Activation of water on the TiO₂ (110) surface: The case of Ti adatoms

Meng Miao,¹ Yingchun Liu,^{1,a)} Qi Wang,¹ Tao Wu,¹ Liping Huang,² Keith E. Gubbins,³ and Marco Buongiorno Nardelli^{4,5}

¹Soft Matter Research Center and Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China

²Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180, USA

³Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695, USA

⁴Department of Physics, North Carolina State University, Raleigh, North Carolina 27695, USA

⁵Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37381, USA

(Received 19 September 2011; accepted 19 January 2012; published online 8 February 2012)

Using first-principles calculations we have studied the reactions of water over Ti adatoms on the (110) surface of rutile TiO₂. Our results provide fundamental insights into the microscopic mechanisms that drive this reaction at the atomic level and assess the possibility of using this system to activate the water dissociation reaction. In particular, we show that a single water molecule dissociates exothermically with a small energy barrier of 0.17 eV. After dissociation, both H⁺ and OH[−] ions bind strongly to the Ti adatom, which serves as an effective reactive center on the TiO₂ surface. Finally, clustering of Ti adatoms does not improve the redox activity of the system and results in a slightly higher energy barrier for water dissociation. © 2012 American Institute of Physics. [doi:10.1063/1.3682781]

I. INTRODUCTION

Hydrogen is emerging as an ideal energy carrier that can be generated from water, biomass, natural gas, or coal (after gasification). In addition to being a clean energy source, it offers versatility, high efficiency, and superior safety.¹ However, for hydrogen to succeed as a potential mass production fuel stock, it is of critical importance to have a clean and sustainable way to produce it from water or other renewable sources. Water is the earth's most abundant compound, and the fact that the oxidation of H₂ yields water means that it can be continually recycled with no emission of greenhouse gases. However, the direct thermal splitting of water, H₂O → H₂ + $\frac{1}{2}$ O₂, which does not generate CO₂ and produces highly pure hydrogen, is limited in practice by the high temperature, in excess of 2000 °C, required for the reaction. This poses major challenges to its practical implementation. Recently, there have been a large number of experimental and theoretical studies that focused on transition metal-based nanostructures as potential high-capacity hydrogen storage media and for their potential in decreasing the activation barriers in water decomposition reactions.^{2–4}

A molecular level understanding of the processes occurring on transition metal surfaces is crucial in order to improve our current knowledge of the heterogeneous catalytic reaction mechanisms and to improve the activity of nanostructured surfaces towards the dissociation of water. Materials based on TiO₂ have widespread applications in a large variety of important fields such as heterogeneous catalysis,

coatings, gas sensors, corrosion, and solar cells.⁵ Since Fujishima and Honda⁶ discovered that water could be photocatalytically split into hydrogen and oxygen on a TiO₂ electrode, enormous efforts have been devoted to the research on TiO₂ materials. The interaction of water with TiO₂ surfaces can be now considered as a model system for the study of water chemical reactions on metal oxide surfaces. The interaction of water with rutile (110), (100), (011), (001) and anatase (101), (001), (100) has been summarized and compared in the work of Sun *et al.*,⁷ while Liu and co-workers⁸ extended the study to liquid water on rutile (110), revealing a strongly inhomogeneous dynamics of the interfacial water molecules. The aqueous film is layered, such that molecules in the contact layer are sluggish towards hydrolysis because of their strong bonding to fivefold-coordinated Ti sites and those in the second layer diffuse rapidly interacting weakly with the substrate. The (110) surface is the most thermodynamically stable crystal face of rutile TiO₂. Water adsorbs molecularly on a defect-free (110) surface and water dissociatively adsorbs in vacancies in the bridging oxygen rows to form two inequivalent bridging hydroxyl groups.^{9,10} However, hydrogen generation efficiency over bare TiO₂ is low. To improve the efficiency, doped Metal/TiO₂ serves as a model for heterogeneous catalysis that has been extensively studied. Systems such as Cu/TiO₂,¹¹ Pt/TiO₂, and Au/TiO₂ (Ref. 12) exhibit energy barriers decreased by 15–19 kcal/mol relative to bare rutile TiO₂. In a combined experimental and theoretical investigation, Xiao *et al.*¹³ showed that dissociative adsorption of water occurs at an oxygen vacancy occupied by a Au atom. Indeed, surface defects are one of the prominent causes for a reduction in activation barriers for water dissociation on oxide surfaces: besides oxygen vacancies, the defect structures

