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Effect of lattice strain on the oxygen vacancy formation and hydrogen adsorption at $CeO_2(111)$ surface

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ABSTRACT

Using first-principles calculation, the effect of lattice strain on the oxygen vacancy formation at $CeO_2(111)$ surface has been investigated. The tensile strain facilitates the oxygen vacancy formation at the surface and the compressive strain hinders the process. This is in part due to the strengthening or weakening of the surface Ce–O bond under the lattice strain. On the other hand, a more open surface with a larger lattice constant can better accommodate the larger Ce^{3+} and thus facilitate the structural relaxation of the reduced surface. The studies on the strain effect on the atomic hydrogen adsorption at the defect-free $CeO_2(111)$ surface show that the adsorption strength monotonously increases with the increase of the lattice strain, further confirming the tunable surface chemical activity by lattice strain.

1. Introduction

CeO_2 has attracted much interest over the past decades both industrially and academically. In catalysis [1,2], CeO_2 serves as a widely used support material and as such helps to improve mechanical and thermal stability as well as activity and selectivity of catalysts (such as Pd, Rh, and Pt). Technologically [2], CeO_2 is relevant in treatment of toxic emissions, for removal of soot from diesel engine exhaust or organics in wastewater. Materials based on CeO_2 play extremely important roles in automotive exhaust treatment, the hydrogen economy and solid oxide fuel cell [3,4]. The widespread applicability mainly originates from the outstanding oxygen storage capacity of CeO_2, i.e., its ability to repeatedly pass through redox cycles rapidly [4,5]. It is believed that this is closely related to the ease in forming and repairing the oxygen vacancy (OV) at the surface of solid CeO_2. Therefore, the in-depth understanding and control of the type, density, and distribution of OVs at CeO_2 surface provide the means to influence the electronic structure and tailor the system's functionality [6,7].

Strain field is unavoidable especially in fabrication of nanostructures and thin films [8,9]. Previously, there were already a lot of works investigating the effect of lattice stain on the chemical activity of a metal surface [10,11]. Recently, much attention has been paid to the strain effect on the behavior of OVs at the surface or in the interior of a transition metal oxide. Using first-principles calculation, Shu et al. systematically studied the formation and diffusion of OVs at rutile $TiO_2(110)$ surface and showed that lattice strain can effectively engineer the distribution of the OVs [12–14]. Recently, during the studies on the optimization of the performance of solid oxide fuel cells, researchers have found that lattice strain has a significant impact on the oxygen ion transport [15–17], OV formation [18–20], and surface adsorption [18,21–23] for the oxide materials. Garcia-Barriocanal et al. experimentally reported that ultrathin (1 nm) YSZ layers (ZrO_2 with 8 mol% Y_2O_3), sandwiched epitaxially between thicker layers of $SrTiO_3$, exhibit conductivities that were higher than bulk YSZ samples by a factor of 10^8 [15]. This enormous increase was ascribed by the authors to the huge (7%) tensile strain in the YSZ films and disorder of oxygen ions at the interface [15]. Through first-principles calculations, Yildiz et al. showed that a 2% tensile strain can lead to a decrease of the OV formation energy by ~1.5 eV on the $LaCoO_3(100)$ surface and a 4% tensile strain makes the O_2 molecule adsorption from chemisorption to physisorption on the same surface [18].

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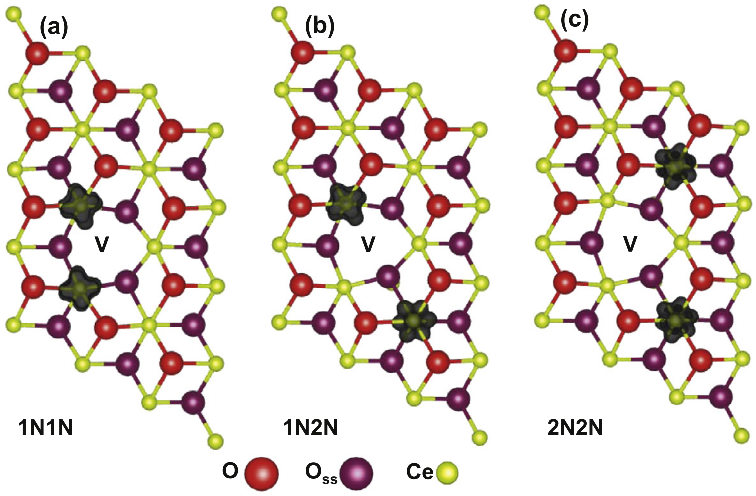

Fig. 1. (Color online.) Calculated structures (top view) of the $CeO_2(111)$ surface containing single surface oxygen vacancy. The O atoms are in red, O atoms at the subsurface in purple, and Ce atoms in yellow. V represents the position of the oxygen vacancy. The isosurface (0.005 $e/bohr^3$) of calculated spin charge densities are in black. They can localize on (a) two first nearest-neighbor Ce^{3+} (1N1N), (b) one first and one second nearest-neighbor Ce^{3+} (1N2N), and (c) two second nearest-neighbor Ce^{3+} (2N2N), with respect to the surface oxygen vacancy.

