

Tailoring of heterostructures in a SnO₂/TiO₂ system by the oriented attachment mechanism

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In order to verify the possibility of forming a heterostructure—i.e., a nanoparticle tailored by the junction of two or more different materials—through the oriented attachment (OA) mechanism, experiments with rutile TiO₂ and cassiterite SnO₂ as candidate materials were done, since they have similar crystallographic parameters. The experiments were carried out in hydrothermal conditions and in an *in situ* observation at the high resolution transmission electron microscopy. The results showed the formation of TiO₂/SnO₂ heterostructures, confirming the coexistence of rotation-alignment and oriented collision mechanisms, hypothesis of OA behavior proposed in previous theoretical works. © 2007 American Institute of Physics. [DOI: 10.1063/1.2779932]

Recent works have focused on nanoheterostructures—i.e., nanoparticles tailored by the junction of two or more different materials¹—as a way to produce different functionalities in a single particle. The heterostructures thus obtained are usually formed only through classical growth strategies;^{2–5} however, advances in the comprehension of nonclassical growth mechanisms^{6–9} can shed light on synthesis strategies for this purpose. A special case is the oriented attachment (OA) mechanism^{10–14} and, in this work, the main goal is to substantiate the mechanism as a way to tailor heterostructures.

In soft chemistry, the simplest strategy to assembly heterostructures is the heterogeneous nucleation of the second phase on the surface of pristine crystalline nanoparticles. Milliron *et al.*² recently investigated this strategy in CdSe/CdS branched heterostructures, forming linear and tetrapod nanoparticles. Using the same strategy, other papers report similar structures and findings.^{3,5} Mokari *et al.*⁴ recently reported an interesting study on CdSe nanorods and tetrapods, tailoring epitaxial Au tips in the structures' terminus. The authors observed a migration of the tips in nanorods from one side to the other, generating a single Au tip in one side; however, this migration was not observed in CdSe tetrapods. Based on these findings, the authors correlated the migration to electron transport into the nanorod structure, allowing for Au oxidation and leading to an oriented dissolution-precipitation mechanism (analogous to Ostwald ripening¹⁵) in tetrapods. However, the high density of defects in the center of the structure may hinder the transport of electrons, preventing migration.

This experiment demonstrates the indispensable need for a thorough understanding of the growth mechanisms involved in the formation of nanoscale heterostructures. However, similar works still focus on classical growth mecha-

nisms, despite the recent interest evinced in nonclassical growth mechanisms. Recent reports^{13,14} have presented kinetic models to describe oriented attachment, a nonclassical approach that has proved important in tailoring anisotropic nanostructures.^{8,9,16,17} By this mechanism, two or more nanoparticles become attached to each other through crystallographic alignment and consequent boundary migration, making the process faster than the classical atom attachment on surfaces. An important conclusion is the statistical nature of the OA mechanism, an implication thereof being that two surfaces will coalesce if the crystallographic alignment can be satisfied, even if the surfaces are not identical, i.e., they have slight energy differences. In fact, several works report events of imperfect OA¹⁰ i.e., cases of attachment of particles without perfect alignment, in which defects remained (twin boundaries, dislocations) in the attachment line across the particles. Thus, OA may result from oriented collisions in a dispersed colloid¹⁸ or from the rotation of a particle over the surface, until alignment occurs.¹⁹ This latter phenomenon was investigated in a SnO₂ nanobelt/nanoparticle structure, in an *in situ* experiment by high-resolution transmission electron microscopy (HRTEM), showing that the incident beam sufficed to promote rotation and alignment.²⁰ It should be noted that the event occurred before any diffusional movement, although the attached nanoparticle presented necking over the nanobelt surface after the OA event.

The statistical nature of OA and its occurrence even with imperfect alignment strongly suggest that the mechanism may be useful for tailoring heterostructures.^{1,21} In principle, two similar structures will have some possibility of forming a heterostructure by OA. To verify this possibility, we chose rutile TiO₂ and cassiterite SnO₂ as candidate materials, since they have similar crystallographic parameters and the same structure, although their densities are very dissimilar and very different surface energies are expected. SnO₂ is also an interesting candidate for evaluating OA due to its extremely

