

An improved method to predict the Wulff shape: An example for $\text{Li}_2\text{CoSiO}_4$



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ABSTRACT

The Wulff construction based on surface energy calculations is an effective tool to understand and predict the shape of nanoparticles. Previous surface energy calculation faces the challenge to precisely deal with the dipole electric field in a slab. Here we propose a method that by fitting the calculated surface energies with no dipole electric field through multivariate linear regression, the separate contributions to the surface energy from the cations coordination loss terms on the surface can be obtained. The fitted results can further be used to estimate the surface energies of slabs with dipole electric field directly and accurately. Using this method, the Wulff shapes of three phases of $\text{Li}_2\text{CoSiO}_4$, a kind of materials with great potential for oxygen evolution reaction (OER) electrocatalysts, are precisely constructed.

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1. Introduction

The surface properties of small particles play great roles on catalysis, gas sensing [1], and chemisorption [2]. Thus a detailed understanding of the morphologies of small particles is important. Wulff construction, originated from the experimental observation of natural crystals by Wulff and the quantitative explanations boosted by von Laue, Dinghas and Herring [3], is able to identify the thermodynamic stable clusters and predict the shape of nanoparticles, including single crystal, alloy [1,3–5], etc. Now it is widely used in nanotechnology to understand and control the shapes of nanoparticles.

Wulff shape can be constructed according to the surface energies, which usually can be obtained by accurate density functional theory (DFT) calculations. For such calculations, there are usually two methods to build the slab. In the first one, the slab is built in the stoichiometry way, and the surface energy is defined as [6]:

$$\gamma = \frac{E_s - NE_b}{2S} \quad (1)$$

where γ , E_s , E_b , N , and S are the surface energy, the total energy of the slab, the energy of unit cell, the number of unit cell in the constructed slab, and the area of the surface, respectively. Its advantage is that the E_b and E_s can be calculated directly, and it doesn't need any other approximations compared with the non-stoichiometry way. However, in some cases, the up surface is not the same as

the bottom surface in the slab, and a dipole electric field would be generated, which doesn't exist in actual nanoparticles [7]. This electric field will bring the extra energy to the E_s term in slab calculation, leading to a bigger surface energy than the real value. Thus the calculated shape would deviate from the actual nanoparticle shape. One way to deal with this problem is to increase the thickness of the slab enough to decrease the dipole electric field, but the corresponding cost for computation would be increased significantly [7]. Moreover, the dipole electric field and the surface energy deviation still exist.

For the second method, the slab is built in a non-stoichiometry way. If the dipole electric field exists in the stoichiometry slab, one layer or few layers of atoms can be added to one side of the surface to make the outmost atoms of the two surfaces the same [8]. This could eliminate the dipole electric field, and the surface energy is defined as:

$$\gamma = \frac{E_s - NE_b + \sum_i n_i \mu_i}{2S} \quad (2)$$

where n_i , μ_i , and i are the number of added atoms, the atomic chemical potential, and the species of atoms. In this method, we should estimate the atomic chemical potentials that the added atoms bring about. Generally, this estimation is not so accurate that it would also bring deviation to the real value of surface energy.

In this work, we develop an improved method through multivariate linear regression to fit the calculated surface energies with no dipole electric field to get the separate contributions to the surface energy from the cations coordination loss terms at the surface. The fitted results can further be used to estimate the surface

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energies of slabs with dipole electric field accurately. Using this developed method, we study the equilibrium crystal shapes of three different phases of $\text{Li}_2\text{CoSiO}_4$ (LCS) named β_{II} -LCS, β_{I} -LCS, and γ_0 -LCS (Fig. S1 in Supplementary Materials), respectively, which belong to a large family of materials known as the tetrahedral structures and are a kind of recently widely studied cobalt redox-active electrode materials for rechargeable lithium batteries [9–11]. They also show a great potential for oxygen evolution reaction (OER) electrocatalysts, thus it is worthy studying their equilibrium crystal shapes to know the mainly exposed surfaces where the OER happens.

2. Methods

All calculations in this work are performed using the plane-wave projector-augmented wave method with an energy cut-off of 520 eV, as implemented in the Vienna ab initio simulation package (VASP) [12–16]. The Perdew-Burke-Ernzerhof (PBE) [17] form of GGA was chosen as the exchange-correlation potential. The PBE+ U approach was employed to take account of the short on-site Coulomb interaction (U) presented in the localized 3d electrons of Co, with the U values set to 3.32 eV for Co [18]. The structures were relaxed until the forces were less than 0.03 eV/Å, and the energy convergent standard was 10^{-5} eV. The k -point meshes of β_{II} -LCS, β_{I} -LCS, γ_0 -LCS unit cells were set to $5 \times 5 \times 6$, $5 \times 3 \times 6$, $5 \times 3 \times 6$, respectively, and β_{II} -LCS, β_{I} -LCS, γ_0 -LCS belongs to $\text{Pmn}2_1$, $\text{Pbn}2_1$, $\text{P}2_1/n$ space group, respectively. For the β_{II} -LCS phase, we use the anti-site structure reported by experiments. The errors for the calculated lattice constants compared with the XRD data for three phases are lower than 1.6% (Supplementary Materials Table S1–S3). A vacuum buffer space of at least 15 Å is set for all slabs.