^{a)} Author to whom correspondence should be addressed. Electronic mail: liuyingch@zju.edu.cn. Fax: +86-571-87951895.

of the (110) rutile surface also include titanium and oxygen atoms in the form of adatoms or interstitial adatoms.¹⁴ Moreover, it has been reported that oxygen adatoms altered the water dissociation and recombination chemistry through two distinctive pathways.¹⁵ On rutile TiO_2 (110), there is an energetically favorable pathway that exists for a Ti interstitial to diffuse to the surface and react with the adsorbed O_2 molecule to form a TiO_2 island on the terrace.¹⁶ It is also believed that the interaction between TiO_2 and metal leads to an electronic perturbation that improves the catalytic activity.¹⁷ In a previous work,^{2,3} we have demonstrated the active role that both a single Ti atom and a dimer adsorbed on C_{60} have in the activation of the water decomposition reaction (energy barriers of 0.19–0.57 eV). Here, the Ti d electrons act as the principal player in the effective reaction center on C_{60} substrate. In this paper, we extend our investigation to the Ti adatom structure on the rutile TiO_2 (110) surface. The paper is organized as follows: after a brief introduction to the methodology (Sec. II), Sec. III A focuses on the activation of water on the clean (110) surface of rutile TiO_2 , Sec. III B discusses the redox properties of a single Ti adatom, and Sec. III C discusses the case of two adatoms. Conclusions are presented in Sec. IV.

II. METHODS

Electronic structure calculations were performed within plane-wave pseudopotential density functional theory as implemented in the QUANTUM-ESPRESSO package.¹⁸ We used the Perdew–Wang 91 gradient-corrected exchange-correlation functional¹⁹ and ultrasoft pseudopotentials with a plane-wave cutoff of 35 Ry and a density cutoff of 350 Ry.

We have alternated the use of a single k -point sampling (Γ) and a denser $4 \times 4 \times 1$ k -point grid for Brillouin zone integration to ensure convergence of the energetics results. A periodic three layers slab model terminated with a (3×1) rutile TiO_2 (110) surface was constructed in orthorhombic supercells of $8.87 \text{ \AA} \times 6.49 \text{ \AA} \times 17.76 \text{ \AA}$, including $10 \text{ \AA}$ of vacuum. All adatoms and substrate layers were allowed to fully relax until the force acting on each atom becomes less than $0.01 \text{ eV/\AA}$. Tests on thicker supercells did not vary adsorption sites and configurations, the adsorption energies of water molecule were found to be in error by about -1.5% for 5 and 3 layers Ti/TiO_2 , which confirmed that our supercell choice was sufficiently converged for the scope of this study. The evaluation of the minimum energy reaction paths (MEP) and transition states has been done using the nudged elastic-band (NEB) method.^{20,21} The reaction energy is defined as $\Delta E = E_{\text{FS}} - E_{\text{IS}}$, where E_{FS} and E_{IS} are the energy of the final and initial state, respectively, so that a negative ΔE indicates an exothermic reaction and a positive ΔE represents an endothermic one. The energy barriers are defined as $E_a = E_{\text{TS}} - E_{\text{IS}}$, where E_{TS} is the energy of the transition state. To characterize the reactions from an electronic point of view, we calculated the partial density of states (PDOS) and charge density differences for the initial, transition, and final state. In all our calculations we have used GGA+U

FIG. 1. Top view of the TiO_2 (110) surface showing the (3×1) supercell used in our calculations. Gray Ti_5 , fivefold-coordinated Ti atoms (Ti_5); gray Ti_6 , sixfold-coordinated Ti atoms (Ti_6); red O_2 , bridging O; and red O_3 , in-plane O. 1 and 2 are the stable adsorption sites for Ti adatoms.

with $U = 4.0 \text{ eV}$ in order to correctly reproduce the correct electronic structure of TiO_2 .^{22–25} Finally, the figures of atomic geometries have been drawn using the XCRYSDEN software.²⁶

