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Anisotropic relaxation of CuO/TiO$_2$ surface under electric field and its impact on visible light adsorption: *ab initio* calculations

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The *ab initio* calculations about the anisotropic relaxation of the CuO/TiO$_2$ surface under the electric fields and the visible light adsorption on these relaxed surfaces are reported. We compare the relaxation of the CuO/TiO$_2$ surface under the electric fields in the direction of [001] or [010]. Fewer Cu-O bonds with the highly coordinated Cu-ions are found in the CuO/TiO$_2$ relaxed surface under the electric field in [010]. The Cu-O bonds in the interface of the CuO/TiO$_2$ surface lead to the improved visible light adsorption in the polarization of [001]. The CuO/TiO$_2$ relaxed surface under the electric field in [010] produces the more effective adsorption over the visible light. However, the electric field in [001] induces more relaxation on the CuO/TiO$_2$ surface so breaks the Cu-O bonds. It leads to the partial reduction of CuO to Cu$_2$O on the CuO/TiO$_2$ relaxed surface under the electric field in [001] and the inefficient adsorption over the visible light is stated on this surface.

1. Introduction

In 1972, Honda and Fujishima discovered the electrolysis of water on the TiO_2 electrodes. [1] Since then, the great attentions have been attracted in the various applications of semiconductor photocatalysts from water and air purification to solar energy conversion. [2-10] Among various oxide semi-conductor photocatalysts, TiO_2 has been considered to be one suitable candidate as the photocatalysts for the water splitting due to its long-term stability photostability, environmental-friendly characteristics, and cost-effectiveness abundant. [12-15] However the photocatalytic performances of TiO_2 are restricted by many factors, such as the low absorption of solar light, rapid recombination of photogenerated electrons and holes on the bare TiO_2. [16, 17] Thus, various novel strategies, including the doping of transitional metal ion and metal oxides, have been extensively employed to modify the TiO_2-based photocatalysts. [18-25]

Copper oxides have served as the composites with TiO_2 owing to their inherent p-type semiconductoring characteristics. The band gaps of CuO and Cu_2O are -1.4 eV and -2.2 eV, lower than 3.0 eV or 3.2 eV of TiO_2, which makes both these materials promising for the conversion of solar light irradiation. [26-36] Bandara et al. reported the fabrication of CuO-deposited TiO_2 photocatalyst for hydrogen production. [37] They found CuO was facilitated the charge separation and considered as an active site for water splitting. Lalitha et al. proposed finely dispersed Cu_2O/TiO_2 to improve the photocatalytic H_2 production. [38] They discovered the interaction of the Cu^+ ions and the TiO_2 surface were in charge of the efficient H_2 production under solar light irradiation. Wu et al. reported the fabrication of different Cu_xO species on TiO_2 to study their roles in photocatalytic H_2 production. [33] They found that the Cu^+ species enhanced the photocatalytic

activity, while the Cu^{2+} species suppressed it. Barreca et al. concluded the reduction of CuO to Cu_2O in the $CuO–TiO_2$ photocatalysts deactivated the photocatalytic hydrogen generation.[39] Sun et al. also reported the deactivation of the efficient $CuO-TiO_2$ photocatalyst due to the reduction of CuO.[16] McFarland et al. synthesized the Cu_xO/TiO_2 heterojunction thin film and received high efficiency on photoelectrolysis.[40] Robert et al. demonstrated the extension of the light-absorption of TiO2 to the visible light on the Cu_2O/TiO_2, Bi_2O_3/TiO_2 and $ZnMn_2O_4/TiO_2$ heterojunctions.[28] The heterojunctions promote the efficient separation of photo-excited electron–hole pairs to avoid the electron–hole recombination. Farbod et al. found CuO nanowires grown at 500 ℃ under an electric field produced the best photocatalytic performance on Methyl Orange and Bromocresol Green dyes.[41] Based on these researches, we focus on the structural relaxations of $CuO-TiO_2$ surface under the electric field and the corresponding impact on the adsorption over visible light in *ab initio* calculations.

