



## Simulation of magnesium hydroxide surface and interface



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### ABSTRACT

The detailed electronic structures of magnesium hydroxide surfaces were determined using density functional theory. The morphology of the nanostructures in experimental magnesium hydroxide products was analyzed. Moreover, molecular simulations were used to investigate the interface between the magnesium hydroxide surface and polyethylene in a canonical (NVT) ensemble using a COMPASS force field. The interaction binding energy was calculated. The results indicate that the most stable surface contained a bonded OH that stretched outward based on the surface simulations for (001), (110), and (101). The dominant (001) face could cause to form nano-lamellar magnesium hydroxide with high thermal decomposition temperature. The nano-structured magnesium hydroxide exhibited better binding energies and mechanical properties when incorporating the magnesium hydroxide into polymers. This compound was a suitable flame retardant additive based on these calculations. The results are significant for understanding the structure and properties of magnesium hydroxide modifications.

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### 1. Introduction

In recent years, inorganic nanostructured materials with special morphologies have garnered increasing attention because of their novel properties and applications in gas sensors, photocatalysis, Li-cells, and wastewater treatment [1,2]. Magnesium hydroxide [Mg(OH)<sub>2</sub>, abbr. as MH] is an important inorganic material with a broad range of applications. MH nanoparticles with various shapes, such as nanoneedle, nanolamellar (or nanoplate), nanorod, or nano-flower-like crystals, can be synthesized using different controlling conditions and used as special function materials. Due to people's increasing environmental consciousness, super-fine MHs are becoming among the most promising halogen-free flame-retardant additives in polymers, such as polyethylene (PE), polyamides and ethylene vinyl acetate, because they are non-toxic, non-corrosive, thermally stable, and smoke-free [3,4]. However, these compounds have some disadvantages most notably the degraded mechanic properties at high additive levels [5].

Recently, experimental researchers have focused on nanostructured MHs with special morphologies. Li et al. [6] proposed a route to synthesize MH nanorods based on hydrothermal reactions with long reaction times and low reactant concentrations. Pang and coworkers [7,8] produced lamellar, rose-like, and torispherical MHs by introducing cations of varying valency (Zn<sup>2+</sup>, Al<sup>3+</sup>, and

Sn<sup>4+</sup>), and they proposed valence bonding to the cations as the differentiating mechanism. Xiang et al. [9–11] studied the structural reengineering of ordinary MH in a CaCl<sub>2</sub> and NaOH medium under hydrothermal conditions. Qu et al. [12,13] individually synthesized needle-, lamellar- and rod-like MH nanoparticles using wet precipitation in the presence of complex dispersants. Furthermore, preparing specific products is still difficult due to the physical and chemical properties of magnesium hydroxide. Hence, studying the reaction mechanism and crystallization process of MH has strong academic and practical significance [14].

The crystal structure of Mg(OH)<sub>2</sub> is of the same type as CdI<sub>2</sub> (trigonal, Space group  $D_{3d}^3 - P3m1$ ,  $Z = 1$ ) with layers of octahedral MgO<sub>6</sub> stacked along the *c* axis. Each O atom is hydrogenated with the O–H bond running along the threefold axis above and below the octahedral layers [15,16]. The interactions between the layers are weak H...H bonds, Ref. to Fig. 2(e). Different crystal surfaces possess different polarities that affect their micro-electronic structures and stability. Products with different morphologies can be produced based on the synthetic conditions. Studying the microstructure through experimentation is difficult; however, such research is simplified by computer models [17–21]. Xiang et al. [22] simulated the adsorption behavior of Ca<sup>2+</sup> and Cl<sup>-</sup> on MH planes using the universal force fields and found that Ca<sup>2+</sup> was easily adsorbed and incorporated onto the (001) plane, which might inhibit growth in the [001] direction to form MH plates with larger diameter to thickness ratios. In this paper, we calculate the electronic structure of various optimized surface from first principles.

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Three different MH morphologies were synthesized experimentally via different methods. The interactions between MH and PE surfaces were studied using molecular dynamics (MD). The results provided insight into how these materials interact with each other and exert influence, and might provide technical guidance for synthesizing and using composite MHs.

## 2. Research methods

### 2.1. Surface model

Slab model was used to study the surface. The initial unrelaxed surface structures were carved out of the fully relaxed bulk crystal, Ref to Fig. 2(a) and (c) for surface (110) and (101). A vacuum layer was set to prevent interactions between internal atoms. The vacuum layer thickness (10 Å, 15 Å, and 20 Å), intercept depth (7.903 Å, 9.483 Å, and 11.064 Å), and supercell size ( $2 \times 2$  with 140 total atoms, or  $3 \times 3$  with 315 total atoms) were tested. According to the test results, the atoms in the bulk and surface can be easily separated when the vacuum layer thickness and intercept depth are above 10 Å and 9.483 Å, respectively. The supercell size had little effect. Therefore, a slab of 29.483–31.064 Å with a relaxation layer of 9.483–11.064 Å was sufficient for a converged surface energy calculation considering the computational precision and efficiency. In our study, only those atoms near the surface were allowed to relax until the forces were less than 0.03 eV/Å. The inner part of the slab is frozen in its bulk position to simulate the bulk material.

The calculations were performed using CASTEP [23,24], an *ab initio* quantum program based on density functional theory (DFT). First, the pseudopotentials (including ultra-soft and norm-conserving), exchange-correlation energies (including PW91, PBE and RPBE), and cut-off energies (from 300 eV to 1000 eV) of the plane wave were tested. The model fits the experimental data well when the cut-off energy was set to 550 eV while using a norm-conserving pseudopotential and PBE. The lattice parameters of the optimized MH are shown in Table 1 and agree with the experimental data [15].

