directions.

The nanocrystals facets surface area for different crystallographic planes plays a major role in the OA events, which can be described as a statistical process that depends on the collision rate. The nanocrystals facets surface area can be determined either thermodynamically or kinetically.

Wulff theorem⁹ describes the nanocrystals geometry at thermodynamic equilibrium as a function of the surface energy distribution for different crystalline planes families, thus indicating the crystal shape for a given volume that would present the minimum surface energy. As the surface energy is related to the plane family bonding configuration, the crystallographic symmetry rules also apply to the surface energy values and to the nanocrystal faceting. *Ab initio* calculation for surface energy¹⁰ indicated that SnO₂ would present the $\langle 110 \rangle$ directions family as the preferential oriented attachment growth direction due to the lower surface energy and higher surface area.

Capping agents can alter the thermodynamic equilibrium shape during the growth process since they stick to the nanocrystal surface in preferential facets, thus preventing the crystal growth along that direction. This capping agent selectivity for different facets is related to its polarity relationship with the exposed crystalline plane. A similar approach is valid for the pH role in the reaction kinetics since its influence depends on the surface charge distribution, which is related to the crystalline planes terminations. Other essential kinetic factors like temperature and pressure are isotropic.

As a consequence of the crystalline symmetry operations for the tetragonal $P4_2/mmm$ special group, it would be expected that the SnO₂ nanocrystals would present an identical faceting behavior for different crystalline planes within the $\{110\}$ plane family both by thermodynamic and kinetic arguments.

In addition, this would ensure an identical OA growth rate along the $\langle 110 \rangle$ directions family since there is no other identified reason for anisotropic growth such as external polarization or orientation relationship.

A Monte Carlo based algorithm was used to simulate the oriented attachment process behavior for equivalent directions. A detailed description of this methodology can be found in the supplementary information. Fig. 3 depicts a comparison between the experimentally observed aspect ratio distribution for SnO₂ nanocrystals (red) and the expected aspect ratio distribution considering randomized attachment events for two identical directions in a 2D model, according to the Monte Carlo based calculation results (green). The aspect

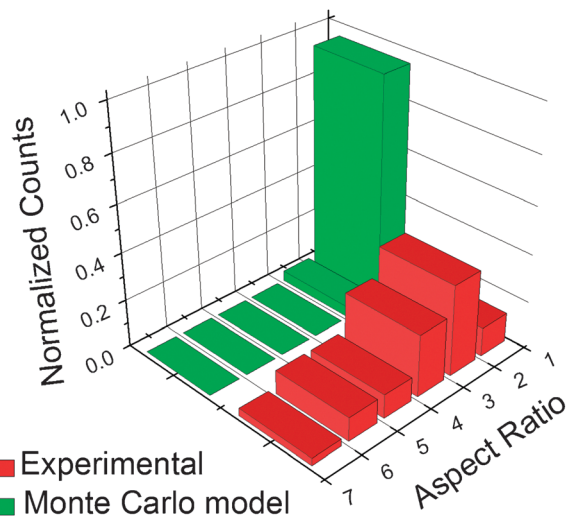


Fig. 3 Comparison between the experimental aspect ratio distribution (red) and the results from a Monte Carlo based algorithm considering equivalent growth directions (green).

ratio distribution comparison shown in Fig. 3 indicates that the SnO₂ nanocrystals present a higher aspect ratio than what would be expected for a statistical growth process along two identical directions. This result demonstrates that a symmetry-breaking event occurs during the crystal growth, which leads to the nanocrystals anisotropic morphology.

This analysis strongly suggests that the observed OA behavior cannot be described as a statistical process controlled by the collision rate. Interactions between the particles, which may be the symmetry-breaking source during the OA events, are highly relevant for the growth mechanism. These interactions must be associated with the van der Waals forces¹¹ such as Keesom, Debye, and London dispersion forces. However, the pairwise forces based on permanent dipoles interaction should not be responsible for the observed anisotropic growth behavior due to the dipoles symmetry concerning identical crystallographic directions. In addition, attractive forces involving interactions between charges and dipole/charge should not be imperative for the present study due to the use of an aprotic organic solvent.

Although a highly anisotropic growth behavior was also reported for metallic and semiconductor systems,¹² a comprehensive description for the OA mechanism in such cases was not achieved. Our findings indicate that the observed growth behavior can be related to the excess energy from the nanocrystal assembly's edges and kinks,¹³ which may have a significant contribution during the OA growth mechanism steps. Considering the OA as a multistep growth mechanism, we believe that this excess energy can induce the nanoparticles rotation¹⁴ at each coalescence event and lead to the preferential attachment on facets which would generate configurations with a lower amount of edges and kinks. This effect would ensure a lower nanocrystals assembly overall energy. In this sense, intermediary steps with elongated configurations ("I-like" structures) could be more favorable than structures with isotropic OA events ("L-like" structures).

The effect of decreasing the overall system energy by the edges and kinks minimization from a smoothing process is reported for highly anisotropic metallic nanowires growth.¹⁵ The occurrence of a smoothing process after attachment events supports our hypothesis as it indicates that the energy contributions from edges and kinks are significant for the

crystal growth mechanism. In addition, as the mentioned smoothing process is not favored for ionic systems with reduced surface diffusion, the excess energy could be responsible for inducing a symmetry-breaking event, which would lead to different growth rates along equivalent crystallographic directions.

The HRTEM characterization indicated that the oriented attachment along the $\langle 110 \rangle$ directions family is the predominant growth mechanism for SnO₂ nanocrystals. However, it was noticed that different directions within the $\langle 110 \rangle$ direction family have different growth ratios and a mean aspect ratio value of 3.24 was observed. A Monte Carlo based simulation showed that this behavior is not likely for a statistical growth process along two identical directions according to the crystallographic symmetry operations.

The observed anomalous anisotropic growth along the $\langle 110 \rangle$ direction family could not be explained using either the classical thermodynamic or kinetic arguments. An OA growth model that includes the edges and kinks excess energies is currently under development and validation for describing these findings.

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