III. RESULTS AND DISCUSSION

A. Water adsorption and dissociation on clean TiO_2 (110) surface

As a first step, we have investigated the possibility of water dissociation on the stoichiometric rutile TiO_2 (110) surface. The (110) face of TiO_2 is composed of alternating rows of fivefold-coordinated Ti atoms (Ti_5) with threefold-coordinated in-plane O atoms (O_3) and twofold-coordinated bridging oxygen atoms (O_2), as indicated in Fig. 1. The sixfold-coordinated Ti atoms (Ti_6) sit below the bridging oxygen atoms, and in-plane O atoms bond to three Ti atoms. Whether water dissociates or molecularly adsorbs on the perfect surface of TiO_2 is still a matter of discussion in both experimental and theoretical studies.^{27–29} In our calculations, we show that water adsorbs preferentially on the fivefold-coordinated surface Ti atom with a distance between the surface Ti and the O atom in the water of $2.27 \text{ \AA}$, in good agreement with existing experimental measurements ($2.21 \pm 0.02 \text{ \AA}$).³⁰ Once water is dissociated, we found that the most stable configuration is the one in which the OH group binds to the fivefold-coordinated surface Ti atom while the remaining H atom binds with the bridging O atom, as shown in Fig. 2(a). After the dissociation, we have explored the possibility of H diffusion to the in-plane O atom and to a neighboring fivefold-coordinated Ti, as shown in Figs. 2(b) and 2(c). However, the relative energy of these configurations ($+0.49 \text{ eV}$ and $+1.15 \text{ eV}$, respectively) would effectively prevent H diffusion from bridging O to the in-plane O and Ti atoms on the surface. Moreover, although the configuration of Fig. 2(a) is found to be stable, the process is still endothermic with a positive energy difference of 0.33 eV , which indicates

FIG. 2. (a) Geometry of the final state for the water dissociation on the ideal TiO₂ (110) surface. (b) H atom diffuses to an in-plane O atom and (c) H atom diffuses to a neighboring fivefold-coordinated Ti. Red, O atoms; gray, Ti atoms; and blue, H atoms.

that water dissociation is energetically unfeasible on the ideal surface of TiO₂.

B. Water adsorption and dissociation on Ti/TiO₂ (110)

It is well known that the (110) surface of rutile TiO₂ can be prepared virtually defect-free only by a careful oxidation process to eliminate the most common oxygen vacancies that play a fundamental role in shaping the electronic and catalytic properties of this surface.¹⁴ Rather than focusing on O vacancies, one could also consider other surface defects, such as Ti adatoms, and study their role and potential in surface reactions. This latter system is the one we have chosen as a prototype for our investigation into the mechanism of water adsorption and dissociation.

First, we have characterized the possible adsorption sites for a single Ti adatom on the stoichiometric TiO₂ (110) surface. The most stable adsorption sites are the ones labeled 1 and 2 in Fig. 1. In configuration 1, the Ti atom binds to two bridging and one in-plane O atoms, while in configuration 2, the Ti atoms binds to one bridging and two in-plane O atoms. Configuration 1 is more stable between the two (energy lower by 0.96 eV). This is in excellent agreement with other theoretical studies.^{14,31}

To elucidate the mechanism of water dissociation on the Ti/TiO₂ surface we have performed NEB calculations with 7 images in order to evaluate the MEP and the transition state energy, as shown in Fig. 3(a). The calculated energy barrier for water dissociation over Ti/TiO₂ is 0.17/ 0.16 eV (spin-unpolarization/spin-polarization) in GGA-PW91 and 0.20 eV in GGA+U, an indication that electron localization does not play a relevant role in this process. These energy barriers are comparable with the one for water dissociation over Ti/C₆₀ (0.27 eV) (Ref. 2) and over Ti/CNT (0.20 eV).³² However, these values are much smaller than the ~5 eV for water splitting in free space, in liquid water (~1 eV),^{4,33} and in reactions catalyzed on the surfaces of Cu, Ni, and Pd (~1 eV).³⁴

In Fig. 3(b) we display the geometries and charge difference plots for the initial, transition, and final state. In the stable adsorption configuration, the Ti–O_{water} bond distance is 2.26 Å, which is close to the 2.27 Å distance on the TiO₂ surface and it is tilted at an angle of about 26°. The molecule-

FIG. 3. Single water dissociation on Ti/TiO₂ (110) surface: (a) Reaction pathway and reaction barrier, and (b) Electron density differences for the initial, transition, and final state.