For CeO_2, previous experiments showed that the change in the lattice parameter of CeO_2 nanostructure ranges from a contraction of 0.32% up to an expansion of 6.8%, depending on the preparation method and the environment to which the particles are exposed before and during the measurement [24–29]. Especially, Hailstone et al. fabricated highly crystalline CeO_2 nanoparticles with predominantly (111) surface [27]. The lattice parameter increases up to an expansion of almost 7% with the decrease of the particle size, for which it has been ascribed to the larger amount of OVs and its associated Ce^{3+} for smaller CeO_2 particles [27]. The similar phenomena have been also observed by Deshpande et al. [29]. Materials based on CeO_2 are well established electrolyte materials due to its high oxygen ion diffusivity and relatively lower reduction temperature [30]. Using static atomistic simulations, based on empirical pair-potentials, De Souza et al. studied the effect of lattice strain on the oxygen diffusivity within ceria [17]. With the same method, Rushton et al. studied the effect of strain on the oxygen diffusion in doped CeO_2 [31]. They showed that a tensile strain always facilitates the oxygen diffusion [17,31]. In addition, Burbano et al. studied the strain effects on the ionic conductivity of Y-doped CeO_2 using dipole-polarizable interatomic potentials derived directly from ab initio calculations [32]. By first-principles calculations, Ahn et al. found that in Gd-doped CeO_2 the formation energy of OV shows the lowest value at tensile strain conditions [33]. Very recently, Sayle et al., based on molecular dynamics simulation, revealed that the chemical reactivity of the surface of CeO_2 nanorods is increased when tensioned and reduced when compressed [34]. Besides, lattice contraction or dilation in solid state ionic materials can be induced by the formation of point defects due to changes in temperature, composition, and surrounding environment, known as chemical expansion [35, 36]. Recently, Marrocchelli et al. have performed lots of studies on the possible factors responsible for the chemical expansion in CeO_2-based materials [37–42]. They found that the chemical expansion in CeO_2 is the result of two competing processes, i.e., the formation of an oxygen vacancy and a change in the cation radius upon reduction [38,39].

Despite these efforts, we find, until now, no studies at the electronic level on the effect of lattice strain on the OV formation at CeO_2 surface, which is more relevant to catalysis and other surface-relevant process [4]. $CeO_2(111)$ is the most thermodynamic stable low-index surface [7]. Therefore, in this study, based on first-principles calculations, we investigate the effect of lattice strain on the OV formation at $CeO_2(111)$ surface, and further the hydrogen atom adsorption at the same surface. For simplicity of interpretation, the surface strain has been imposed isotropically for all calculations even though it is not a realistic strain condition.

2. Computational details

We employed the density functional theory (DFT) as implemented in the VASP code within the generalized gradient approximation (GGA) of PBE to perform all the calculations [43,44]. The projector augmented wave method (PAW) was used to describe the electron–ion interaction [45,46]. The cerium $5s$, $5p$, $5d$, $4f$, and $6s$ electrons, the oxygen $2s$ and $2p$, and the hydrogen $1s$ electrons were considered as valence electrons with the cutoff energy of 500 eV for the plane-wave basis set. $DFT + U$ was chosen as our computational approach, since it can describe the structural, electronic (band structure) and redox properties of CeO_2, Ce_2O_3, and CeO_{2-x} in an acceptable way. In the $DFT + U$ method [47,48], a Hubbard parameter, U, is introduced for the Ce $4f$ electrons to describe the onsite Coulomb interactions and the U value is chosen to be 5.0 eV, since it is found previously that for $U = 5$ eV and greater, the localization of the Ce $4f$ electrons in the partially reduced ceria can be properly described [49,50].

The $CeO_2(111)$ surface has been studied in this work, since it is the most stable among the low-index surfaces. The surfaces were modeled as slabs, periodically repeated in the z direction perpendicular to the surface and separated from their images by a vacuum gap of $\sim$15 Å. Each slab consisted of a stack of (O–Ce–O) sandwiches, including 9 atomic layers in each slab with oxygen terminations. A rather big $p(3 \times 4)$ lateral cell with corresponding $(1 \times 1 \times 1)$ Monkhorst–Pack (MP) k-point mesh was used [51]. Two-dimensional-planar lattice strain was imposed isotropically by elongating or contracting the simulation cell in the x and y directions and relaxing the cell configuration and dimension in the z direction. The structure optimizations were performed until the force on each atom was less than 0.02 eV/Å, with the bottom three atomic layers fixed to mimic the bulk.

3. Results and discussion

We first present the results on the unstrained defective $CeO_2(111)$ surface with the calculated equilibrium lattice parameter of 5.47 Å, which is in a good agreement with the experimental value of 5.41 Å [52]. For $CeO_2(111)$, previous theoretical and experimental works [53–55] have demonstrated that electrons left