We investigated all the basic low index faces ((100), (010), (001), (110), (101), (011), and (111)) and some other possible high index faces with low surface energies (e.g., (120), (210), and (130)). The general rule of cutting face should minimize the ion coordination loss at the surface. We performed crystal orbital Hamilton populations (COHP) [19,20] bond analysis in the unit cell of β_{II} -LCS (Table S4), which can be used to estimate the bond strength. The results show that the strength of Si–O, Co–O, and Li–O bonds follows: Si–O > Co–O > Li–O, and the bond length also follows this trend. For the situation of LCS materials, the rules are:

- (1) For the same cutting plane with different terminal atoms, we choose the way that breaks less bonds as far as possible;
- (2) The breaking of Si–O bond would increase the surface energy greatly, so we choose the way that does not break the Si–O bond as far as possible;
- (3) If the number of the broken Co–O bonds is the same with the broken Li–O bonds, we choose to break Li–O bonds, as the Li–O bonds are weaker than the Co–O bonds;
- (4) In some faces, we choose the zigzag way to minimize the number of broken bonds;
- (5) The priority of the above four rules decreases successively.

Because the surfaces with dipole electric field would reconstruct beyond simple geometrical relaxations, we also have calculated the surface energies using a larger slab (2×2 of primary slab) for β_{II} -LCS phase (Table S5), and found that the difference between the results from primary slab and the results from the larger slab is quite small.

3. Results and discussion

All the three structures (β_{II} -LCS, β_{I} -LCS, γ_0 -LCS) we studied are vertex-connected tetrahedron networks. Different from the full octahedron (e.g., layered LiMO_2) and octahedron/tetrahedron hybrid structures (e.g., Co_3O_4 and olivine LiCoPO_4) with coplanar or collinear, the cobalt tetrahedra are cross-linked by silicate groups in LCS. Fig. 1 shows the atomic structure and the examples of cutting planes of β_{II} -LCS. We take the stoichiometry ratio way to cut the lattice plane, which guarantees the electric neutrality of slab. Almost half of the slabs with no perpendicular dipole belong to the “type I” and the “type II” surfaces [21], and dipole exists on another half of slabs along the direction of the surface normal, including some vanishing dipole slabs and great dipole slabs. We considered all the different situations in three different phases. There are two non-equivalent ways to cut the (010) lattice plane (Fig. 1b), which would lead to different terminated atoms. Specifically, the (010)-1 cutting way breaks the Si–O bonds and the Li–O bonds, and the (010)-2 cutting way breaks the Co–O bonds and the Li–O bonds. Our calculations show that the surface energy of (010)-2 is smaller than (010)-1, so we use the data of (010)-2 as the final data for Wulff construction. For (100) and (001) lattice plane, there is only one non-equivalence cutting way.

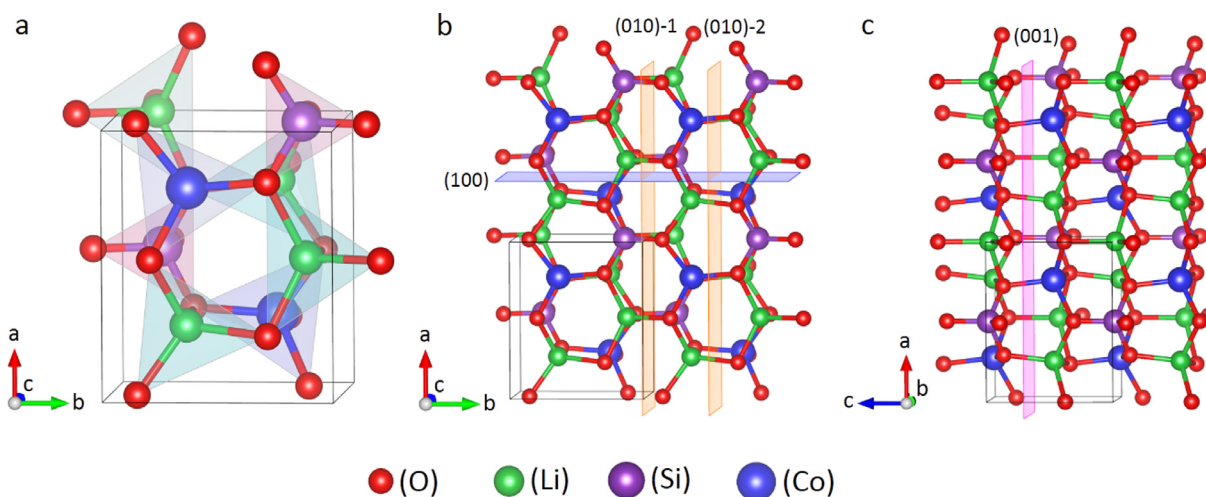


Fig. 1. (a) The unit cell of β_{II} -LCS phase. (b) The cutting way of (010) and (100) lattice plane of β_{II} -LCS phase. (010)-1 and (010)-2 are two non-equivalence ways of cutting (010) lattice plane. (c) The cutting way of (001) lattice plane of β_{II} -LCS phase.

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