

A Theoretical Study of Twinning Boundaries of Gold using Evolutionary Algorithms and Reactive Force Field Molecular Dynamics

Ting Nie, Xue-Qing Gong*

^aLaboratories for the advanced Materials, Center for Computational Chemistry and Research Institute of Industrial Catalysis, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, People's Republic of China.

*Corresponding author: +86-21-64253457, xgong@ecust.edu.cn

Abstract:

Evolutionary algorithm is a global search optimization algorithm, which is based on Darwin's theory of evolution, to solve optimization problems by selection, heredity and mutation operators. In recent years, it has been widely applied in computational simulation of catalytic material structures.

In our work, we study the specific structures of gold nanomaterial, and simulate the twinning boundaries observed in experiments using evolutionary algorithms and reactive force field¹ molecular dynamics. Many different structures can be obtained. The results are vital to deeply understanding the relationship between energies and structures and catalytic activities of such unique materials.

Keywords: Twinning Boundaries, Evolutionary Algorithm, Reactive Force Field.

1. Introduction

Twinning is one of the most common crystal defects. During the last several decades, many scientists have devoted to studying the unique properties of twinning crystals. Many experimental literatures have emerged in the past twenty years, but the theoretical studies about twinning crystals are very limited. In recent years, there are some reports about the investigation of five-fold twinning nanorods. Chen *et al.*² have performed thorough researches on twinning structures of pentagonal metal nanorods. Experiments³ show that gold nanorods grow along [110] direction, with feature of five-fold twinning structure, which is obtained by rotating {111} crystal for five times (see Fig. 1). So the twinning boundaries in cross section widen obviously, and have a certain angle of about 7.5°.

2. Theoretical

In our work, we mainly studied twinning boundaries of gold nanorods. In order to correctly obtain possible structures of gold twinning boundaries, we performed General Utility Lattice Program (GULP) calculations aided by evolutionary algorithm (EA) optimization.

After halting criterion is achieved, many different structures can be obtained. According to the calculated total energies, these optimized structures can be classified, and the lowest-energy structure is determined. We set the range of energy difference and cosine distance to screen and extract structures.

Then we analyze the extracted structures. We use three methods (the Euclidean distance, the cosine distance and the quasi-entropy) to describe fingerprint and bond characterization matrix (BCM)⁴ of a structure, thus describe structural (dis)similarity.

3. Results and discussion

For the gold twinning boundaries, we use USPEX code⁵ to perform structural evolution with almost 100 generations, which produces thousands of structures altogether. From the structures in Fig. 2, it is clear that the twinning boundaries of five configurations are different. The lowest-energy structure has the most ordered atomic arrangement. As the disordered atoms of twinning boundary increase, the energy of the structure is also raised, and the structure is less stable. Therefore, according to these different configurations, we can conclude the relationship between energy and structure. Moreover, we can predict the catalytic activity of twinning boundaries.

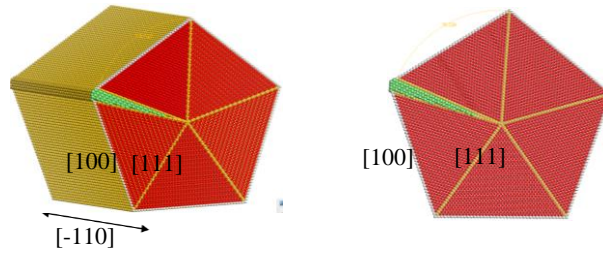


Figure 1. The theoretical model constructed according to experimental five-fold twinned nanorod.

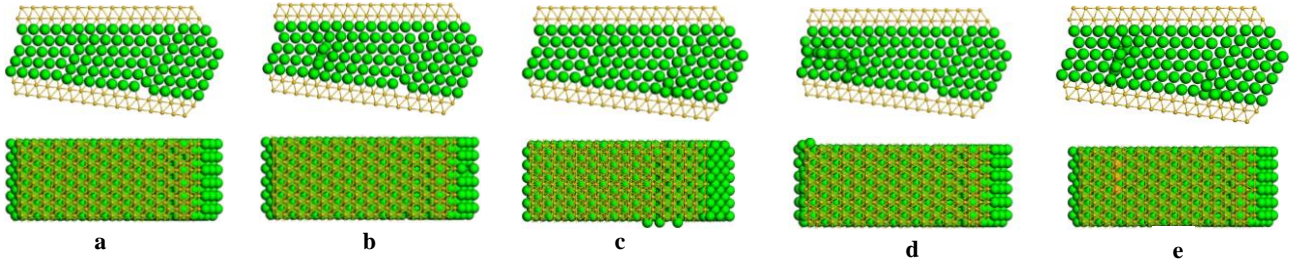


Figure 2. The structures of twinning boundaries obtained in an evolutionary run.

Model No.	Relative energy (eV)	Relative average energy of each atom ($\times 10^{-3}$ eV/atom)
1 (Fig. 2a)	0	0
2 (Fig. 2b)	3.26	2.10
3 (Fig. 2c)	7.30	4.70
4 (Fig. 2d)	8.02	5.17
5 (Fig. 2e)	10.90	7.02

Table 1. Relative energy and average energy of each atom of five structures. The structure Fig 2a is taken as a reference.

4. Conclusions

According to the simulation results and structural analyses, we can preliminarily draw the following conclusions:

First, twinning boundaries are the preferential positions of anisotropic growth. From thermodynamic perspective, the atomic arrangement of twinning boundaries always tends to achieve the stable condition with the lowest energy. Moreover, with the process of growth, crystals can often adjust the growth rate of each facet.

Second, the atoms in twinning boundaries will be firstly arranged in the close-packed mode to maximize local atomic density by contracting towards the interior of nanorods.

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