adatom distance is slightly larger than the one observed for water on Ti/C₆₀ (2.17 Å) (Ref. 2) and on Ti/CNT (2.15 Å),³² an indication of the variation of the chemical environment felt by the Ti adatom in different systems. At the transition state, the Ti–O_{water} distance is 2.30 Å, slightly longer than the 2.26 Å in the initial state, and the water molecule is now located on top of the Ti adatom. The two O–H bonds become asymmetric, one slightly longer than the other, (1.01 Å compared to 0.97 Å in the initial state, and the other is shortened to 0.98 Å compared to 1.00 Å in the initial state). After the longer bond breaks, the hydrogen atom and the hydroxyl group are bonded to the Ti adatom at a distance of 1.85 Å and 1.81 Å, respectively. From these results it is clear that during the dissociation process the bonds between the O–Ti, O–H, and Ti–H evolve in the three configurations. In the final state, H moves to Ti, resulting in H–O bond breaking and H–Ti bond forming, similar to the process of water dissociation on Ti/C₆₀ (Ref. 2) and Ti/CNT.³² More insight on the electronic processes involved in the dissociation process can be gleaned from the evaluation of the electron density differences plots, $\Delta\rho = \rho(\text{H}_2\text{O}/\text{Ti}/\text{TiO}_2) - \rho(\text{Ti}/\text{TiO}_2) - \rho(\text{H}_2\text{O})$ shown as isosurfaces in Fig. 3(b): red isosurfaces indicate electron accumulation and blue ones indicate electron depletion. From the analysis of these plots we can clearly identify transfer of electrons from the Ti adatom to the water molecule as the primary mechanism for the molecular dissociation. A similar conclusion is obtained by the more quantitative analysis of the PDOS for the initial, transition, and final state, as shown in Fig. 4.

FIG. 4. Projected density of states (PDOS) for the initial, transition, and final state of water dissociation on Ti/TiO₂ (110). (The vertical dotted line indicates the Fermi level).

The largest change between the initial and final state PDOS comes from the Ti *d* orbitals, which clearly contribute to bonding, while Ti 3*s* and 3*p* orbitals lie very low in energy and are unaffected by bonding. The main difference here is the decrease of the Ti *d* electron peak around the Fermi level, a signature of the formation of the bonds with H and OH, a picture that is indeed consistent with the analysis of charge transfer in Fig. 3, and confirms the role of Ti 3*d* states as catalyst of the dissociation reaction already observed in Ti/C₆₀ (Ref. 2) and Ti/CNT.³²

The evolution of the *p* orbitals of O from three in the initial state to two in the final state is the product of the hybridization between Ti *d* and O *p* orbitals. In the final state O(2*s*) and Ti(3*d*), O(2*p*) and Ti(3*d*), as well as H(*s*) and Ti(3*d*), all have overlapping peaks at -20.45 eV, -8.45 eV, and -2.95 eV, respectively, which indicate the formation of the Ti–OH and Ti–H bonds. Finally, this interpretation is further confirmed by the analysis of the Lowdin charges on the Ti site, which shows a decrease consistent with the behavior observed in the PDOS. Our results are also in agreement with Deskins *et al.*'s work³⁵ where they identified defects in titanium dioxide (including oxygen vacancies, bridging row hydroxyls, and interstitial Ti) as active centers for redox chemistry.

Finally, we have considered the possibility of the H atom diffusion on the TiO₂ surface in Fig. 5. However, the possible paths for hydrogen diffusion to the bridging O and in-plane O are energetically unfavorable, with an energetic cost of 0.94 eV and 1.03 eV, respectively, leaving the dissociation on the Ti adatom the only exothermic reaction.

C. Water adsorption and dissociation on 2Ti/TiO₂ (110)

In order to explore the effect of Ti adatom clustering on the energetics of water dissociation on the rutile TiO₂ (110) surface, we added a second Ti atom as shown in Fig. 6(a). After a careful structural optimization we found that the surface restructured. The location of one bridging O atom bonding

FIG. 5. Illustration of the mechanism of water dissociation and diffusion of H on Ti/TiO₂(110) surface: (a) Initial dissociation, (b) Hydrogen atom diffuses to a bridging O, and (c) Hydrogen atom diffuses to an in-plane O.

to the two titanium adatoms simultaneously changed, the two titanium adatoms sit in a Ti (adatom)–O (bridging)–Ti (adatom) configuration that is similar to that of the perfect surface. The threefold-coordinated in-plane O atoms bonding to titanium adatoms relax away from the sixfold-coordinated Ti atoms, increasing the Ti–O bond lengths. Meanwhile, the in-plane O atoms on the other side relax toward the sixfold-coordinated Ti atoms, thereby shortening the Ti–O bond lengths. In Fig. 6(b) we show the energy profile for water dissociation and hydrogen atom diffusion processes calculated using the NEB method with 7 images. Note that the configurations used in NEB calculations were determined by choosing the lowest-energy one among different adsorption sites and orientations after series searching. In the initial state, the water molecule is adsorbed on one of the titanium adatoms with a bond length of 2.22 Å. The dissociation process takes place in steps that are very similar to the ones we have observed in the case of a single Ti adatom: both the