2. Methods

The $2\times1\times2$ supercells (a = 9.188 Å, b = 4.594 Å, c = 5.918 Å) are built as the initial structure model on the primitive cell of the perfect rutile TiO_2 (a = b = 4.594 Å, c = 2.959 Å). We firstly cleave the supercells at (0 0 1) plane and build the TiO_2 layer (a = 9.188 Å, b = 4.594 Å, c = 4.438 Å) as shown in Fig. 1(b). The perfect CuO of the $2\times1\times2$ supercells (a = 9.306 Å, b = 3.410 Å, c = 10.216 Å) are built on the primitive cell of the perfect CuO (a = 4.653 Å, b = 3.410 Å, c = 5.108 Å). The supercells are cleaved at (0 0 -1) plane in order to build the CuO layer (a = 9.306 Å, b = 3.410 Å, c = 5.038 Å) as shown in Fig. 1(a). The TiO_2 layer and the CuO layer are assembled into the CuO/TiO_2 layer with the vacuum slabs of 5 Å at both sides as shown in Fig. 1(c). Avoiding for

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the much mismatch of the lattice constants, we set the lattice constants of the TiO$_2$ layer (a = 9.188

Å, b = 4.594 Å, γ=90°) as the reference. So we get the final lattice constants of the CuO/TiO$_2$

layer (a = 9.188 Å, b = 4.594 Å, c = 2.959 Å, $\alpha = \gamma = 90°$, $\beta = 94.58°$). We further construct the

2×3 surface on the initial CuO/TiO$_2$ layer. The CuO/TiO$_2$ surface would be relaxed under the

electric field of 10.4 MV/cm at the direction of [001] or [010]. We call the relaxed surface under

the electric field in [001] and [010] as CuO/TiO$_2$-Z and CuO/TiO$_2$-Y, respectively.

We perform the first-principles calculations on Dmol^3 program based on the density functional

theory.[42] The PBE formulation (Perdew, Burke, and Ernzerh) of the generalized gradient

approximation (GGA) are always used to describe exchange-correlation energy.[43] The spin

polarization method is necessary for TiO$_2$ to produce the semiconducting phenomenon.

Double-numeric quality basis set with the polarization functions (DNP) is employed in the value

of 3.5. The full Brillouin zone is defined with 3×3×2 meshes of Monkhorst-Pack k points.[44] A

thermal smearing of 0.01 Ha (1 Ha = 27.2114 eV) is used to accelerate the geometric optimization.

The convergence tolerances for the self-consistent field (SCF) energy and displacement in the

geometric optimization are set to $1.0×10^{-5}$ Ha and $5 ×10^{-3}$ Å. These geometries are relaxed under

the electric field of 10.4 MV/cm at the direction of [001] or [010]. When the geometric

optimization converged, these properties, such as the band structure, density of the states, and the

Mulliken charge are determined by Dmol^3 program.

The adsorption spectras are calculated in CASTEP program.[45] The ultrasoft pseudopotentials

are used to describe the electrons-ions interaction. The wave basis set with a cutoff energy of

400.0 eV is adopted. The k-points are set to 5×3×2 meshes. The polarization directions of [001]

and [010] are selected to address the impact of the polarization directions on the optical properties.

3. Results and discussion

Fig. 2 shows (a, b) the un-relaxed structures of the CuO/TiO$_2$ surface, (c, d) the CuO/TiO$_2$-Z

structures, (e, f) the CuO/TiO$_2$-Y structures. The left column (a, c, e) is in the side view of the

direction [0 1 0], the right column (a, c, e) in the [1 1 0]. The width along the [001] in Fig. 2(c, d)

is 11.475 Å, larger than that of 11.115 Å in Fig. 2(e, f) and 8.880 Å in Fig. 2(a, b). One reason is

the electric field induces the CuO/TiO$_2$ surface relaxed towards the two vacuum slabs. In the

interface of the CuO/TiO$_2$ surface, the more Cu-O$_{TiO2}$ bonds are found in Fig. 2(e) than in Fig. 2(c)

as shown in the circle boxes with the blue color. Moreover, the higher coordinated Cu-ions are

also observed in the blue rectangle boxes of Fig. 2(e). So, the electric field in [001] leads to more

relaxation.

