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Atomic-scale aspects of oriented attachment

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HIGHLIGHTS

- TiO_2 nanocrystal aggregation mechanisms are quantified using molecular dynamics.
- In vacuum, TiO_2 nanocrystal aggregation is directed by electrostatics.
- In water, TiO_2 nanocrystals exhibit oriented attachment.
- Oriented attachment is facilitated by adsorbed water and surface hydroxyls.

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ABSTRACT

Oriented attachment (OA), or the non-random aggregation of crystallites to form single or twinned crystals, has been observed is a variety of different systems during crystal growth. OA is believed to underlie the growth of anisotropic and potentially useful nanostructures, such as wires and plates, as well as complex hierarchical nanostructures. However, its origins are poorly understood. I review insights into OA that we gained in two sets of molecular-dynamics simulation studies of titanium dioxide (anatase) nanocrystals. In the first set of studies, we focused on the role of intrinsic nanocrystal forces in facilitating nanocrystal alignment and aggregation in vacuum. These studies show that, although nanocrystal aggregation occurs in a predictable way, OA is not a common outcome. In a second set of studies, we used the ReaxFF reactive force field to study anatase nanocrystal aggregation in an aqueous (humid) environment. OA occurs in these studies and is mediated by adsorbed water and surface hydroxyls. The OA mechanisms that we find for anatase may be common to other aqueous metal-oxide systems.

1. Introduction

Solution-phase syntheses have been extensively studied and employed to fabricate solid nanocrystals with well-defined sizes and shapes. Studies of the growth of these nanocrystals are both interesting and beneficial. From a fundamental standpoint, many crystals in solution grow via Ostwald (1897) ripening, in which the larger nanocrystals grow, atom-by-atom, at the expense of smaller crystallites. An alternate or parallel mechanism is cluster aggregation, which often leads to the formation of random and ill-formed agglomerates. However, cluster aggregation is not always random. As Penn and Banfield (1999) demonstrated, cluster aggregation can occur along specific crystallographic directions and lead to the formation of single or twinned crystallites. This non-random aggregation is known as oriented attachment (OA).

Since the initial discovery of OA, there have been numerous studies of this fascinating phenomenon (Niederberger and Cölfen, 2006; Q. Zhang et al., 2009; Zhang et al., 2010). From a practical perspective, OA frequently underlies the growth of complex architectures ranging from quasi-one- and two-dimensional structures (Tang and Kotov, 2005; Cho et al., 2005; Tian et al., 2012; Yu et al., 2005; Sharma et al., 2009; Halder and Ravishankar, 2007; G. Zhang et al., 2009; Schliehe et al., 2010; Liu et al., 2012; Yuwono et al., 2010), such as nanowires, nanoribbons, and nanosheets, to hierarchical two- or three- dimensional superstructures (Heiligtag et al., 2011; Zitoun et al., 2005; Yang and Zeng, 2004). In the interest of achieving controlled bottom-up (and often surfactant-free) synthesis of these potentially useful structures, a strong fundamental understanding of OA is highly beneficial.

How does OA come about? Many studies cite the reduction of interfacial energy as the driving force for OA. For example, if the aggregation of two nanocrystals occurs on the facets with the highest surface energies, then these interfaces are eliminated and the aggregate has a reduced interfacial energy. Although this may be an appropriate driving force in many systems, it does not

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explain, mechanistically, what makes two nanocrystals move toward each other and choose a specific orientation (from the very large set of all possible orientations) that causes them to join in perfect registry. Very recent experiments (Li et al., 2012) with high-resolution transmission electron microscopy (HRTEM) in a liquid cell have allowed for *in situ* imaging of OA and can provide insight into its origins. However, such experiments do not provide chemically and spatially detailed information on species at the interfaces where OA occurs, which are probably vital for a true understanding of its origins.

Atomic-scale investigations could contribute significantly to understanding OA. Although it is currently challenging to simulate the aggregation of nanometer-sized particles in solvent using first-principles methods, this can be done in classical molecular dynamics (MD) simulations (Zhu and Averback, 1995; Raut et al., 1998; Zhang and Banfield, 2004; Spagnoli et al., 2008; Alimohammadi and Fichthorn, 2009; Sathiyanarayanan et al., 2011; Zhou and Fichthorn, 2012; Raju et al., 2014). MD simulations can also be used to resolve interparticle forces (Qin and Fichthorn, 2003; Fichthorn and Qin, 2006; Qin and Fichthorn, 2006a,b; Qin and Fichthorn, 2007; Fichthorn and Qin, 2008). Provided that MD simulations are based on sufficiently realistic force fields, they can potentially furnish many details of OA that are not accessible experimentally.