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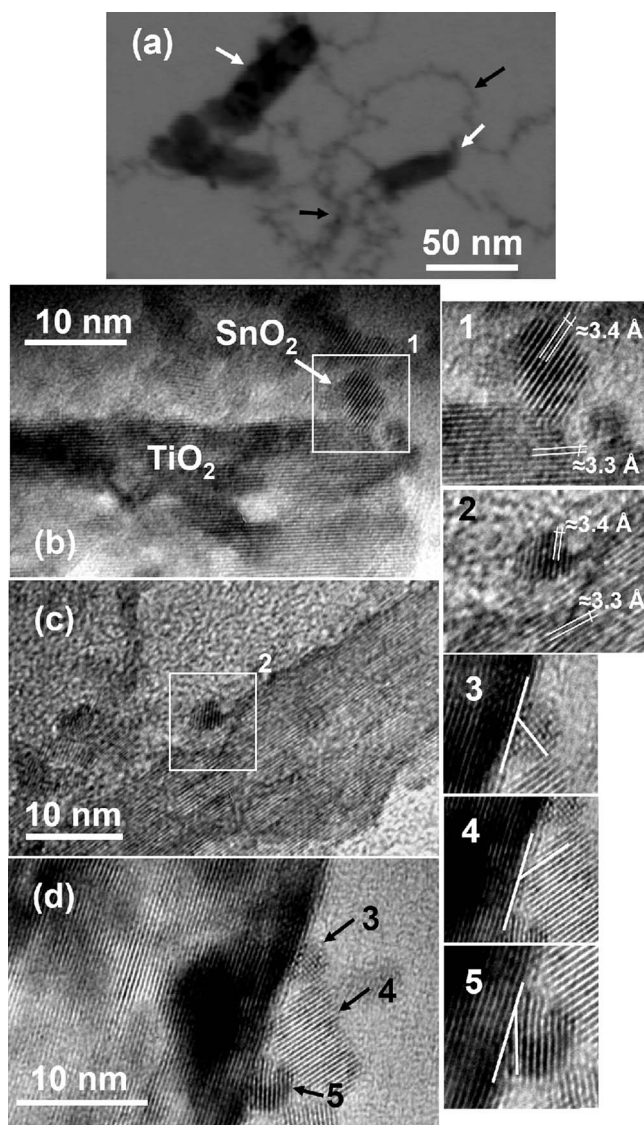


FIG. 1. As-hydrothermally TiO₂/SnO₂ heterostructures: (a) bright field transmission electron microscopy showing TiO₂ particles (white arrows) evolved by SnO₂ nanoparticles (black arrows) and (b) SnO₂ coalesced at the top of a TiO₂ nanorod. The inset (1) shows the crystallographic alignment, identifying the planes (110)=3.4 Å in SnO₂ and (110)=3.3 Å in TiO₂; (c) SnO₂ coalesced at the side of TiO₂ nanorod, showing in inset (2) the alignment; (d) SnO₂ nanoparticles attached at the side of a single TiO₂ nanorod; the insets (3), (4), and (5) show the imperfect oriented attachment in all the cases, highlighted by the white lines.

low solubility.¹³ TiO₂ was synthesized by decomposition of a peroxotitanium complex under hydrothermal conditions, as described in detail by Ref. 22. The method allowed for the precipitation of highly crystalline rutile nanorods, with diameters of around 12 nm and length of ≈20 nm, oriented in the [110] direction. The SnO₂ nanoparticles were obtained by hydrolysis of SnCl₂ in ethanolic solution, followed by dialysis versus de-ionized water for Cl⁻ elimination.¹⁸ The particles thus obtained were almost spherical, with a diameter smaller than 5 nm. Strongly diluted colloidal suspensions of the oxides were mixed ultrasonically, and the resulting suspension was aged under hydrothermal conditions for 24 h at 200 °C. The system was observed in a high resolution transmission electron microscopy (HRTEM) (Phillips CM200).

The particles are identifiable by their morphological characteristics shown in Fig. 1(a). The white arrows indicate TiO₂ nanoparticles that evolved from fine SnO₂ nanopar-