Fig. 3 shows the fine structures of the CuO/TiO$_2$ surface in the rectangle boxes with the green

color in Fig. 2(d) and 2(f). The data in the black color marks the number of each atom. The

electric field in [010] in Fig. 3(a) induces the formation of the O(9)-Cu(3) bonds and the

O(13)-Cu(5) bonds, while only the O(9)-Cu(3) bonds are found in Fig. 3(b) as the electric field in

[001]. The bonds between the O(11) and O(12) with the Ti(10) are not formed in both relaxed

structures. Figs. 3(c) and 3(d) show the deformation electron density of the interface in the

CuO/TiO$_2$ surface. The spectrum of deformation electron density is set to the blue-green-red from

-0.1 to 0.1 electron/Å^3 with the bands of 128. The blue color and the red color indicate the electron

deficiency and the electron enrichment, respectively. It clearly shows the evitable difference of the

electron clouds around the Cu(5) ion. In Fig. 3(c), the electron clouds around Cu(5) ion are shared

by three nearby O-ions, while only by two O-ions in Fig. 3(d).

The distances between the Ti-ions and Cu-ions with the O-ions are found in Fig. 4. The number of

1-14 in X axis means the bonds of the Cu-ions or Ti-ions with the O-ions as shown in the

sub-table of Fig. 4(a). The number of 15-18 in X axis also indicates the Cu(X)-Cu(Y) as shown in

the sub-table of Fig. 4(b). The distance between the Cu(5) ion and the O(13) ion in the

CuO/TiO_2-Z structure shows the 1.5 times larger than that in the CuO/TiO_2-Y structure. The lower

coordinated Cu(5) ion induces the shorter bonds among the nearby O(14) ion , O(16) ion and O(13)

ion with the Cu-ions or Ti-ions. The length of the Cu(3)-O(9) bond shows shorter in the

CuO/TiO_2-Z structure than that in CuO/TiO_2-Y structure. The shorter Cu(3)-O(9) bond lead to the

larger distance between the O(11) ion and O(12) ion with the Ti(10) ion, especially to the O(11)

ion. It means the O(11) ion and O(12) ion move away from the Ti(10) ion,. The shorter distance

between the Cu(5) ion and Cu(7) ion are also found as the lower coordinated Cu(5) ion in the

CuO/TiO_2-Z structure. It produces the more distorted structures as shown in Fig. 3(b).

Fig. 5 shows the Mulliken charges of the Cu-ions and Ti-ions in the relaxed structures.[46, 47] The

number of 1-9 indicates the Cu-ions and Ti-ions as shown in the sub-table of Fig. 5. The 0.735 eV

and the 1.721 eV mean the Mulliken charges of the Cu-ions in perfect CuO and the Ti-ions in

perfect rutile TiO_2, respectively. All the Mulliken charges of Ti-ions and Cu-ions are less than

those in the perfect oxides. The Mulliken charges of the Cu(2) ion, Cu(4) ion, and Cu(6) ion show

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larger than those of the other Cu-ions. The Mullken charge of the Cu(4) ion in the CuO/TiO$_2$-Y

structure is larger than that in the CuO/TiO$_2$-Z structure. It means that the Cu(4) ion loss more

electrons to the O-ions to form the Cu-O$_{CuO}$ bonds. So, we observe the higher coordinated Cu-ions

in the CuO/TiO$_2$-Y structure as shown in the blue rectangle boxes of Fig. 2(e). The Mulliken

charges of the Cu(1) ion and Cu(7) ion produce little variation as the electric field in [001] and

[010]. In Fig. 6, we could find the Cu-Cu bonds between the Cu-ions liked the Cu(1) ion and the

Cu(7) ion. The occurrences of the Cu-Cu bonds decrease their Mulliken charges. Moreover, the

angle of the O-Cu(7)-O bond is 159.770°, which is larger than 103.34° of the O-Cu(1)-O bond. It

means the weak polarization in O-Cu(1)-O bond. So, the Cu(1) ion loss the more electrons than

the Cu(7) ion do. The electric field in [010] and [001] show the evitable impact on the Mulliken

charges of the Cu(3) ion and the Cu(5) ion, especially to the Cu(5) ion. The Mulliken charge of the