All calculations were performed in reciprocal K-space. A  $5 \times 5 \times 4$  k-point mesh was chosen to ensure that the total ground-state energy converged via the Monkhorst–Pack method [25]. The SCF of every atom was set to  $1.0 \times 10^{-6}$  eV using the Pulay density mixing method. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [18,26] was used to optimize the model. The lattice parameter, *c*, was underestimated slightly because the methods assume the weak interactions between layers to be insufficient. However, the relative error for all of the calculated properties is below 2%, which fully complies with the required accuracy for simulations (<3%).

### 2.2. The interface model between PE and MH

The interactions between the PE and MH surfaces were calculated using amorphous cell (AC) and the Discover module in the Materials Studio software package with COMPASS force fields [27]. COMPASS is an *ab initio* force field because most of its parameters are initially derived based from *ab initio* data. Both Discover and Forcite support COMPASS force fields. AC is a comprehensive model-building tool for simulating a wide range of amorphous materials, such as plastics, glasses, and chemicals. AC has been designed to build realistic models of chained molecules to enable the rapid prediction of properties such as density, mechanics, and diffusivity. In this paper, PE was constructed and optimized using AC. The modeled interactions at the PE and MH interface consisted of three layers, an upper vacuum layer, a middle PE layer generated via AC, and the bottom MH slab model built via the method described above.

Simulation details of MD are shown in Table 2. All of these calculations were performed on supercomputers.

**Table 1**  
The lattice parameters of the optimized Mg(OH)<sub>2</sub>.

	Exp. [15]	Cal. [28]	This work	Err. (%)
<i>a</i> (Å)	3.150	3.146	3.161	0.356
<i>c</i> (Å)	4.770	5.354	4.696	1.566
<i>V</i> (Å <sup>3</sup> )	40.99	45.89	40.63	0.875
$\alpha$	90.00	90.00	90.00	0
$\gamma$	120.00	120.00	120.00	0
<i>Z</i> <sub>H</sub>	0.413	–	0.419	1.423
<i>Z</i> <sub>O</sub>	0.220	–	0.218	0.980
H–O (Å)	0.958	0.953	0.943	1.606
Mg–O (Å)	2.100	2.103	2.093	0.343
H...H (Å)	1.997	2.250	1.977	1.000

## 3. Results

### 3.1. Electronic structure of crystal MH

The band structure and partial density of state (PDOS) for the optimized MH are shown in Fig. 1. The band gap was 3.645 eV. The band structure can be divided into three parts, bands near –17.5 eV caused primarily by the O-s orbital, bands below the Fermi level caused primarily by the O-p orbital, and bands in the conduction area caused by Mg-s, Mg-p and H-s orbitals. The outermost oxygen electrons most affect the total DOS. The Mulliken bond population analysis shows that the bond lengths of H–O and Mg–O were 0.943 Å and 2.093 Å, respectively, with populations of 0.65 and 0.61, respectively, which indicate MH is a typical covalent crystal. However, the H...H distance was 1.977 Å with a population of –0.06, which indicates the interactions between layers were relatively weak.

### 3.2. Surface study

According to the crystal symmetry and standard XRD diffraction spectra (PDF7-239) of MH, five surfaces with high symmetry and low indices, i.e., (001), (100), (101), (102) and (110), were chosen for the energy calculations and structure analyses. The results are shown in Table 3, where the “Area” is the MH crystal surface area in different cleaving directions, and “*E<sub>s</sub>*” is the energy per area per mole of molecules calculated by CASTEP via an energy minimization. Both the surface area and energy differ with the direction, and the energy is completely correlated to the surface with larger surface areas having more energy, which destabilizes them. Therefore, three surfaces (001), (101), and (110), were selected for further study. The positions of each atom in the crystal surface both before (a for (110) and c for (101)) and after (b for (110), d for (101), and e for (001)) the structural optimization are shown in Fig. 2.

Surface (110) cleaved through Mg–O–H. The relative positions of the surface atoms changed greatly, especially the OH group (Fig. 2(a) and (b)). The H–O–Mg angle was 119.3° for the initial crystal, and 121.0° and 129.9° for the optimized crystals. This change was not big, but the direction changed and tended to protrude from the surface.

For technical reasons, several cleaving surface might be formed when surface (101) was simulated. Minimizing the energy of these models indicates the system energy is relatively high when surface (101) is cut through the H or O atoms, which creates an unbonded H or O because of the broken OH bond. The system energy is still high when surface (101) is cut through the Mg atom because the naked Mg destabilizes the system despite there being no broken OH. The most stable surface is shown in Fig. 2(c). The initial and optimized (shown in Fig. 2(d)) H–O–Mg angles are 119.3° and 125.7°, respectively, while the O–Mg–O angles are 98.1° and 109.8°, respectively. All of the OH protrudes from the surface. The atoms in this sublayer do not change significantly.

For surface (001), each atom in the surface changes positions only slightly (shown in Fig. 2(e)). Therefore, we only show the optimized model of surface (001).

For all three surfaces, the height of the outmost layer is less than the inner layers. This height shrinks from 1.523–1.389 Å for surface (110), 2.361–2.337 Å for surface (101), and 4.763–4.714 Å for surface (001). This decreased distance strengthens the atomic interactions of the outmost atoms.

The MH band structure and DOS for different cleaving surfaces are similar to those of the bulk MH shown in Fig. 1, which is close to the D’Arco’s simulation results [28]. However, the surface band gap is less than that of the bulk MH (3.645 eV), and the

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