OA has been observed for various oxide materials (Penn and Banfield, 1999; Niederberger and Cölfen, 2006; Q. Zhang et al., 2009; Zhang et al., 2010; Yuwono et al., 2010; Li et al., 2012). Indeed, some of the most detailed experimental studies to date have been carried out for this class of materials (Li et al., 2012), so that complementary theoretical studies will be useful. In the work I will discuss below, we focused on the aggregation of the anatase polymorph of TiO_2. OA was first observed in experimental studies of the crystallization of colloidal (hydrothermal) anatase (Penn and Banfield, 1999). In a colloidal system, there are several phenomena that could affect the alignment of two approaching nanocrystals, including intrinsic forces between nanoparticles, selective adsorption and surface chemistry of liquid-phase molecules at the nanoparticle–liquid interface, and solvent-mediated interactions. In this paper, I will discuss insights into OA that we gained in two sets of MD-simulation studies. In the first set, we focused on the role of intrinsic nanocrystal forces in facilitating anatase nanocrystal alignment and aggregation, by studying the aggregation of two anatase crystals in vacuum (Alimohammadi and Fichthorn, 2009). Although these studies indicate that intrinsic nanocrystal forces can induce specific (and non-random) aggregation of anatase, we do not observe OA in vacuum. In a second set of studies, we probed the influence of water on anatase nanocrystal aggregation (Raju et al., 2014). Interestingly, OA does occur in this system and I will discuss its origins.

2. Aggregation of anatase nanocrystals in vacuum: the role of intrinsic nanocrystal forces

To understand the role of intrinsic nanocrystal forces in promoting OA, we consider the aggregation of anatase nanocrystals that possess variations of the experimentally observed (Penn and Banfield, 1999) and theoretically predicted (Lazzeri et al., 2001; Barnard and Zapol, 2004) Wulff shapes. As shown in Fig. 1(a), nanocrystals with the Wulff shape contain both {101} and {001} facets. In addition, we considered three possible off-Wulff shapes that could occur during crystal growth (Alimohammadi and Fichthorn, 2009) and an example containing a {112} facet is shown in Fig. 1(b). {112} facets have been experimentally observed to play a significant role in the OA of colloidal anatase (Penn and Banfield, 1999), so by including these we can investigate this possible role. All together, we studied five different nanocrystals: a large (3774 atoms) and a small (816 atoms) Wulff-shaped crystal and three off-Wulff crystals with 2958, 3141, and 3528 atoms. The longest dimensions of these nanocrystals ranged from 6 nm for the two nanocrystals shown in Fig. 1 to 3 nm for the small Wulff crystal.

To describe interactions between the nanocrystals, we use the Matsui–Akaogi force field (Matsui and Akaogi, 1991). In this force field, the interaction energy U between atoms i and j separated by a distance of r_{ij} has the form

$$U(r_{ij}) = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{r_{ij}}. \tag{1}$$

The Matsui–Akaogi force field assigns fixed partial charges q of $+2.196$ and -1.098 to titanium and oxygen, respectively ($q_O = -q_{Ti}/2$). These effective charges were obtained by Traylor et al. (1971) by fitting to the experimentally observed phonon dispersion of rutile. In addition to the electrostatic term, the first two terms in Eq. (1) constitute a Buckingham potential. The parameters for the Buckingham potential, A_{ij}, ρ_{ij} and C_{ij}, are given in Matsui and Akaogi (1991).

We justified our use of the Matsui–Akaogi force field in a previous paper (Alimohammadi and Fichthorn, 2009). Briefly, in a study of nine promising force fields by Collins and Smith (1996), this potential was shown to be the best at reproducing the lattice energy, polymorphic structures, elastic and dielectric constants, and relative surface energies of TiO_2. Further, this potential has been useful in a wide variety of applications (Eithiraj and Geethalakshmi, 2013; Houska et al., 2012; Salameh et al., 2012; Oliver et al., 1997; Bandura and Kubicki, 2003; Hamad et al., 2005; English et al., 2006; Dubrovinskaia et al., 2001). The Matsui–Akaogi force field has also been shown to perform similar to a more complex and computationally demanding variable charge model (Swamy and Gale, 2000; Swamy et al., 2001; Thomas et al., 2004).

We note that electrostatic interactions dominate inter-particle forces in the Matsui–Akaogi force field (Alimohammadi and Fichthorn, 2009). Considering the nature and influence of electrostatic interactions on OA, we note that dipole–dipole interactions have been proposed to be the driving force for directed aggregation in some previous studies (Niederberger and Cölfen, 2006; Q. Zhang et al., 2009; Tang et al., 2002; Talapin et al., 2007). To assess the possible role of dipole interactions in aggregation, we calculated the dipole moments of all the crystals. The dipole moment μ is given by $\mu = \sum_i q_i \overline{r_i}$, where q_i and $\overline{r_i}$ are the charge and the position vector of ion i, respectively. While nanocrystals with the Wulff shape do not possess a permanent dipole moment due to their symmetry, the off-Wulff nanocrystals that we considered all have permanent dipole moments. For example, the Matsui–Akaogi force field predicts that the nanocrystal shown in Fig. 1(b) has a permanent dipole moment of $\mu = 75$ Debye and the direction of its dipole vector is shown in the figure. By creating nanocrystals with different magnitudes and directions of dipole moments, we could study the role of dipole interactions in aligning the nanocrystals prior to their aggregation to see if this alignment is an important mechanism of OA.

As a second way of characterizing inter-particle electrostatic interactions, we made maps of the electrostatic potential surrounding the nanocrystals. To calculate the electrostatic potential, we set up a grid of points in a plane parallel to each nanocrystal facet and summed the electrostatic interactions between a positive charge and all the nanocrystal ions at each grid point. Fig. 2 shows the electrostatic maps for a Wulff and an off-Wulff nanocrystal. As we will discuss below, these electrostatic maps were useful in understanding nanocrystal aggregation.

To link these measures with aggregation mechanisms, we used the DL-POLY package (Smith and Forester, 1996), version 2.18, to