Cu(5) ion is even lower than the Cu-ions of 0.425 eV in the Cu$_2$O. It implies the unsteady bonds

between the Cu(5) ion with the adjacent O-ions in the CuO/TiO$_2$-Z structure. By contrast to the

Ti-ions in the perfect TiO$_2$, the Ti(10) ion and the Ti(15) ion loss the fewer electrons. Their

Mulliken charges show lower than those in the perfect TiO$_2$. However, the electric field in [001]

leads to the higher Mulliken charge of the Ti(10) ion and the Ti(15) ion than in [010]. It indicates

the Ti-O bond in the CuO/TiO$_2$-Z structure.

Fig. 6 shows the partial side view of the fine structures in the CuO/TiO$_2$-Y structure (a) and the

CuO/TiO$_2$-Z structure (b). The blue color indicates the Ti-O bonds in Fig. 6(a). In contrast, these

blue bonds are not found in Fig. 6(b). The dark arrows mean the formation of the Cu-Cu bonds in

the two relaxed structures.

Fig. 7 shows the UV−Visible light absorption spectra of the two relaxed structures in the polarization direction of [001] (a), [010] (b), their total spectras (c). The structure of the perfect TiO_2 is shown in Fig. 1(b). In Fig. 7, the UV light adsorption of the perfect TiO_2 shows larger than that of the CuO/TiO_2 surface. The CuO/TiO_2-Y structure and the CuO/TiO_2-Z structure in Fig. 7(a) improve the visible light adsorption at the range of 460 nm -800 nm and 520 nm -800 nm, respectively. By contrast, the former structure induces the more effective adsorption over the visible light. In Fig. 7(b), these relaxed structures only enhance the adsorption at the narrower range of 620 nm – 800 nm. It shows that these relaxed structures can effectively improve the adsorption over the visible light in the polarization of [001] rather than in [010]. In Fig. 7(c), it shows the CuO/TiO_2-Y structure and the CuO/TiO_2-Z structure also improve the visible light adsorption at the range of 600 nm -800 nm and little difference could be found between them.

Fig. 8 shows the partial density of states (PDOS) for the CuO/TiO_2-Z structure (a-d) and the CuO/TiO_2-Y structure (e-h). The first row (a, e) indicates the PDOS of the whole relaxed structures, the second row (b, f) for the layer 1, the third (c, g) for the sum of the layer 2 and 3, and the fourth (d, h) for the layer 2. The three layers are marked in Fig. 2. The dash lines at 0 eV indicate the relative Fermi energy level. In the comparison of Fig. 8(b) and 8(f), we find a small peak consisted of Cu-3d states lie below the Fermi energy level. Another minor peak of the defect energy level would be found on the top of the valence band maximum in Fig. 8(g), which is composed of the O-2p states. The above two peaks mean the formation of the fewer Cu-O bonds in the CuO/TiO_2-Y structure. In Fig. 8(h), we could also find the defect energy levels on the top of

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the valence band maximum. It means the O-ions locate in the layer 2. In Fig. 8(b), the peak of the

PDOS lies at -1.7 eV, while at -2.2 eV in Fig. 8(f). It means the PDOS in Fig. 8(f) shift to the

lower energy. In contrast, the PDOS moves to the higher energies in Figs. 8(c, d) and 8(g, h). The

defect energy levels induced by the formation of the excess $Cu-O_{TiO2}$ bonds could lead to the

improved adsorption on the CuO/TiO_2-Y structure in the polarization of [001].

Figs. 9 (a, b) show the fine structures of the CuO/TiO_2 surface in the small rectangle boxes with

the blue color in Fig. 2(e) and (c). Figs 9 (c, d) show the fine structure of the perfect CuO and

Cu_2O. It's clearly seen that the un-bonding between the Cu(2) ion and O(2) ion leads to the broken

bond of the Cu(4) ion and O(3) ion. The bond of the Cu(4) ion and O(3) isn't found in Fig. 9(d).

