XIX SBQT
Simpósio Brasileiro de Química Teórica 2017
12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil

Computational Study of the Interactions between TiO_2 Anatase Nanoparticles

Uallisson Silva Santos and André Farias de Moura

Department of Chemistry – Federal University of São Carlos – Rodovia Washington Luís km 235 – CP 676 – CEP 13565-905 – São Carlos – SP

Abstract: Experimental and theoretical studies have shown that the aggregation of TiO_2 anatase nanoparticles (NPs) occurs with preferential crystallographic orientation between the NPs by the so-called oriented attachment (OA) mechanism.[1] TiO_2 anatase NPs exhibit a truncated bipyramid shape with eight (101) faces and two (001) faces. The interaction between TiO2 anatase NPs was described by a classical forcefield comprising Buckingham and Coulomb potentials.[2] Although the size of the model NPs and the numerical efficiency of the classical force field should allow direct simulation to be accomplished with either molecular dynamics simulations or Monte Carlo methods, preliminary investigations of the potential energy landscape revealed multiple minima with energy differences larger than 10^2 kJ/mol, usually separated by barriers higher than 10^3 kJ/mol, potentially leading to kinetically trapped NPs dimers, with a very restricted sampling of the available phase space. We then devised an alternative approach to perform a thorough and uniform sampling of the phase space of TiO_2 NPs at contact distance, which amounts to the actual calculation of a partition function. The microstates of the system were obtained by placing one NP on previously chosen points of a regular grid around the other NP, then allowing the former NP to rotate and pivot around the latter, with both NPs treated as rigid bodies. The profile of Helmholtz energy obtained for the (101) face of one NP around the other (Figure 1) was computed with a solvent accessible surface grid with 6886 points, allowing the second NP to rotate at 492 different directions and to pivot at 10° intervals, amounting to a partition function with 121 964 832 independent microstates explicitly calculated. Color scheme indicates favorable Helmholtz energies in darker red (lowest value being -875 kJ/mol) whereas darker blue stands for most positive Helmholtz energies (up to 569 kJ/mol). Similar grids have been calculated for other combinations of faces, edges and corners of the NPs and they point out to the interaction between two (001) faces as the most stable thermodynamically. This finding might be considered to be at odds with previous investigations that consider the interaction between two (001) faces as the most probable outcome of an oriented attachment for TiO_2 anatase NPs. This apparent contradiction is most likely due to the small ration between the (001):(101) areas, so we are extending the modeling to include other sizes and shapes of the TiO_2 NPs. But even at the present status of the investigation, the most important conclusion is already sound and clear: the usual picture of a well-defined surface free energy describing the self-assembling in general and the oriented attachment as simple surface area

minimization might be naïve, since there are hot spots separated by thermodynamically unfavorable regions, and thus there are a few preferred positions and orientations. So decreasing the exposed area is no longer an acceptable explanation, since there is a very large number of possible dimers which have a decreased surface area and yet have prohibitively larger free energies.

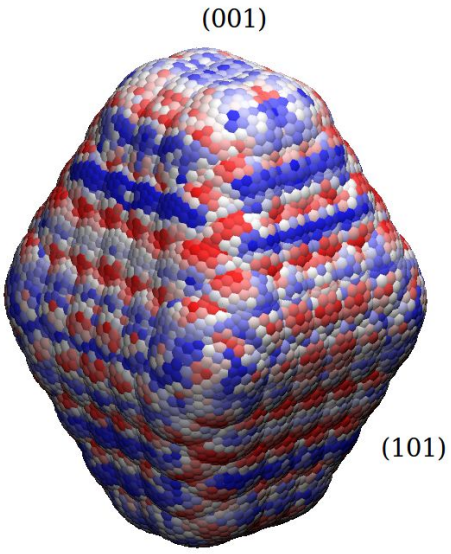

Figure 1: Profile of Helmholtz energy for the interaction of one (101) face around the reference TiO_2 NP. Red spots stand for the most negative values whereas blue spots stand for the most positive.

Key-words: oriented attachment, nanoparticles, TiO_2 anatase, free energy.

Support: The authors are indebted to FAPESP for the financial support (2012/15147-4, 2013/07296-2). USS thanks CNPq for a scholarship. AFM thanks MEC/PET for a fellowship. The authors acknowledge the National Laboratory for Scientific Computing (LNCC/MCTI, Brazil) for providing HPC resources of the SDumont supercomputer, which have contributed to the research results reported within this communication. URL: http://sdumont.lncc.br

References:

[1] LV, W.: HE, W.; WANG, X.; NIU, Y.; CAO, H.; DICKERSON, J. H. & WANG, Z. "Understanding the oriented-attachment growth of nanocrystals from an energy point of view: a review". Nanoscale, **6**: 2531, 201.

[2] MATSUI, M. & AGAKOI, M. "Molecular dynamics simulation of the structural and physical properties of the four polymorphs of TiO_2". Mol. Simul., **6**: 239, 1991.