FIG. 6. Selected intermediate states (a) and reaction energy profile (b) for water dissociation on 2Ti/TiO₂ (images 1–3 for the initial, transition, and final state) and H diffusion process (images 3–5 for the initial, transition, and final state of H diffusing from one Ti atom to other Ti atom).

hydrogen atom and the hydroxyl group are bonded to the same titanium adatom and the energy barrier for this process is 0.89 eV (see images 1–3 in Fig. 6(a)). For the transition state in the water dissociation process (image 2), the angle between the hydrogen and hydroxyl group is small and the distance between them is short. From image 3, both Ti–OH and Ti–H distances are 1.82 Å, the orientation of the hydroxyl group and hydrogen is similar to the final state in Fig. 3(a). After dissociation, an energy barrier of 0.36 eV is estimated for H diffusion from one of the Ti adatoms to the other (images 3–5). For the transition state in the H diffusion process (image 4), the bridging O can be seen moving toward the opposite direction of the H atom and then coming back again in the final state (image 5).

Comparing with the case of a single Ti adatom, the energy barrier for water dissociation is larger, an indication that in the 2Ti geometry, the single adsorption site loses some of the ability to exchange electronic charge with the water molecule, since it is involved into a more stable bonding with the bridging O, one that resembles much more closely the ideal stoichiometry of TiO₂. Furthermore, we have checked that the adsorption energies of Ti adatom is 5.92 eV and 5.95 eV for Ti/TiO₂ and 2Ti/TiO₂, the adsorption energy of the second Ti adatom is slightly larger than the first one. However, when a water molecule was involved, the adsorption energy of water molecule is reduced by 12.3% (0.81 eV vs 0.71 eV) between Ti/TiO₂ and 2Ti/TiO₂ systems, which indicate that the interaction between 2Ti/TiO₂–water is weaker than Ti/TiO₂–water, thus there is a larger barrier for 2Ti/TiO₂. Nevertheless, these energy barriers are much smaller than the 5 eV needed for splitting water in free space⁴ and the reactions are exothermic with large releases of energy. This indicates that Ti adatoms on TiO₂ (110) can effectively promote water dissociation.

IV. CONCLUSIONS

In summary, using first-principles calculations, we have studied the redox properties of titanium adatoms on the rutile TiO₂ (110) surface towards the water dissociation reaction. Our results show a reduction of one order of magnitude in the energy barriers with respect to the bare TiO₂ surface (0.17 eV vs. 2.2 eV) when the reaction happens on a single Ti adatom. Upon clustering, i.e., when a second Ti adatom was added on the TiO₂ surface, the energy barrier of water dissociation increased to 0.89 eV due to the more stable bonding of the two Ti atoms to the underlying surface.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation (Grant No. 20876132), MOE (J20091551 and 2011QNA3014) of China, and ZJU-

2011XZZX002. L.H. and K.E.G. were supported by the National Science Foundation of USA under Grant Nos. CHE-1012719 and CHE-1012780, respectively. M.B.N. has been supported in part by BES and U.S. Department of Energy (DOE) at ORNL (DE-FG02-98ER14847 and DE-AC05-00OR22725 with UT-Battelle, LLC).