Consequently, it means the parts of CuO in CuO/TiO2-Y are reduced to Cu_2O in CuO/TiO_2-Z. So,

the occurrence of the Cu_2O deactivates the adsorption of the visible light in the structure of

CuO/TiO_2-Z.

4. Conclusions

We successfully address the different relaxations of the CuO/TiO_2 surface under the electric field

at two directions and these impacts on the visible light adsorption in *ab initio* calculations. The

CuO/TiO_2 surfaces are relaxed under the electric field in the direction of [001] or [010]. We find

the relaxation under the electric field in [010] give rise to the fewer Cu-O bonds in both the

interface and the bulk of the CuO/TiO_2 surface. The occurrence of the defect energy levels

induced by the Cu-O bonds in the interface of the CuO/TiO_2 surface improves visible light

adsorption in the polarization of [001]. The more effective adsorption over the visible light is

found in the CuO/TiO$_2$ surface relaxed under the electric field in [010]. By contrast, the partial

reduction of CuO to Cu$_2$O leads to the inefficient adsorption over the visible light on the

CuO/TiO$_2$ surface relaxed under the electric field in [001].

Acknowledgements

References

1 A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37–38.

2 M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69–96.

3 B. ORegan and M. Gratzel, *Nature*, 1991, **353**, 737–740.

4 J. G. Yu and B. Wang, *Appl. Catal. B*, 2010, **94**, 295–302.

5 M. Ksibi, S. Rossignol, J. M. Tatibouet, and C. Trapalis, *Mater. Lett.*, 2008, **62**, 4204–4206.

6 S. W. Liu, J. G. Yu, and M. Jaroniec, *J. Am. Chem. Soc.*, 2010, **132**, 11914–11916.

7 H. G. Yang, G. Liu, S. Z. Qiao, C. H. Sun, Y. G. Jin, S. C. Smith, J. Zou, H. M. Cheng, and G.

   Q. Lu, *J. Am. Chem. Soc.*, 2009, **131**, 4078–4083.

8 J. G. Yu, Y.R. Su, and B. Cheng, *Adv. Funct. Mater.*, 2007, **17**, 1984–1990.

9 V. Gombac, L. Sordelli, T. Montini, J. J. Delgado, A. Adamski, G. Adami, M. Cargnello, S.

   Bernal, and P. Fornasiero, *J. Phys. Chem. A*, 2010, **114**, 3916–3925.

10 J. H. Park, S. Kim, and A. J. Bard, *Nano Lett.*, 2006, **6**, 24–28.

12 M. Ni, M. K. H. Leung, D. Y. C. Leung, and K. Sumathy, *Renew. Sust. Energy Rev.*, 2007, **11**,

   401–425.

13 A. A. Nada, M. H. Barakat, H. A. Hamed, N. R. Mohamed, and T. N. Veziroglu, *Int. J. Hydrogen Energy*, 2005, **30**, 687–691.