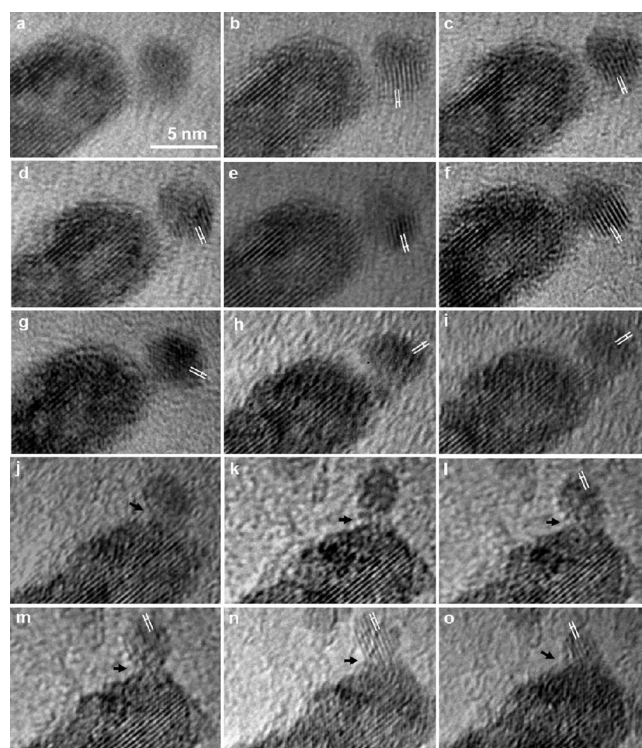


FIG. 2. Spontaneous orientation by rotation alignment of SnO₂ over TiO₂ tip. The white bars show SnO₂ planes and are a guide to the eyes in the rotation. Each image corresponds to a time interval of 1 min. (a)–(i) show the rotation, with the OA and necking (black arrows) in (j)–(o).

ticles on the surface. The general view of the particles shows the “pearl necklace” distribution of SnO₂ nanoparticles on the TiO₂ tips is clearly visible at several points, as indicated by the black arrows. Figure 1(b) shows a heterostructure of a SnO₂ nanoparticle attached to a TiO₂ tip, which was formed during aging. The planes identified in inset (1) are consistent with the (110) plane in cassiterite and the (110) plane in TiO₂ rutile. Initially, this type of structure appears to be more frequent; however, some laterally attached particles are also visible, as indicated in Figs. 1(c) and 1(d). These cases are evidence of OA produced by oriented collision, since the hydrothermalized colloid was very stable, without segregation. The preferential OA on TiO₂ tips is consistent with the assumption of the existence of “active” surfaces, where the event is more likely to occur in response to a favorable surface energy, as proposed previously.¹⁴ In fact, previous works have shown that (110) is the lowest energy plane in TiO₂ rutile. Hence, this being the predominant plane on surfaces, it is probable that OA events are more likely to occur on tips (high energy planes).

However, an important observation is the agglomeration of particles in a quasioiented fashion, though not coalesced—as depicted in Fig. 2(a). The SnO₂ nanoparticle is close to the TiO₂ nanoribbon, but there is no evidence of coalescence at this stage (this fact is still under investigation). Interestingly, after 1 min of electron irradiation, the nanoparticles began a spontaneous counterclockwise rotational motion. This movement is illustrated in Fig. 2(b) by the alignment of the particle, revealing the (110) plane. Taking 1 image/min, one can observe the orientation of the SnO₂ nanoparticle until it reaches a favorable attachment position [Figs. 2(b)–2(j)]. The necking, highlighted by the black arrows, indicates the final stage of coalescence, which

is given by the movement of a surface discordance formed in the attachment line. Finally, after 15 min, the particle undergoes some diffusional motion, relaxing the surface and concluding the OA process. This event clarifies the process as it unfolds to form a heterostructure: rotation and alignment are in line with the model proposed by Moldovan *et al.*,¹⁹ and confirm that surface accordance is the only requisite for OA—that can be linked with the findings of Penn and Banfield.²³ Another interesting feature is the similarity with the OA event shown in Fig. 1(b). Finally, the occurrence of OA in twinning is an indication that the phenomenon needs only a local minimum of energy, even in a metastable condition. This fact (or, in general, the occurrence of imperfect oriented attachment) is similarly observable in the insets (1)–(5) in Fig. 1, and may be correlated to the contamination of the surfaces in aqueous media, as observed by Penn and Banfield.¹¹

In summary, this letter offers evidence of the tailoring of heterostructures by OA, similarly to what has been observed in the formation of anisotropic nanoparticles. The coexistence of rotation-alignment and oriented collision mechanisms is confirmed, reinforcing the hypothesis of OA behavior proposed in previous theoretical works. The importance of surface energy accordance, i.e., a local minimum of energy in crystallographic alignment, is also observed and is an indicative of a selective behavior in the heterostructure formation. Finally, the importance of this mechanism is highlighted, opening up an avenue of investigation for the construction of functional anisotropic nanostructures.

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