- ¹T. N. Veziroğlu and S. Şahin, *Energy Convers. Manage* **49**, 1820 (2008).
- ²L. P. Huang, Y. C. Liu, K. E. Gubbins, and M. B. Nardelli, *Appl. Phys. Lett.* **96**, 063111 (2010).
- ³Y. C. Liu, L. P. Huang, K. E. Gubbins, and M. B. Nardelli, *J. Chem. Phys.* **133**, 084510 (2010).
- ⁴M. A. Henderson, *Surf. Sci. Rep.* **46**, 1 (2002).
- ⁵U. Diebold, *Surf. Sci. Rep.* **48**, 53 (2003).
- ⁶A. Fujishima and K. Honda, *Nature (London)* **238**, 37 (1972).
- ⁷C. H. Sun, L. M. Liu, A. Selloni, G. Q. Lu, and S. C. Smith, *J. Mater. Chem.* **20**, 10319 (2010).
- ⁸L. M. Liu, C. J. Zhang, G. Thornton, and A. Michaelides, *Phys. Rev. B* **82**, 161415 (2010).
- ⁹S. Wendt, J. Matthiesen, R. Schaub, E. K. Vestergaard, E. Lægsgaard, F. Besenbacher, and B. Hammer, *Phys. Rev. Lett.* **96**, 066107 (2006).
- ¹⁰Z. Zhang, O. Bondarchuk, B. D. Kay, J. M. White, and Z. Dohnalek, *J. Phys. Chem. B* **110**, 21840 (2006).
- ¹¹S. P. Xu, J. W. Ng, X. W. Zhang, H. W. Bai, and D. D. Sun, *Int. J. Hydrogen Energy* **35**, 5254 (2010).
- ¹²S. F. Peng and J. J. Ho, *Int. J. Hydrogen Energy* **35**, 1530 (2010).
- ¹³X. Tong, L. Benz, S. Chrétien, H. Metiu, M. T. Bowers, and S. K. Buratto, *J. Phys. Chem. C* **114**, 3987 (2010).
- ¹⁴E. J. Sanville, L. J. Vernon, S. D. Kenny, R. Smith, Y. Moghaddam, C. Browne, and P. Mulheran, *Phys. Rev. B* **80**, 235308 (2009).
- ¹⁵Y. Du, N. A. Deskins, Z. Zhang, Z. Dohnalek, M. Dupuis, and I. Lyubintsky, *Phys. Rev. Lett.* **102**, 096102 (2009).
- ¹⁶S. Wendt, P. T. Sprunger, E. Lira, G. K. H. Madsen, Z. S. Li, J. Ø. Hansen, J. Matthiesen, A. Blekinge-Rasmussen, E. Lægsgaard, B. Hammer, and F. Besenbacher, *Science* **320**, 1755 (2008).
- ¹⁷V. Subramanian, E. E. Wolf, and P. V. Kamat, *J. Am. Chem. Soc.* **126**, 4943 (2004).
- ¹⁸See <http://www.pwscf.org> for electronic structure calculations and materials modeling at the nanoscale.
- ¹⁹J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
- ²⁰G. Mills, H. Jonsson, and G. K. Schenter, *Surf. Sci.* **324**, 305 (1995).
- ²¹H. Jonsson, G. Mills, and K. W. Jacobsen, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B. J. Berne, G. Cicciotti, and D. F. Coker (World Scientific, Singapore, 1998).
- ²²Z. P. Hu and H. Metiu, *J. Phys. Chem. C* **115**, 5841 (2011).
- ²³S. Chrétien and H. Metiu, *J. Phys. Chem. C* **115**, 4696 (2011).
- ²⁴J. Stausholm-Møller, H. H. Kristoffersen, B. Hinnemann, G. K. H. Madsen, and B. Hammer, *J. Chem. Phys.* **133**, 144708 (2010).
- ²⁵B. J. Morgan and G. W. Watson, *J. Phys. Chem. C* **114**, 2321 (2010).
- ²⁶See <http://www.xcrysden.org/> for a crystalline and molecular structure visualization program, it can display isosurfaces and contours.
- ²⁷L. A. Harris and A. A. Quong, *Phys. Rev. Lett.* **93**, 086105 (2004).
- ²⁸P. J. D. Lindan and C. J. Zhang, *Phys. Rev. B* **72**, 075439 (2005).
- ²⁹M. A. Henderson, *Surf. Sci.* **355**, 151 (1996).
- ³⁰F. Allegretti, S. O. Brien, M. Polcik, D. I. Sayago, and D. P. Woodruff, *Phys. Rev. Lett.* **95**, 226104 (2005).
- ³¹A. M. Asaduzzaman and P. Krüger, *J. Phys. Chem. C* **112**, 19616 (2008).
- ³²Y. Lei, Z. X. Guo, W. G. Zhu, S. Meng, and Z. Y. Zhang, *Appl. Phys. Lett.* **91**, 161906 (2007).
- ³³M. K. Kostov, E. E. Santiso, A. M. George, K. E. Gubbins, and M. B. Nardelli, *Phys. Rev. Lett.* **95**, 136105 (2005).
- ³⁴A. A. Phatak, W. N. Delgass, F. H. Ribeiro, and W. F. Schneider, *J. Phys. Chem. C* **113**, 7269 (2009).
- ³⁵N. A. Deskins, R. Rousseau, and M. Dupuis, *J. Phys. Chem. C* **114**, 5891 (2010).