14 M. H. Zhou, J. G. Yu, S. W. Liu, P. C. Zhai, and B. B. Huang, *Appl. Catal. B*, 2009, **89**, 160–166.

15 P. V. Kamat, *J. Phys. Chem. C*, 2007, **111**, 2834–2860.

16 S. P. Xu and D. D. Sun, *Int. J. Hydrogen Energy*, 2009, **34**, 6096–6104.

17 J. Yu, Y. Hai, and M. Jaroniec, *J. Colloid Interface Sci.*, 2011, **357**, 223–228.

18 W. Y. Choi, A. Termin, and M. R. Hoffmann, *J. Phys. Chem.*, 1994, **84**, 13669–13679.

19 D. Dvoranova, V. Brezova, M. Mazur, and M. Malati, *Appl. Catal. B: Environ.*, 2002, **37**, 91–105.

20 A. W. Xu, Y. Gao, and H. Q. Liu, *J. Catal.*, 2002, **207**, 151–157.

21 N. L. Wu and M. S. Lee, *Int. J. Hydrogen Energy*, 2004, **29**, 1601–1605.

22 C. C. Chen, X. Z. Li, W. H. Ma, and J. C. Zhao, *J. Phys. Chem. B*, 2002, **106**, 318–324.

23 H. S. Park, D. H. Kim, S. J. Kim, and K. S. Lee, *J. Alloy. Compd.*, 2006, **415**, 51–55.

24 D. Beydoun, H. Tse, R. Amal, G. Low, and S. McEvoy, *J Mol Catal A: Chem*, 2002, **177**, 265–272.

25 Y. X. Li, G. F. Ma, S. Q. Peng, G. X. Lu, and S. B. Li, *Appl. Surf. Sci.*, 2008, **254**, 6831–6836.

25 G. K. Mor, O. K.Varghese, R. H. T. Wilke, S. Sharma, K. Shankar, T. J. Latempa, K. -S. Choi, and C. A. Grimes, *Nano Lett.*, 2008, 8, 1906–1911.

26 M. Dahl, Y. Liu, and Y. Yin, *Chem. Rev.*, 2014, **114**, 9853–9889.

27 S. J. A. Moniz, S. A. Shevlin ,D. J. Martin, Z. X. Guo, and J. Tang, *Energy Environ. Sci.*, 2015, **8**, 731–759.

28 Y. Bessekhouad, D. Robert, and J. V. Weber, *Catal. Today*, 2005, **101**, 315–321.

29 S. Chu, X. Zheng, F. Kong, G. Wu, L. Luo, Y. Guo, H. Liu, Y. Wang, H. Yu, and Z. Zou, *Mater. Chem. Phys.*, 2011, **129**, 1184–1188.

30 L. Liu, X. Gu, C. Sun, H. Li, Y. Deng, F. Gao, and L Dong, *Nanoscale*, 2012, **4**, 6351–6359.

31 M. S. Dieckmann and K. A. Gray, *Water Res.*, 1996, **30**, 1169–1183.

32 M. K. I. Senevirathna, P. K. D. D. P. Pitigala, and K.Tennakone, *J. Photochem. Photobiol. A*, 2005, **171**, 257–259.

33 Y. Wu, G. Lu, and S. Li, *Catal. Lett.*, 2009, **133**, 97–105.

34 Z. Li, J. Liu, D. Wang, Y. Gao, and J. Shen, *Int. J. Hydrogen Energy*, 2012, **37**, 6431–6437.

35 Z. Wang, Y. Liu, D. J. Martin, W. Wang, J. Tang, and W. Huang, *Phys. Chem. Chem. Phys.*, 2013, **15**, 14956–14960.

36 H.-J. Choi and M. Kang, *Int. J. Hydrogen Energy*, 2007, **32**, 3841–3848.

37 J. Bandara, C. P. K. Udawatta, and C. S. K. Rajapakse, *Photochem. Photobiol. Sci.*, 2005, **4**, 857–861.

38 K. Lalitha, G. Sadanandam, V. D. Kumari, M. Subrahmanyam, B. Sreedhar, and N. Y. Hebalkar, *J. Phys. Chem. C*, 2010, **114**, 22181–22189.

39 D. Barreca, G. Carraro, V. Gombac, A. Gasparotto, C. Maccato, P. Fornasiero, and E. Tondello, *Adv. Funct. Mater.*, 2011, **21**, 2611–2623.

40 W. Siripala, A. Ivanovskaya, T. F. Jaramillo, S. -H. Baeck, and E. W. McFarland, *Sol. Energy Mater. Sol. Cells*, 2003, **77**, 229–237.

41 M. Farbod, N. M. Ghaffari, and I. Kazeminezhad, *Ceram. Int.*, 2014, **40**, 517–521.

42 L. Li, W. S. Li, A. M. Ji, Z. O. Wang, C. Y. Zhu, L. J. Zhang, J. F. Yang, and J. F. Mao, *Eur. Phys.*

J. B, 2014, **87**, 1–8.

43 J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple,

Phys. Rev. Lett., 1996, **77**, 3865.

44 H. J. Monkhorst and J. D. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B*,

1976, **13**, 5188.

45 M. D. Segall, P. L. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clarke, and M. C.

Payne, *J. Phys.: Condens. Matter*, 2002, **14**, 2717–2744.

46 M. D. Segall, C. J. Pickard, R. Shah, and M.C. Payne, *Mol. Phys.*, 1996, **89**, 571–577.

47 M. D. Segall, R. Shah, C. J. Pickard, and M. C. Payne, *Phys. Rev. B*, 1996, **54**, 16317–16320.

Figure Captions

Fig. 1 Configuration of the cleaved TiO_2 layer (a), the cleaved CuO layer (b), and the assembled

TiO_2/CuO surface with the vacuum slabs of 5 Å at both sides (c). The gray balls, the red balls, and

the pink balls indicate the Ti-atoms, the O-atoms, and the Cu-atoms, respectively.

Fig. 2 (a, b) the un-relaxed structures of the CuO/TiO_2 surface, (c, d) the CuO/TiO_2-Z structure, (e,

f) the CuO/TiO_2-Y structure. The left column (a, c, e) is in the side view of the direction [0 1 0],

the right column (a, c, e) in the [1 1 0].

Fig. 3 (a, b) Fine structures of the CuO/TiO_2 surface in the rectangle boxes with the green color in

Fig. 2(f) and 2(d); (c, d) Deformation electron density of the interface in the CuO/TiO_2 surface.

The data in the black color marks the number of each atom. The gray balls, the red balls, and the

pink balls indicate the Ti-atoms, the O-atoms, and the Cu-atoms, respectively. The spectrum of

deformation electron density is set to the blue-green-red from -0.1 to 0.1 electron/Å^3 with the bands of 128.

Fig. 4 (a) Distances between the Ti-ions and Cu-ions with the O-ions; (b) Distances between the Cu-ions.

Fig. 5 Mulliken charges of the Cu-ions and Ti-ions in the each relaxed structures.

Fig. 6 Partial side view of the fine structures in the CuO/TiO_2-Y structure (a) and the CuO/TiO_2-Z structure (b). The gray balls, the red balls, and the pink balls indicate the Ti-atoms, the O-atoms, and the Cu-atoms, respectively.

Fig. 7 UV−Visible light absorption spectra of the two relaxed structures in the polarization direction of [001] (a) and [010] (b) , their total spectras (c).

Fig. 8 Partial density of states (PDOS) for the CuO/TiO_2-Z structure (a-d) and the CuO/TiO_2-Y structure (e-h). The first row (a, e) indicates the PDOS of the whole relaxed structures, the second row (b, f) for the layer 1, the third (c, g) for the sum of the layer 2 and 3, and the fourth (d, h) for the layer 2. The three layers are marked in Fig. 2.

Fig. 9 (a, b) Fine structures of the CuO/TiO_2 surface in the small rectangle boxes with the blue color in Fig. 2(e) and (c); (c, d) Fine structures of the perfect CuO and perfect Cu_2O. The gray balls, the red balls, and the pink balls indicate the Ti-atoms, the O-atoms, and the Cu-atoms, respectively.

(a)

(b)

(c)

Ti

O

Cu

Ti

O

Cu

(a)

(b)   8.880 Å

(c)

(d)   Layer 1

Layer 2   11.475 Å

Layer 3

(e)

(f)   Layer 1

Layer 2   11.115 Å

Layer 3

(a)

Number			
1	Cu(2)-O(8)	8	Cu(3)-O(9)
2	Cu(3)-O(8)	9	Cu(5)-O(13)
3	Cu(4)-O(14)	10	O(9)-Ti(10)
4	Cu(3)-O(14)	11	O(13)-Ti(10)
5	Cu(5)-O(14)	12	O(13)-Ti(15)
6	Cu(5)-O(16)	13	O(11)-Ti(10)
7	Cu(6)-O(16)	14	O(12)-Ti(10)

(b)

Number	
15	Cu(1)-Cu(3)
16	Cu(5)-Cu(7)
17	Cu(2)-Cu(4)
18	Cu(4)-Cu(6)

CuO/TiO$_2$-Z

CuO/TiO$_2$-Y

Ti

O

Cu